Macromolecules **2006,** *39,* 1681−1692

Articles

Efficient Synthesis of *ω*-(*p*-Vinylbenzyl)polystyrene by Direct Functionalization of Poly(styryl)lithium with *p*-Vinylbenzyl Chloride in Hydrocarbon Solvent with Lithium 2,3-Dimethyl-3-pentoxide

Roderic P. Quirk,*,[†] Joseph M. Pickel[⊥,†] Mark A. Arnould,[‡,§]
Kathleen M. Wollyung,[‡,#] and Chrys Wesdemiotis[‡]

Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, and Department of Chemistry, The University of Akron, Akron, Ohio 44325-3601

Received June 3, 2005; Revised Manuscript Received December 29, 2005

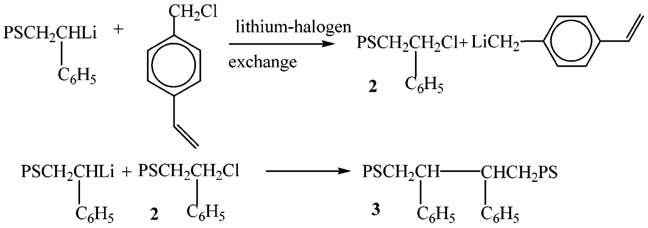
ABSTRACT: The direct functionalization of poly(styryl)lithium ($M_n \approx 2000$ g/mol) with *p*-vinylbenzyl chloride (VBC) has been investigated in hydrocarbon solvent. With a 9-fold excess of VBC and normal addition, the predominant product (55% yield) was the corresponding head-to-head dimer; the macromonomer was formed in only 20% yield as determined by ^{1}H NMR analysis. MALDI-TOF MS analysis of the products showed that the other major side reaction products resulted from addition of PSLi to the vinyl group of VBC. However, in the presence of excess lithium halides (LiCl, LiBr) the amount of dimer formation was reduced (30%), but the yield of macromonomer was increased only slightly (27%). The principal impurity was the corresponding nonfunctional polystyrene attributed to hydrogen abstraction from VBC by PSLi. A high yield (≥98%) of *ω*-(*p*-vinylbenzyl)-polystyrene macromonomer was obtained when the functionalization was effected in the presence of 10 equiv of lithium 2,3-dimethyl-3-pentoxide. No dimer formation was observed by SEC analysis, but the presence of a small amount (≤2%) of nonfunctional polystyrene was detected by MALDI-TOF MS analysis of the product.

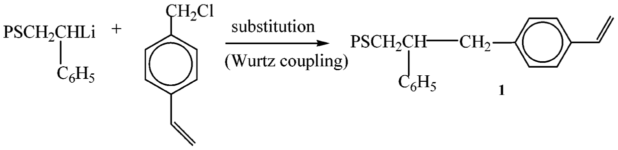
Introduction

Styrene is readily polymerized by most polymerization mechanisms, i.e., anionic, cationic, free radical, and transition-metal catalyzed.[1] Polymer chains which are functionalized with a polymerizable styrene moiety, i.e., styryl-functionalized macromonomers, offer a convenient route to polymers with novel architectures, in particular comb-branched polymers. Such macromonomers have been synthesized by a number of methods including free radical, anionic, and cationic functionalizations and postpolymerization transformations.[2−7] The reactivity of these macromonomers in homopolymerization and copolymerization has been extensively investigated.[4,6,8−12]

Living polymerizations provide the maximum degree of control for the synthesis of macromonomers with predictable, well-defined structures.[7,10] Among living polymerization methods, anionic polymerization is one of the most reliable and useful methods for the controlled synthesis of macromonomers with low degrees of compositional heterogeneity.[2,3,7−12] In principle, the synthesis of *ω*-styryl-functionalized polymers using anionic polymerization techniques can be accomplished most directly by the reaction of a polymeric organolithium with an appropriate styrene-substituted alkyl halide, as such compounds are relatively inexpensive and readily available. For *ω*-(*p*-vinylbenzyl)-functionalized polymers, in particular, the alkyl halide of choice is *p*-vinylbenzyl chloride (VBC), as shown in eq 1. Unfortunately and in general, the reactions of organolithium compounds with alkyl halides are complicated by side reactions such as lithium−halogen exchange and Wurtz-type coupling which form dimeric species (Scheme 1).[13,14] It is noteworthy that there is evidence for an electron-transfer mechanism for both of these reactions.[13] For example, the reaction of a benzene solution of poly(styryl)lithium with a tetrahydrofuran (THF) solution of VBC produced the corresponding *ω*-(*p*-vinylbenzyl)-substituted polystyrene macromonomer in only 50% yield; the other major product was the corresponding polystyrene dimer (50%).[15] Asami and co-workers[16,17] have also investigated these reactions with simple and polymeric benzyl chlorides and have proposed an electron-transfer mechanism for these reactions.

Scheme 1





(1)

[†] Maurice Morton Institute of Polymer Science.

[‡] Department of Chemistry.

[§] Current address: Xerox Analytical Services, 800 Phillips Road, Webster, NY 14580.

[⊥] Current address: Oak Ridge National Laboratory PO Box 2008, Oak Ridge, TN 37831-6197.

[#] Current address: Perkin-Elmer Life and Analytical Sciences, 3985 Eastern Road, Norton, OH 44203.

10.1021/ma0511604 CCC: $33.50

Currently there are only a few methods available for the efficient synthesis of styryl-functionalized polymers using anionic techniques. To circumvent unwanted side reactions associated with these end-functionalization reactions, it has been necessary to modify reaction conditions to decrease the reactivity and/or improve the selectivity of the anionic chain ends. Milkovich and co-workers[18−20] demonstrated the effectiveness of end-capping polymeric organolithium compounds with ethylene oxide prior to reaction with various halogen compounds to produce macromonomers. The end-capping reaction of poly(styryl)potassium with 1,1-diphenylethylene in THF at −70 °C prior to reaction with *p*-bromomethylstyrene was also shown to be effective for the efficient synthesis of *ω*-(*p*-vinylbenzyl)polystyrene macromonomers.[21] Although end-capping can be used to decrease the reactivity of a polymeric organolithium chain end, it would be desirable to develop a functionalization method which does not require an end-capping step. *ω*-(*p*-Vinylbenzyl)-functionalized macromonomers have been prepared without end-capping by terminating poly(styryl)lithium and poly(styryl)sodium with *p*-vinylbenzyldimethylchlorosilane. This reaction proceeds efficiently to form the macromonomer in quantitative yield.[22−24]

Asami and co-workers[15] investigated the effect of solvent and temperature on the direct reaction of poly(styryl)lithium with VBC. Quantitative macromonomer synthesis was achieved when THF (17 vol %) was added to poly(styryl)lithium before addition to a 13 M excess of VBC in THF at −10 °C. Hirao and co-workers[25,26] have reported quantitative syntheses of *ω*-styryl-functionalized macromonomers by addition of poly(styryl)lithium to 4-(haloalkyl)-substituted styrenes in THF at −78 °C. The incorporation of polar additives has proven to be useful for the synthesis of dendritic[27] and graft[28] polymers from polymeric organolithiums with VBC.

In summary, none of the available *p*-vinylbenzyl chloride-based functionalization methods for the synthesis of *ω*-(*p*-vinylbenzyl)polystyrene macromonomers utilize optimal conditions for alkyllithium-initiated polymerizations, i.e., hydrocarbon solution at room temperature and above. Under these conditions it is possible to effect maximum control of polymer structure, including the ability to obtain polydienes with high 1,4-microstructure. Herein, optimal conditions for the quantitative synthesis of *ω*-styryl-functionalized macromonomers are described by functionalization of poly(styryl)lithium with VBC in benzene solution at room temperature.

Experimental Section

Chemicals and Solvents. Styrene (99%, Aldrich), benzene (certified ACS, EM Science), and tetrahydrofuran (reagent grade, Fisher) were purified as described previously.[29] 2,3-Dimethyl-3-pentanol (99%, Aldrich) was used as received. Solutions of *sec*-butyllithium (1.45 M; FMC, Lithium Division, 12 wt % in cyclohexane) were used as received after analysis by the Gilman double titration using allyl bromide.[30] Lithium chloride (>95%, Fisher) or lithium bromide (99%, Aldrich) was placed in the reactor prior to the addition of initiator or monomer and heated to 150 °C under vacuum. Inhibitors were removed from *p*-vinylbenzyl chloride (VBC; 90%, Aldrich) by passing a cyclohexane solution of VBC through a column of aluminum oxide (calcined, 99+%, Aldrich). The eluent was condensed, dried over calcium hydride, and distilled into calibrated ampules, and the ampules were flame-sealed from the high-vacuum line. Methanol (certified ACS grade, Fisher) was degassed on the vacuum line.

Polymerizations. *sec*-Butyllithium-initiated polymerizations of styrene (10 vol %) in benzene were effected in all-glass, sealed reactors with break-seals and high-vacuum techniques.[31] Aliquots of poly(styryl)lithium were removed and terminated with degassed methanol for base polymer samples. Polymers were precipitated into methanol, filtered, and dried in a vacuum oven overnight.

Functionalizations. Styrene (10.6 mL, 9.63 g) polymerization in benzene (250 mL) was initiated with *sec*-butyllithium (3.15 mL, 0.0048 mol, 1.53 M) at room temperature and proceeded for 24 h, after which the solution was divided into flame-sealed samples for individual reactions. In experiments without additives, poly(styryl)lithium (75 mL, ∼0.0020 mol) was added to VBC (4.0 mL, 0.0284 mol) in benzene (75 mL). After 24 h at room temperature, the polymer was isolated from solution by precipitation into methanol, filtered, and dried. All functionalized polymer samples were purified by silica gel column chromatography to remove excess functionalizing agent.

For a typical functionalization in the presence of lithium halides, lithium bromide (2.66 g, 0.0306 mol) was added to a reactor using a small funnel and heated at 160 °C for 1 h under vacuum. After cooling, *sec*-butyllithium (4.0 mL, 0.006 12 mol, 1.53 M) was added followed by the distillation of benzene (300 mL). The reactor was flame-sealed from the vacuum line, and then styrene (13.5 mL, 12.27 g) was added. After 12 h at room temperature the solution was divided into flame-sealed samples for individual reactions. Functionalizations were effected by adding poly(styryl)lithium solution (85 mL, ∼0.0087 mol) to a solution of VBC (4.0 mL, 0.0284 mol) in benzene (100 mL). After 24 h at room temperature, the polymer was isolated by precipitation into methanol, filtered, and dried in a vacuum oven.

For a typical functionalization in the presence of lithium alkoxide, 2,3-dimethyl-3-pentanol (2.5 mL, 0.0179 mol) was injected into a reactor under an argon purge, followed by the slow addition of *sec*-butyllithium (14.7 mL, 0.0224 mol, 1.53 M) with periodic cooling with ice water to control the exothermicity. After the addition of benzene (300 mL), the reactor was flame-sealed from the line under full vacuum, and then styrene (10.8 mL, 9.82 g) was added. After 24 h, the solution was divided into smaller ampules for further reactions. Poly(styryl)lithium (85 mL, 0.001 275 mol) was added to a reactor containing *p*-vinylbenzyl chloride (4.0 mL, 0.0284 mol) and benzene (50 mL). After 30 h at room temperature, the polymer was isolated from solution by precipitation into methanol twice and dried in a vacuum oven.

Macromonomer Reaction with Poly(styryl)lithium. Dried macromonomer (0.47 g, 2.4×10^{-4} mol; $M_n \approx 1800$ g/mol) in 10 mL of benzene was added to 2 equiv of poly(styryl)lithium (4.4×10^{-4} mol; $M_n = 6000$ g/mol) in benzene. After 12 h at room temperature, degassed methanol was added by smashing the corresponding break-seal. The polymer was isolated by methanol precipitation and analyzed by SEC.

Characterization. SEC analyses were performed on a Waters 150C-Plus system equipped with an automatic injector and four Phenomenex Phenogel columns (500, 10^3, 10^4, 10^5 Å), a Waters differential refractometer, and a Viscotek viscometry detector (model 150R). Samples were prepared by making 10 mg/mL solutions in tetrahydrofuran and filtering through a 0.45 μm Teflon filter. The experiments were done at 32 °C in THF, with a flow rate of 0.60 mL/min. Results were analyzed using TriSEC SEC software (SEC-viscometry module version 3.0, Viscotek Corp.). UV−vis spectra were recorded using a Hewlett-Packard 84552A diode array spectrophotometer. Quantitative analyses of macromonomer functionality by UV−vis spectroscopy were effected for cyclohexane solutions of macromonomer products using the molar absorptivity of *p*-methylstyrene [$\epsilon = 1.64 \times 10^4$ L/(mol cm) at $\lambda = 250$ nm][15] as a model for the macromonomer functionality and a molar absorptivity of 133 nm for polystyrene as described by Asami and co-workers.[15]

^{1}H and ^{13}C NMR spectra were obtained on a Varian 300 spectrophotometer (300 MHz). Solutions for NMR analysis were prepared as follows. For ^{1}H NMR, 100 mg of polymer was dissolved in 0.7 mL of deuterated chloroform (Cambridge Isotopes). For ^{13}C NMR and attached proton tests up to 200 mg of polymer was dissolved in deuterated chloroform. Tetramethylsilane was added to the deuterated solvent as an internal reference.

Table 1. Results for the Functionalization Reactions of PSLi with VBC in Hydrocarbon Solvent at Room Temperature[a]

sample	M_n (g/mol) (M_w/M_n)	additive (equiv)	[VBC]:[PSLi]	functionality f^c (SEC)[d]	functionality f^c (NMR)[e]
1[b]	1700 (1.13)		10	45	20
2	1700 (1.13)		10	60	21
3	2400 (1.02)	LiBr (5)	15	70	25
4	5700 (1.01)	LiBr (20)	30	49	56
5	3000(1.03)	LiCl (2)	10	40	14
6	5800 (1.01)	LiCl (10)	10	62	26
7	2700 (1.03)	DMPOLi (4)	20	84	54
8	5700 (1.01)	DMPOLi (5)	14	80	47
9	1700 (1.01)	DMPOLi (10)	20	100	81

[a] Reactions effected using inverse addition techniques (PSLi added to VBC) unless otherwise noted [b] Reaction effected using normal addition technique. [c] Percent functionalized polymers. [d] Functionality as indicated by weight percent of nondimer product. [e] Functionality determined by analysis of ^{1}H NMR spectrum.

MALDI-TOF mass spectrometry experiments were run on a Bruker REFLEX-III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with a LSI Model VSL-337ND pulsed nitrogen laser (337 nm, 3 nm pulse width), a single-stage pulsed extraction ion source, and a two-stage gridless reflector. Most spectra were obtained in reflector mode. Separate solutions of dithranol (20 mg/mL), polymer (10 mg/mL), and silver trifluoroacetate (10 mg/mL) were made in tetrahydrofuran. These solutions were mixed in the ratio of matrix: cationizing salt:polymer (10:1:2). Samples of 0.5 μL were deposited onto the sample holder. Attenuation of the laser was set at 70%.

Results and Discussion

Reaction of PSLi with VBC in Benzene. In the initial experiments, poly(styryl)lithium (PSLi, $M_n = 1.7 \times 10^3$ g/mol, $M_w/M_n = 1.13$) was reacted with 10 mol equiv of p-vinylbenzyl chloride (VBC) in hydrocarbon solvent at room temperature by the normal addition mode (VBC added to PSLi; sample 1, Table 1). The use of a large excess of VBC was based on the previous investigations of Asami and co-workers[15] on optimization of this functionalization reaction. Upon addition of the VBC to PSLi, the color of the solution immediately changed from the characteristic orange-red of PSLi solutions to faint yellow within 5 s. The excess VBC was removed from all macromonomer samples by silica gel column chromatography. The SEC chromatogram of the resulting polymer (Figure 1) exhibits a bimodal distribution, and the major product (55%) exhibits a retention volume corresponding to a molecular weight that is twice that of the base polymer. The styryl functionality was determined to be only 20% using ^{1}H NMR spectroscopy (Figure 2) using the ratio of the integral for the vinyl protons (2 H, δ 4.8−5.7 ppm) and the integral for the *sec*-butyl initiator fragment (6 H, δ 0.9 ppm). A styryl functionality of 26% was determined by UV−vis spectroscopy. From the SEC and the styryl functionality determinations, it is obvious that a significant amount of side reaction products (ca. 21%) are formed that have approximately the same molecular weight as the functionalized polymer and the base polymer. Unfortunately, these analyses did not provide definitive information about the nature of these side reaction products nor have previous studies.[15]

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) techniques provide a method for the determination of the absolute molecular weight of polymeric components and for the definitive characterization of functional end groups. For relatively low molecular weight samples, a typical spectrum will show resolved isotopic peaks for each oligomer. In contrast, with higher molecular weight samples, individual isotopic peaks are usually not resolved because the instrument resolving power is insufficient or because resolution is sacrificed to maximize sensitivity. To facilitate analysis, polymers with low molecular weights ($M_n \sim 2000$ g/mol) were used in this investigation.

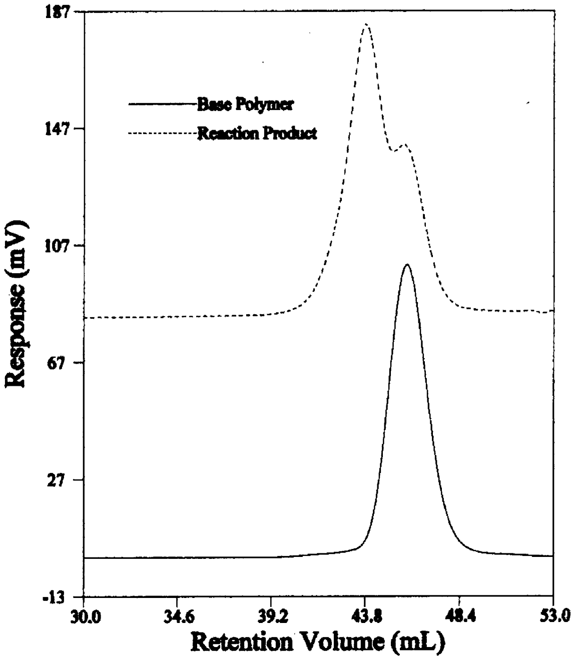


Figure 1. SEC chromatogram of the products from functionalization of PSLi with VBC in the absence of additives (top) and the corresponding base polymer (bottom) (sample 1, Table 1).

The MALDI-TOF mass spectrum for the products resulting from the previously described reaction of PSLi and VBC is shown in Figure 3. Multiple distributions are observed in the mass spectrum clearly illustrating the presence of dimeric and trimeric products; however, it is obvious that the observed peak intensities for the dimeric distribution vs the base distribution are moderated by their relative volatility (see Figure 1 for comparable SEC weight fraction distributions). Each distribution has peaks separated by m/z 104.1, corresponding to the molar mass of a styrene repeat unit. The region of most interest is that corresponding to the molecular weight of the base polymer (~1700 g/mol). The styryl-functionalized polymer would be expected to be observed in this m/z region. An enlargement of this area (m/z 1710−1960) is shown in Figure 4. The primary distribution of peaks corresponds to the macromonomer product. A representative peak for this distribution (labeled **1** in Figure 4) at m/z 1737.85 corresponds to a 14-mer of styryl-functionalized polystyrene having one butyl end group and one vinylbenzyl group with a silver ion from the cationizing agent: calculated monoisotopic mass $\{57.0704\ (C_4H_9) + 14 \times 104.0626\ [(C_8H_8)_{14}] + 117.0704\ (C_9H_9) + 106.9045\ (^{107}Ag^+)\} = 1737.92$ Da. This product results from the desired Wurtz

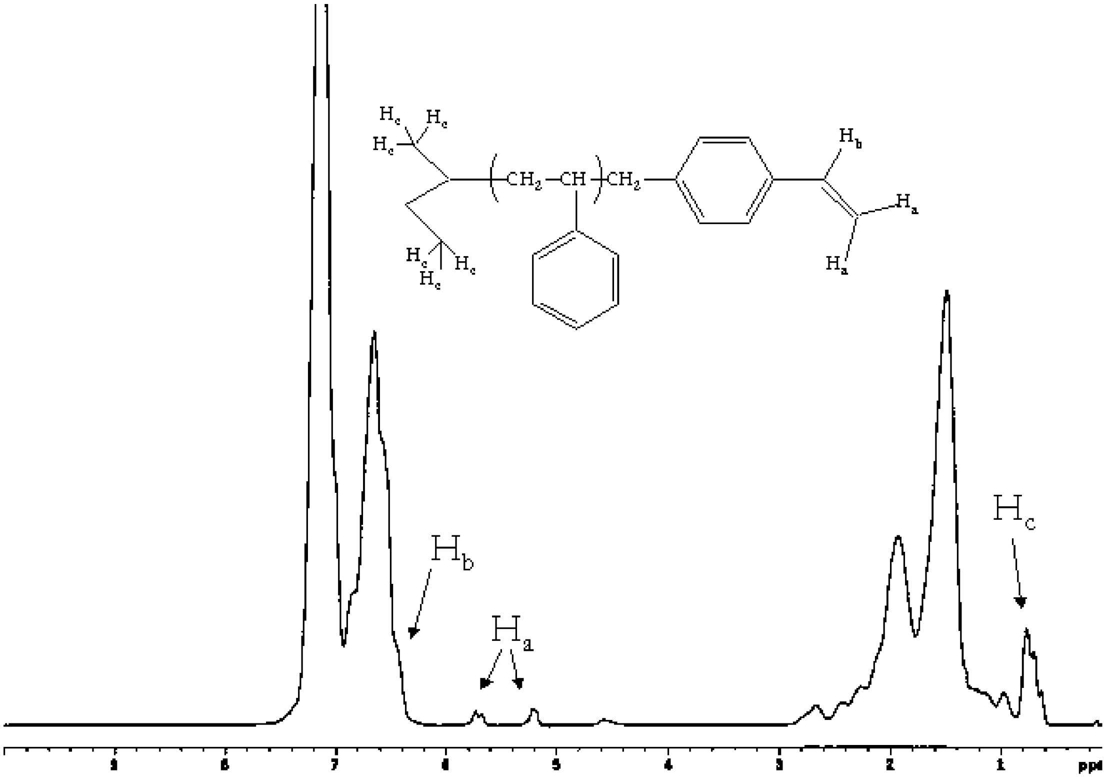


Figure 2. ^{1}H NMR spectrum of purified ω-styryl-functionalized polystyrene (sample 1, Table 1).

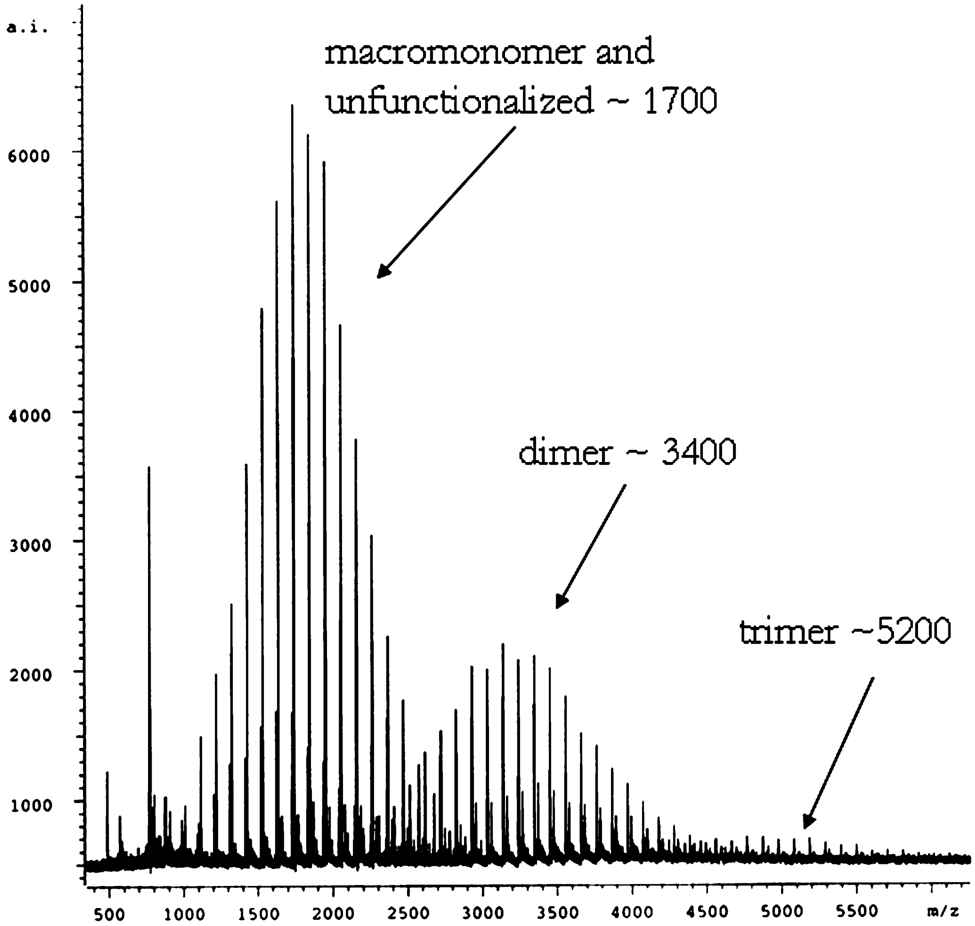


Figure 3. MALDI-TOF mass spectrum of functionalization reaction product (sample 1, Table 1).

coupling of PSLi with VBC (see eq 1). Another peak corresponding to the next largest distribution is also shown in this expanded region (**4** in Figure 4, *m*/*z* 1723.86), and it has the exact mass of the silver adduct of a PS 15-mer with one butyl group and missing a proton: calculated monoisotopic mass {57.0704 (C_4H_9) + 15 × 104.0626 [$(C_8H_8)_{15}$] − 1.0078 (H) +

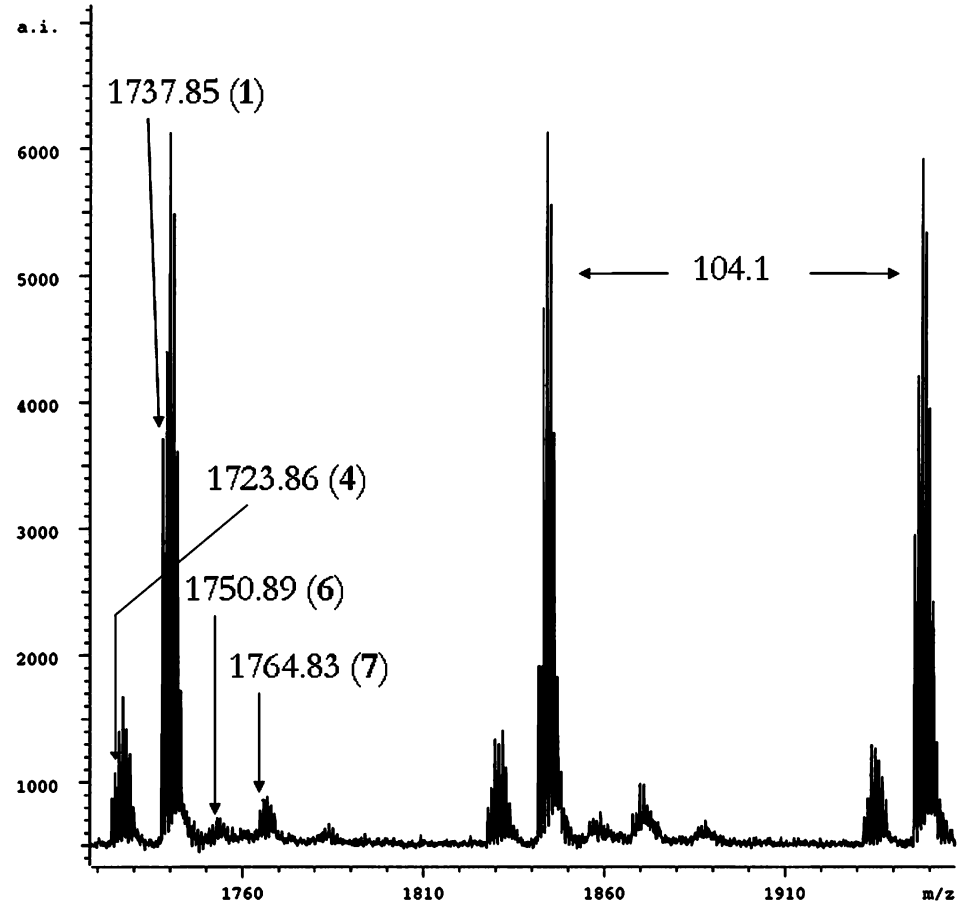
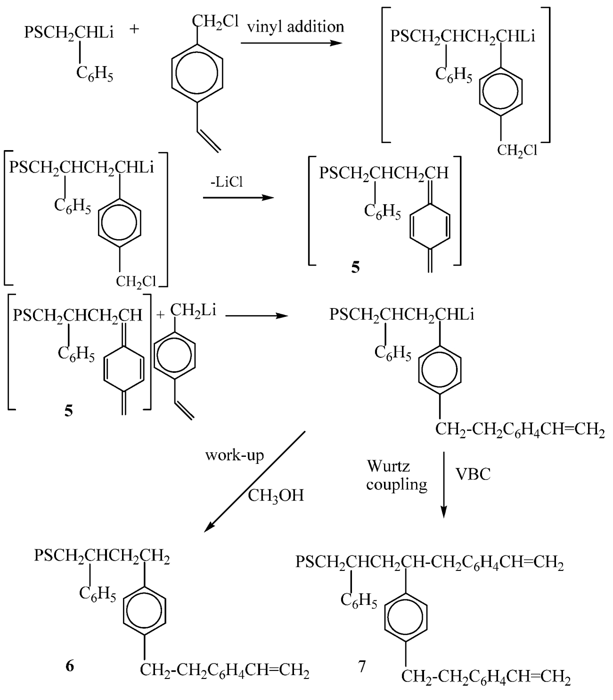
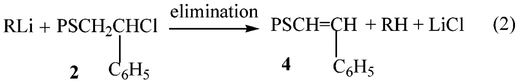


Figure 4. Enlargement of main product distribution in Figure 3 (m/z 1720−1950).

106.9045 ($^{107}Ag^+$)} = 1723.91 Da. Formation of product **4** could result from lithium−halogen exchange to form **2** (Scheme 1), followed by dehydrohalogenation of **2** by an organolithium base to form a vinyl chain end (see eq 2). In addition to the styryl-functionalized and vinyl-end-substituted polymers there are two other smaller series of peaks observed in the mass spectrum. An example of a peak from one of these series is labeled **6** in the expanded region. We speculate that this peak (m/z 1750.89) corresponds to the silver adduct of a PS 13-mer with one butyl group and two vinylbenzyl groups: calculated monoisotopic mass {57.0704 (C_4H_9) + 13 × 104.0626 [$(C_8H_8)_{13}$] + 2 × 117.0704 [$(C_9H_9)_2$] + 106.9045 ($^{107}Ag^+$)} = 1750.93 Da. Another minor series is represented by peak labeled **7** at m/z 1764.83, which has the exact mass of the silver adduct of a PS 12-mer with one butyl group and three vinylbenzyl groups: calculated monoisotopic mass {57.0704 (C_4H_9) + 12 × 104.0626 [$(C_8H_8)_{12}$] + 3 × 117.0704 [$(C_9H_9)_3$] + 106.9045 ($^{107}Ag^+$)} = 1763.94 Da. Possible mechanisms for formation of structures **6** and **7** are shown in Scheme 2. The key steps in these mechanisms are vinyl addition of PSLi to VBC followed by 1,6-elimination of lithium chloride to form the p-xylylene-end-functionalized polystyrene, **5**. Earlier reports indicate that 1,6-elimination is possible for *para*-substituted styrenes and 1,1-diphenylethylenes containing a CH_2 group in the *para* position between the phenyl ring and an oxygen substituent that can serve as a leaving group.[32−37]

Scheme 2





$$\underset{\mathbf{2}}{\mathrm{RLi + PSCH_2\underset{C_6H_5}{\underset{|}{C}}HCl}} \xrightarrow{\text{elimination}} \underset{\mathbf{4}}{\mathrm{PSCH{=}\underset{C_6H_5}{\underset{|}{C}}H}} \mathrm{+ RH + LiCl} \qquad (2)$$

The m/z region corresponding to twice the molecular weight of the base polymer (m/z 3090−3410) shows two significant series of peaks, as shown in the expanded view (Figure 5). One of the peaks in the major distribution in the high molecular weight region (**3**, m/z 3342.69) corresponds to the silver adduct of a 30-mer polystyrene dimer with two butyl end groups: calculated monoisotopic mass {2 × 57.0704 [$(C_4H_9)_2$] + 30 ×

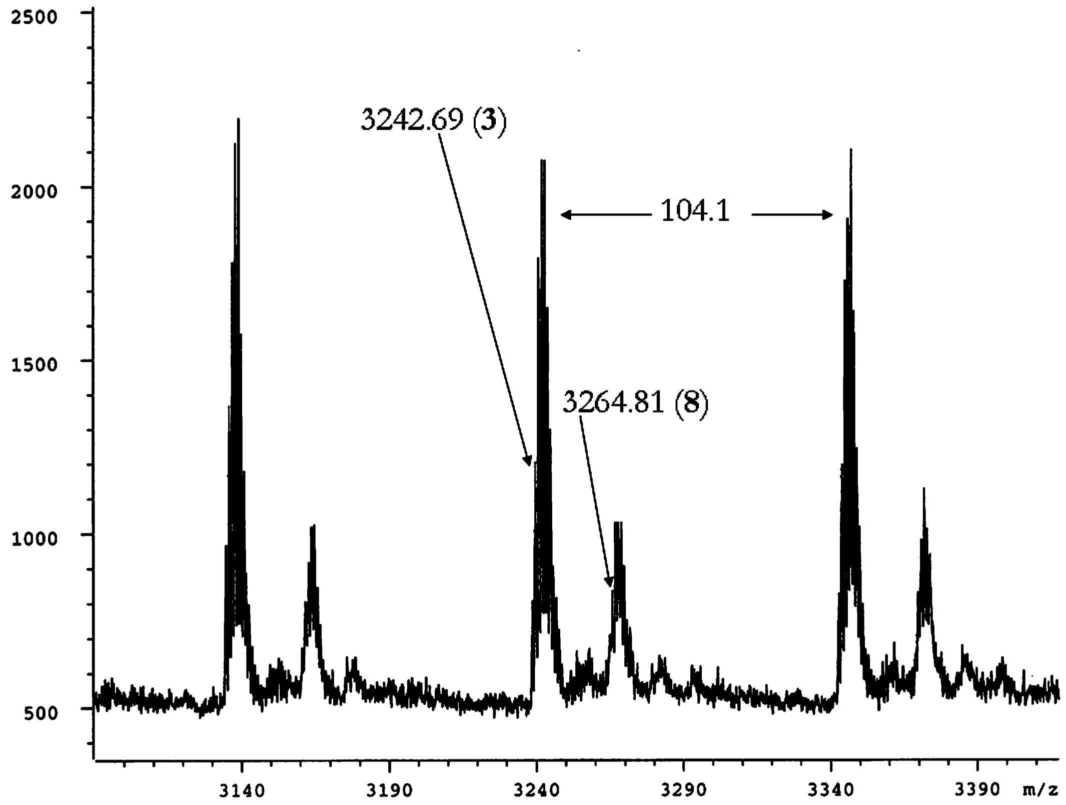
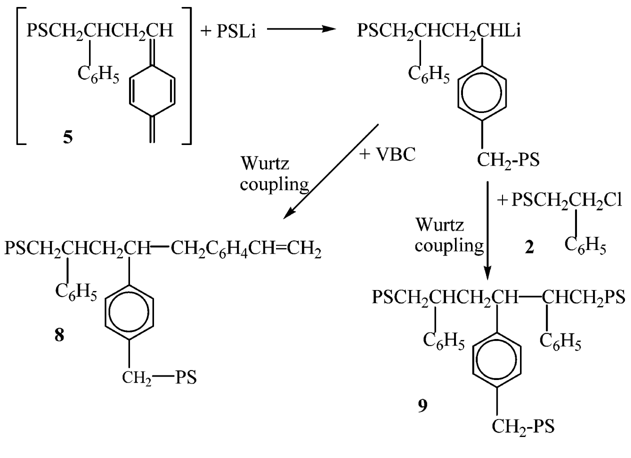


Figure 5. Enlargement of dimer region (m/z 3090−3410) from Figure 3.

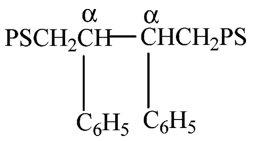
104.0626 [$(C_8H_8)_{30}$] + 106.9045 ($^{107}Ag^+$)} = 3342.92 Da. This product (**3**) is presumably the head-to-head dimer resulting from the coupling of the lithium chloride exchange product (**2**) with PSLi, as shown in Scheme 1. The minor distribution of the higher molecular weight region (**8** in Figure 5) (m/z 3264.81) has the exact mass of the silver adduct of a polystyrene 27-mer with two butyl groups and two vinylbenzyl groups: calculated monoisotopic mass {2 × 57.0704 [$(C_4H_9)_2$] + 27 × 104.0626 [$(C_8H_8)_{27}$] + 2 × 117.0704 [$(C_9H_9)_2$] + 106.9045 ($^{107}Ag^+$)} = 3264.88 Da. It is proposed that formation of **8** could involve addition of PSLi to the *p*-xylylene intermediate, **5** (see Scheme 2), followed by Wurtz coupling with VBC, as shown in Scheme 3. A number of the smaller peaks observed in this region are actually metastable peaks. These peaks did not appear when the MALDI experiment was run in the linear mode, indicating that the peaks probably represent fragments of larger molecules formed during the ion collection process.

A small distribution corresponding to a component with 3 times the molecular weight of the base polymer was found, albeit in small quantities as shown in Figure 3. This distribution was not resolved in the SEC trace of the polymer. An enlargement of this area (m/z 4830−5100, Figure 6) shows at least one product distribution, although the high molecular weight prevents better resolution. A representative peak (**9**) at m/z 4977.65 corresponds to a polystyrene 44-mer with three butyl groups and one vinylbenzyl group: calculated average mass {3 × 57.1159 [$(C_4H_9)_3$] + 44 × 104.1521 [$(C_8H_8)_{44}$] + 117.1711 (C_9H_9) + 107.87 (Ag^+) = 4979.08 Da}. Formation of **9** may result from addition of PSLi to the *p*-xylylene intermediate, **5** (see Scheme 2), followed by Wurtz coupling with **2** (see Scheme 1), as shown in Scheme 3.

Scheme 3



The structure of the major component in the dimer fraction was confirmed by analysis of the ^{13}C NMR spectrum of the reaction products (Figure 7). Rinaldi and co-workers[38] have previously reported that the ^{13}C NMR resonance corresponding to the two adjacent methine carbons in the head-to-head dimer of polystyrene (see carbons labeled α in structure below) has a calculated $\delta = 48.9$ ppm and experimental $\delta = 48.5, 49.5$ ppm. The ^{13}C NMR spectrum of the functionalization products clearly shows two peaks at δ 48,49 ppm, which is consistent with head-to-head dimer formation in this functionalization reaction.



$$\mathrm{PSCH_2}\underset{\substack{|\\ C_6H_5}}{\overset{\alpha}{\mathrm{CH}}}-\underset{\substack{|\\ C_6H_5}}{\overset{\alpha}{\mathrm{CH}}}\mathrm{CH_2PS}$$

Asami and co-workers[15] determined that the mode of addition affected the efficiency of this reaction. When an inverse addition mode was used (PSLi added to VBC), it was found by SEC analysis that the amount of dimer formation was reduced from 55% to 40%, although the macromonomer functionality was not increased (see sample 2, Table 1). Therefore, all further reactions were effected using the inverse addition mode.

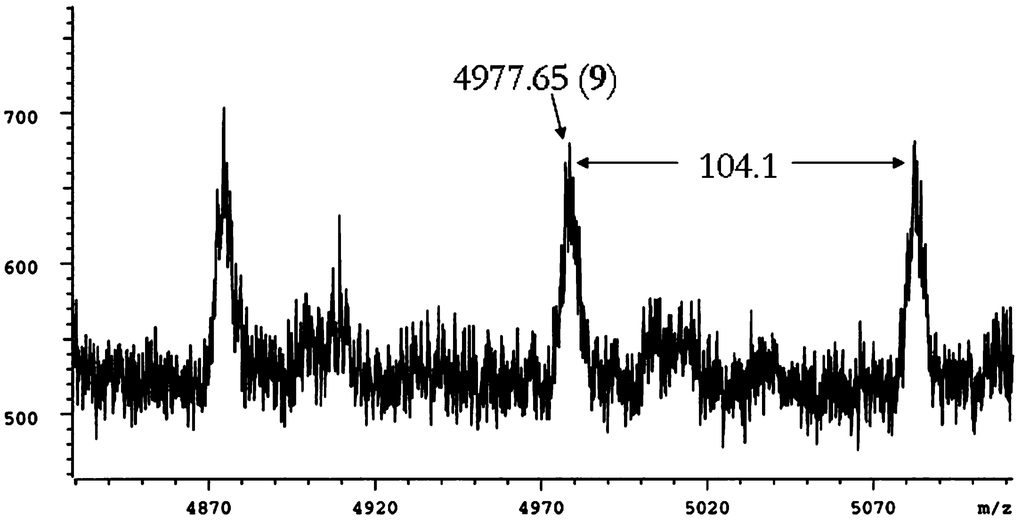


Figure 6. Enlargement of trimer region (*m*/*z* 4840−5110) shown in Figure 3.

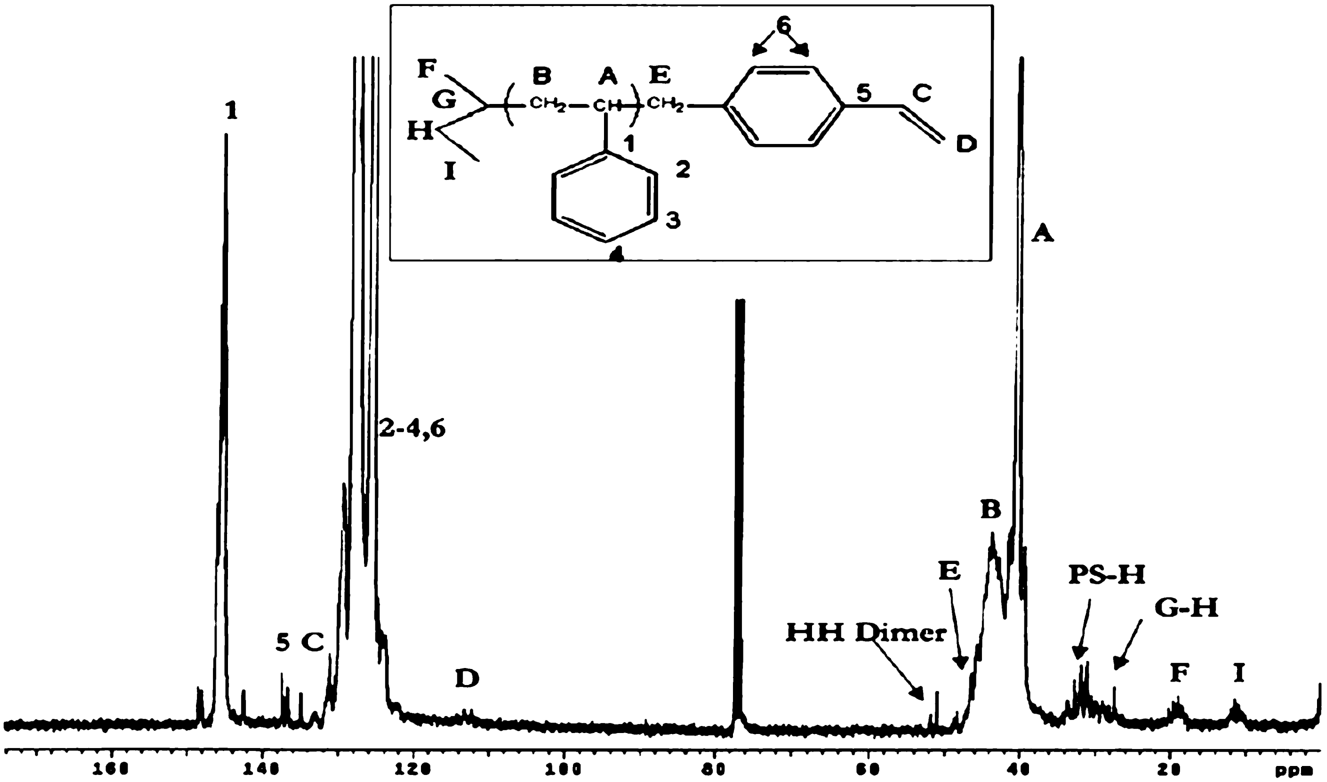


Figure 7. ^{13}C NMR spectrum of styryl-functionalized polystyrene (sample 1, Table 1).

On the basis of the SEC, ^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS results, it is clear that a variety of products are formed from the reaction of PSLi with VBC in benzene and that this is not an efficient procedure for the synthesis of the styryl-functionalized macromonomer. The reactions leading to the formation of macromonomer and side products were Wurtz coupling, lithium−halogen exchange, and addition to the vinyl group. On the basis of the structures of the side reaction products, it is concluded that all three of these reactions must occur, sometimes in combination. It is noteworthy that although previous investigations of this reaction have shown SEC evidence for the formation of significant amounts of dimer, the structures of the dimeric products, and the structures of the non-macromonomer, nondimer fractions have not been previously elucidated.

Reaction of PSLi with VBC in Benzene in the Presence of Lithium Halides. The use of additives to modify the reactivity and/or selectivity of PSLi was considered as a means of increasing the yield of functionalized product. In particular, Tochtermann[39] recognized that salt-free solutions of lithium compounds are more reactive than those containing salts. Glaze and West[40] found that mixtures of alkyllithium compounds with lithium halides form complexes of significantly decreased reactivities, so much so that such solid complexes were not reactive in air although they would decompose in water.

Previous reports have shown that lithium chloride effectively controlled the alkyllithium-initiated polymerization of acrylates.[41−44] In an example that has particular relevance to the current topic, lithium chloride has also been used as an additive in functionalization reactions where it has been found

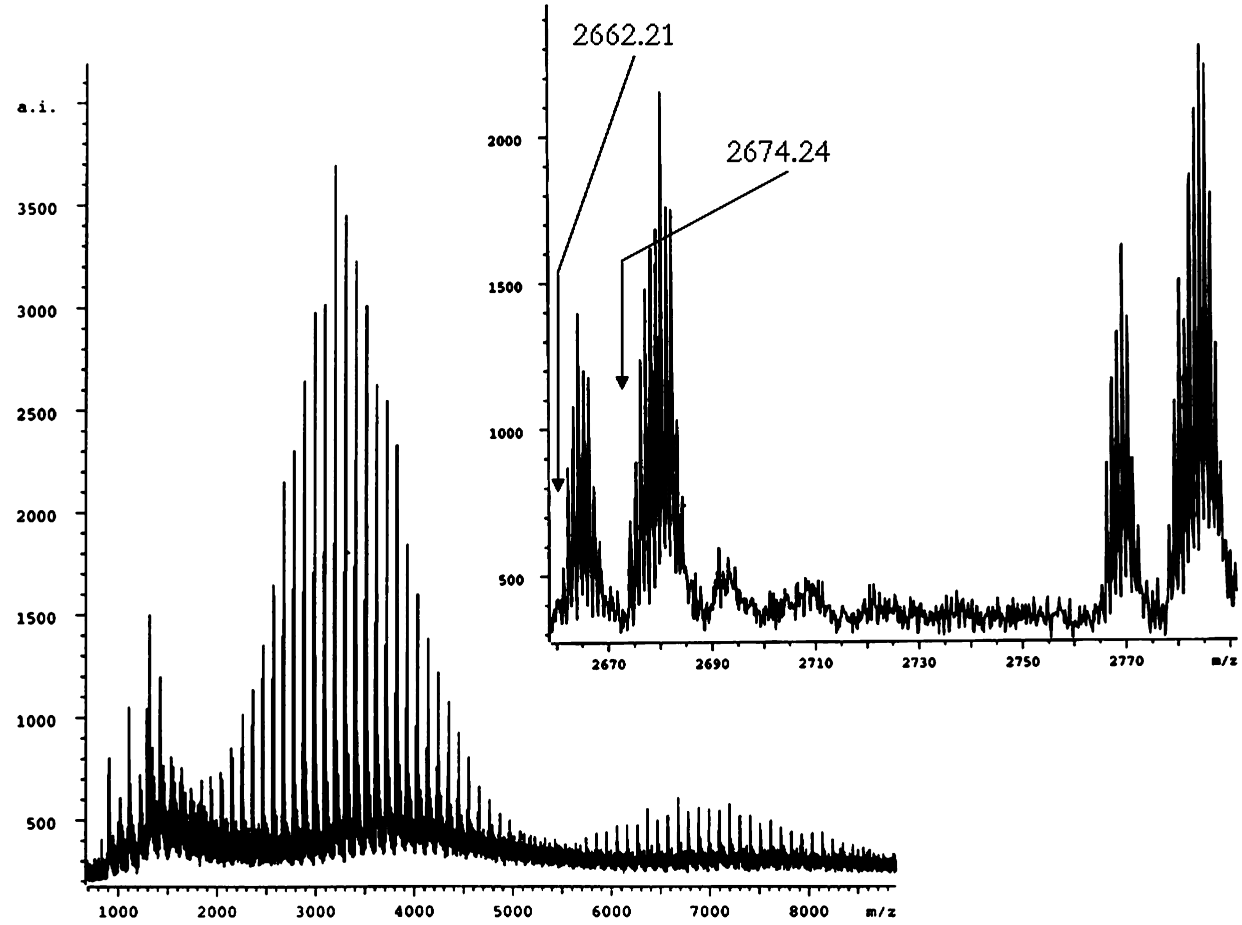


Figure 8. MALDI-TOF mass spectrum of PSLi functionalized with VBC (10 equiv) in the presence of lithium chloride (2 equiv) (sample 5, Table 1) and expansion of the region between *m*/*z* 2660−2790.

to slow the rates of reaction as well as to increase the selectivity. In particular, when the reaction of poly(styryl)lithium with 3-(dimethylamino)propyl chloride was effected in hydrocarbon solvent at room temperature, the resulting product distribution consisted of 67% of the amine-functionalized polystyrene, 23% of the nonfunctionalized polystyrene dimer, and 10% hydrogen-terminated product.[14] It was proposed that the dimer was formed by lithium halogen exchange followed by Wurtz coupling with PSLi while the hydrogen-terminated product resulted from an E_2-type elimination of hydrogen chloride from the alkyl halide by hydrogen transfer to PSLi. However, the tertiary amine-functionalized polymer was quantitatively formed when the same reaction was effected in the presence of 1 equiv of lithium chloride.[45] Thus, it was of interest to investigate the effect of added lithium chloride on the analogous functionalization of PSLi with VBC.

From SEC analysis of the products from the reaction of PSLi and VBC (10 equiv), it was found that added lithium chloride (1.5−10 equiv relative to *sec*-BuLi) decreased the amount of dimer product from 55% (see Figure 3 and Table 1) in the absence of LiCl to 40% (sample 6, Table 1). However, the styryl macromonomer functionality was not significantly improved (26% functionality with 10 equiv of LiCl vs 21% in the absence of LiCl). However, in the presence of the more soluble lithium salt, LiBr (20 equiv), the amount of dimer formation was still high (51%), but the styryl macromonomer functionality increased to 56% using 30 equiv of VBC (sample 4, Table 1).

The MALDI-TOF mass spectrum of polymers produced in the presence of 2 equiv of lithium chloride is shown in Figure 8 (sample 5, Table 1). There are two series of peaks, and within each series individual peaks are separated by *m*/*z* 104.1, corresponding to a styrene repeat unit. The main series of peaks are assigned to the polystyrene macromonomer (**1**). For example, the peak at *m*/*z* 2674.24 corresponds to a polystyrene 23-mer with one butyl group and one vinylbenzyl group: calculated monoisotopic mass $\{57.0704\ (C_4H_9) + 23 \times 104.0626\ [(C_8H_8)_{23}] + 117.0704\ (C_9H_9) + 106.9045\ ({}^{107}Ag^+)\} = 2674.49$ Da. The second series of peaks corresponds to the hydrogen-terminated polymers. For example, the peak at *m*/*z* 2662.21 corresponds to a polystyrene 24-mer with one butyl group and a proton: calculated monoisotopic mass $\{57.0704\ (C_4H_9) + 24 \times 104.0626\ [(C_8H_8)_{24}] + 1.0078\ (H) + 106.9045\ ({}^{107}Ag^+)\} = 2662.49$ Da. The formation of nonfunctionalized polystyrene may result from the abstraction of a proton from the benzyl group on the functionalization agent by PSLi. A precedent for this reaction has been reported from the reaction of benzyl chloride with organolithium compounds.[46,47] It is interesting to note that this product was not formed in the absence of LiCl, although many other products were formed. It is also noteworthy that no products were formed from multiple additions to VBC (**6**, **7**) or from elimination of the lithium−halogen exchange product (**4**) as observed for the analogous reaction effected in the absence of LiCl. Thus, addition of lithium chloride dramatically changed the chemistry for the reaction of PSLi with VBC.

The MALDI-TOF MS was also used in the analysis of the region corresponding to twice the molecular weight of the base polymer. Figure 9 is an expanded view of this higher molecular weight region. It is noteworthy that although the polymer sample

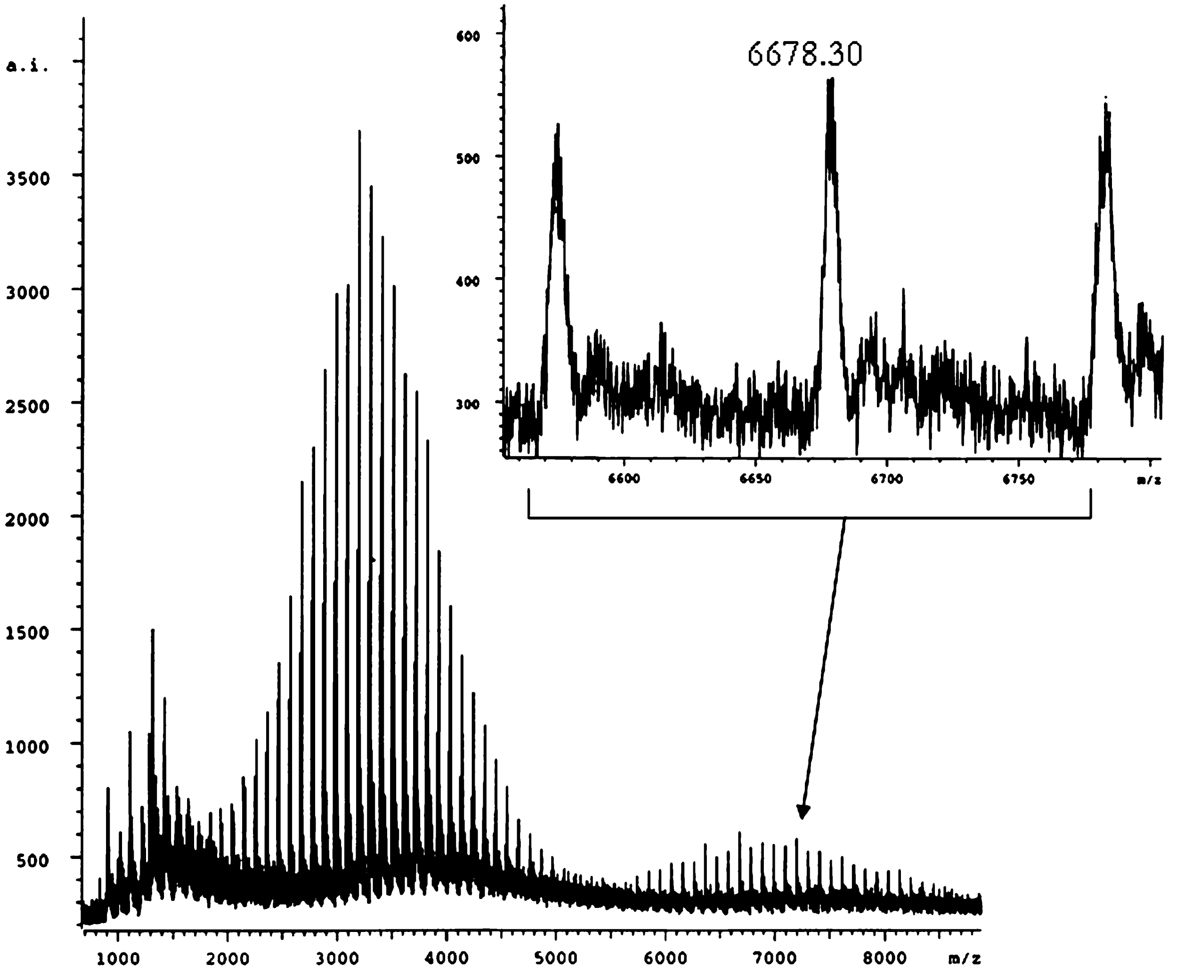


Figure 9. MALDI-TOF MS spectrum of functionalization product (sample 5, Table 1) and expansion of the region corresponding to dimer.

analyzed was determined to contain ~35% dimer by SEC, the dimer region in the mass spectrum is diminished compared to the reaction in the absence of LiCl (Figure 3). The enlargement of this region shows one distribution of peaks, differing by *m*/*z* 104.2 units. The peak at $m/z = 6678.30$ corresponds to a polystyrene 62-mer with two butyl groups $\{2 \times 57.1159\ [(C_4H_9)_2] + 62 \times 104.1521\ [(C_8H_8)_{62}] + 107.87\ (^{107}Ag^+)\} =$ 6679.53 Da. This is analogous to the dimer region observed in the absence of lithium chloride and presumably corresponds to a head-to-head dimer (**3**) resulting from a lithium−chlorine exchange reaction as discussed previously (see Scheme 1). In conclusion, although the use of lithium halides seems to increase the selectivity for the functionalization reaction, it does not lead to the formation of high yields of the desired macromonomer.

Reaction of PSLi with VBC in Benzene in the Presence of Lithium 2,3-Dimethyl-3-pentoxide. The effect of lithium alkoxides on the reaction of PSLi with VBC was also investigated. In general, lithium alkoxides are always present to some extent when performing alkyllithium-initiated polymerizations. Lithium alkoxides are formed by the reaction of organolithium compounds with hydrolytic impurities and oxygen.[13] For example, water will react with organolithium compounds to form lithium hydroxide.[48] The reaction of organolithium compounds with oxygen can also form alkoxides.[49,50] When utilized as an adjuvant in the functionalization of polymeric organolithiums, lithium alkoxides were observed to improve the selectivity of the nucleophilic chain end. For example, Quirk and Jiang[51] reported that the addition of 5 equiv of lithium alkoxide decreased the amount of dimer formation from 48% to less than 3% for the reaction of polymeric organolithiums with 3-glycidoxypropyltrimethoxysilane in hydrocarbon solvent at room temperature. With this background, the effect of lithium

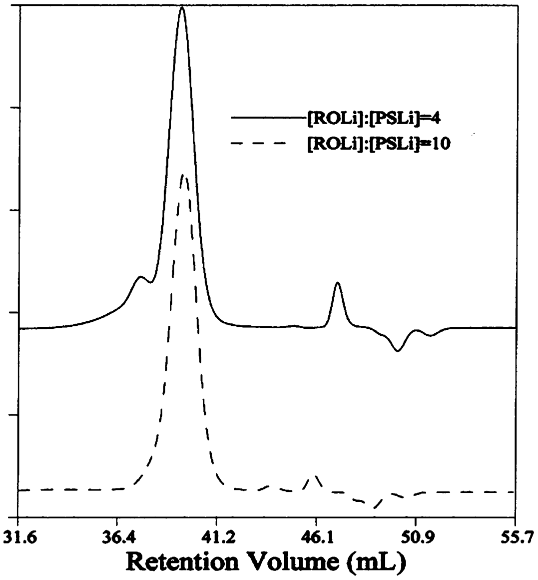


Figure 10. SEC chromatograms for products from functionalization of PSLi with VBC in the presence of lithium 2,3-dimethyl-3-pentoxide (samples 7 and 9, Table 1): Conditions: [DMPOLi]:[VBC]:[PSLi] = 4:20:1 (top); [DMPOLi]:[VBC]:[PSLi] = 10:20:1 (bottom).

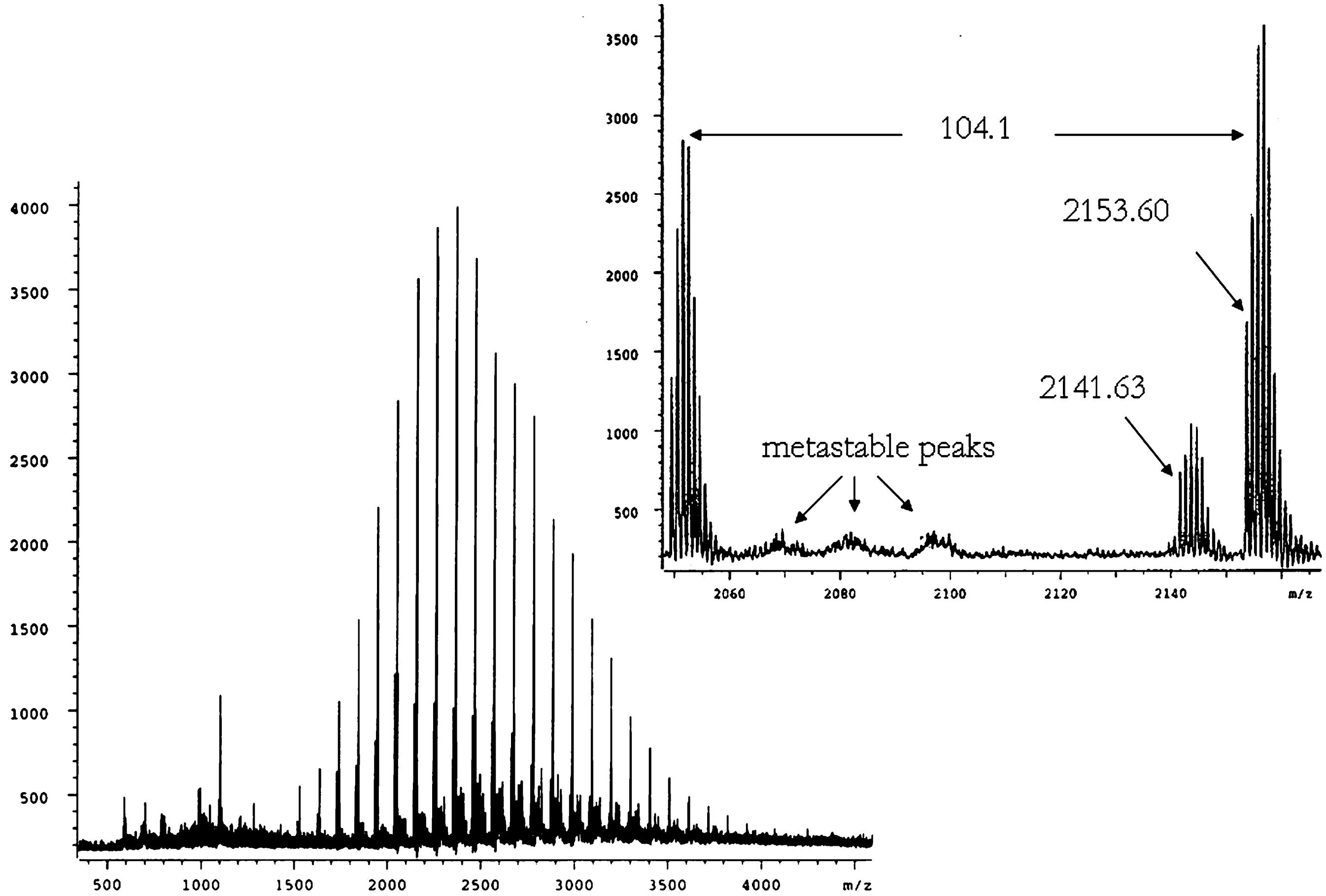


Figure 11. MALDI-TOF mass spectrum of macromonomer functionalized in the presence of 4 equiv of lithium 2,3-dimethyl-3-pentoxide (sample 7, Table 1).

alkoxide on the reaction of PSLi with VBC was investigated.

The lithium alkoxide chosen for investigation was lithium 2,3-dimethyl-3-pentoxide (DMPOLi) because of its solubility in hydrocarbon solvent.[52−55] DMPOLi was readily generated in situ by reacting the corresponding alcohol with *sec*-butyllithium. When 4 equiv of alkoxide relative to *sec*-butyllithium was used in the reaction of PSLi with VBC (sample 7, Table 1), it was found that the amount of dimer was reduced to ≈10 wt % as determined by SEC analysis (Figure 10). No dimer was observed by SEC analysis when the ratio of DMPOLi to *sec*-BuLi was increased to 10 (sample 9, Table 1). The styryl functionalities of the resulting macromonomers as determined by ^{1}H NMR were 54% and 81% using 4 and 10 equiv of DMOPLi, respectively; the functionalities determined by UV−vis spectroscopic analyses were 57% and 98% using 4 and 10 equiv of DMOPLi, respectively. Thus, there is a discrepancy between the macromonomer functionality determined by ^{1}H NMR compared to UV−vis analyses. In general, it has been observed that analysis by ^{1}H NMR usually underestimates the macromonomer functionality.

Polymer samples that had been functionalized in the presence of lithium alkoxides were analyzed by MALDI-TOF MS. The MALDI-TOF mass spectrum in Figure 11 corresponds to the product from the functionalization of a poly(styryl)lithium (M_n = 2700 g/mol; M_w/M_n = 1.03) with VBC in the presence of 4 equiv of DMPOLi (sample 7, Table 1). Two resolved series of peaks can be seen in this spectrum. Within each series the peaks are separated by *m*/*z* 104.1, corresponding to a styrene repeat unit. The larger series of peaks can be assigned to the macromonomer product. For example, the peak at *m*/*z* 2153.60 corresponds to a polystyrene 18-mer with a vinylbenzyl group and a butyl group: calculated monoisotopic mass {57.0704 (C_4H_9) + 18 × 104.0626 [$(C_8H_8)_{18}$] + 117.0704 (C_9H_9) + 106.9045 ($^{107}Ag^+$)} = 2154.17 Da. The smaller series of peaks corresponds to hydrogen terminated polystyrene. For example, the peak at *m*/*z* 2141.63 corresponds to the silver adduct of a hydrogen terminated polystyrene 19-mer having one butyl group and a proton: calculated monoisotopic mass {57.0704 (C_4H_9) + 19 × 104.0626 [$(C_8H_8)_{19}$] + 1.0078 (H) + 106.9045 ($^{107}Ag^+$)} = 2142.17 Da. Smaller, unresolved bumps can also be observed in the expanded region, and these correspond to metastable peaks.

The mass spectrum for products of the functionalization of PSLi (M_n = 1700 g/mol; M_w/M_n = 1.01) effected in the presence of 10 equiv of DMPOLi exhibits only two series of peaks as well (Figure 12). Within each series, peaks are separated by *m*/*z* 104.1, corresponding to one styrene repeat unit. The dominant series of peaks corresponds to styrene-functionalized macromonomer. For example, the peak at *m*/*z* = 1737.96 corresponds to a polystyrene 14-mer with one butyl group and one vinylbenzyl group: calculated monoisotopic mass {57.0704 (C_4H_9) + 14 × 104.0626 [$(C_8H_8)_{14}$] + 117.0704 (C_9H_9) + 106.9045 ($^{107}Ag^+$)} = 1737.92 Da. The smaller series of resolved peaks represents a small amount of hydrogen-terminated polymer. For example, the peak at *m*/*z* 1725.93 corresponds to the silver adduct of a polystyrene 15-mer with one butyl group and a proton: calculated monoisotopic mass {57.07042 (C_4H_9) + 15 × 104.0626 [$(C_8H_8)_{15}$] + 1.0078 (H) + 106.9045 ($^{107}Ag^+$)} = 1725.92 Da. Comparison of Figure 10 with Figure 13 shows that the relative amount of nonfunctionalized polystyrene is much less in the presence of the larger amount of DMPOLi (10 vs 4 equiv). In agreement with the

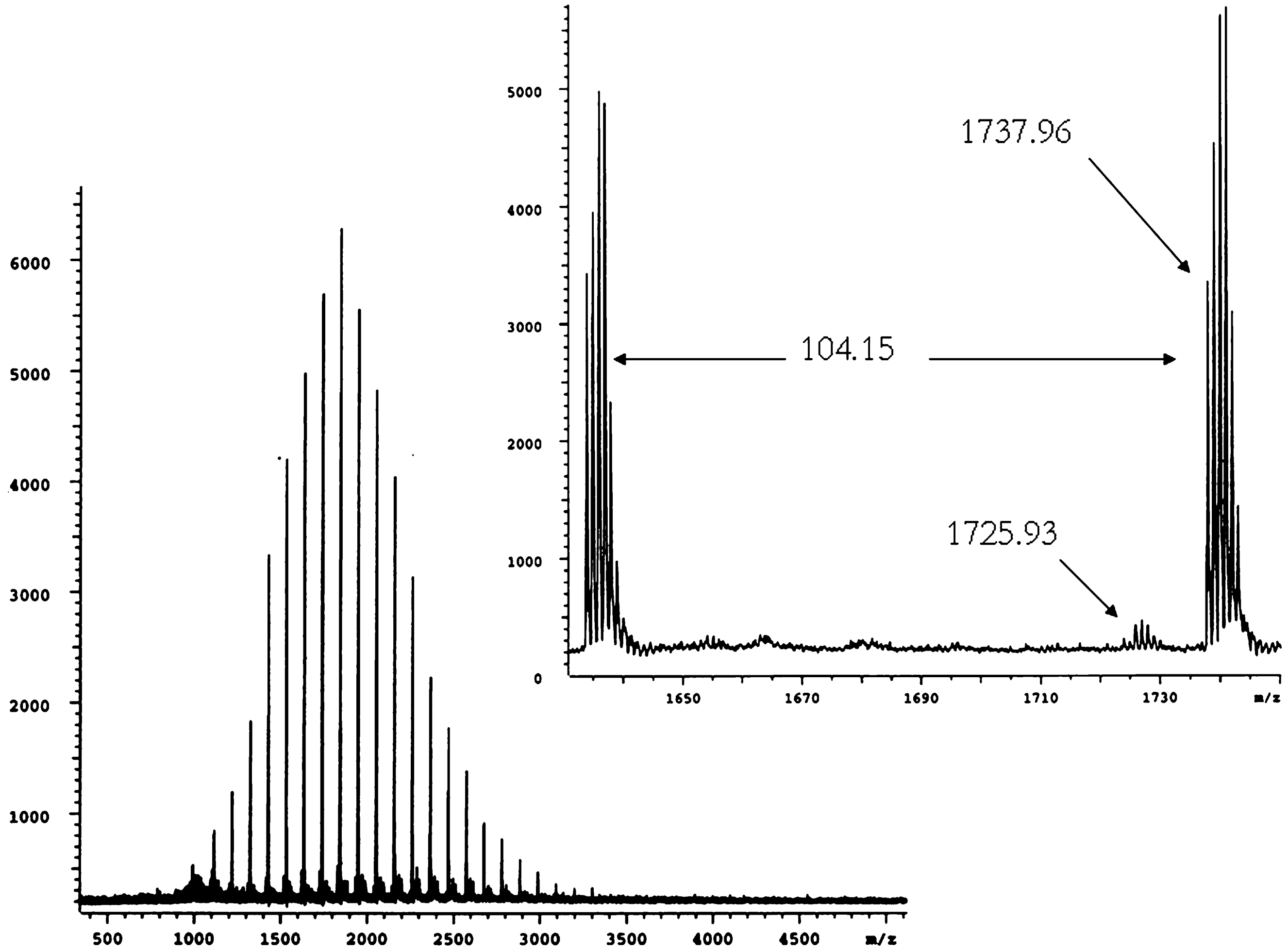


Figure 12. MALDI-TOF mass spectrum of macromonomer functionalized in the presence of 10 equiv of lithium 2,3-dimethyl-3-pentoxide (sample 9, Table 1).

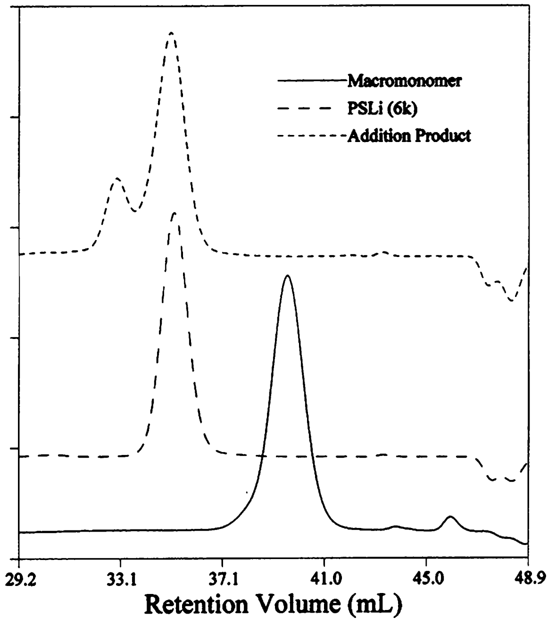


Figure 13. SEC addition study showing peaks of styrene-terminated macromonomer (sample 9, Table 1; 2K), poly(styryl)lithium (6K), and addition product.

SEC results shown in Figure 10, the mass spectrum for macromonomer synthesized in the presence of 10 equiv of DMPOLi also shows no evidence for dimer formation, in striking contrast to polymer products formed either without additives or in the presence of lithium chloride (see Table 1).

Thus, the MALDI-TOF mass spectrometry results combined with the SEC results are consistent with the ability of added lithium alkoxide (DMPOLi) to suppress not only dimer formation but also the formation of side products resulting from addition to the vinyl group of VBC and hydrogen abstraction. The ^{1}H NMR analysis of the functionalizations of PSLi with VBC effected in the presence of 4 and 10 equiv of DMPOLi indicated functionalities of 54 and 81%, respectively. However, the apparent lower functionality obtained by ^{1}H NMR analysis for the sample prepared in the presence of 10 equiv of DMPOLi is believed to be erroneous based on the functionality determined by UV−vis analysis of this sample (98%). From the ratios of the intensities for the monoisotopic peaks for the nonfunctional compared to the macromonomer in Figure 12, the amount of nonfunctional polymer corresponds to only ca. 2%.

To further investigate the functionality of the macromonomer, the macromonomer produced in the presence of 10 equiv of DMPOLi (sample 9, Table 1) was reacted with 2 equiv of PSLi (M_n = 6000 g/mol; M_w/M_n = 1.01) in benzene for 12 h. After quenching with degassed methanol and precipitation into methanol, the polymer products were analyzed by SEC. As shown in the SEC chromatograms in Figure 13, only two peaks are observed; one peak corresponds to the product from addition of PSLi to the macromonomer, and the other peak is assigned to the base polymer corresponding to the excess PSLi. No peak is observed at the elution volume corresponding to the macromonomer. These results are consistent with the MALDI-TOF MS results, indicating that the macromonomer is formed in high yield (≥98%) from the reaction of PSLi with VBC in the presence of 10 equiv of lithium alkoxide.

It is noteworthy that the purity of the VBC used in this study was 90% (Aldrich). Purification of this material consisted of passage through a column of calcined aluminum oxide followed by storage and distillation from calcium hydride under vacuum. From the high yield of macromonomer obtained and the absence of detectable products resulting from incorporation of other organic residues into the polymeric products, it is concluded that no deleterious impurities were present in VBC after purification.

Conclusions. The functionalization of poly(styryl)lithium with vinylbenzyl chloride in hydrocarbon solution without additives is an inefficient method for the synthesis of the corresponding styryl-functionalized macromonomer. The desired macromonomer is obtained in only 21% yield; other products include the corresponding head-to-head dimer and products from addition of PSLi to the double bond of vinylbenzyl chloride. Addition of lithium halides decreases the amount of dimer formation and eliminates the products resulting from addition of PSLi to the vinyl group of VBC. However, the yield of macromonomer was still low (56%). The addition of lithium 2,3-dimethyl-3-pentoxide dramatically decreased the amount of dimer formation, and nearly quantitative (≥98%) functionalization was observed in the presence of 10 equiv of this salt.

Acknowledgment. The authors thank Dynasol Elastomeros and Sartomer for financial support and FMC Corp., Lithium Division, for samples of *sec*-butyllithium and dibutylmagnesium.

References and Notes

(1) Odian, G. G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: New York, 2004.
(2) Kawakami, Y. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1987; Vol. 6, p 195.
(3) Percec, V.; Pugh, C.; Nuyken, O.; Pask, S. D. Macromonomers, Oligomers and Telechelic Polymers. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Elmsford, NY, 1989; Vol. 6, p 281.
(4) Yamashita, Y. *Chemistry and Industry of Macromonomers*; Huthig and Wepf Verlag: Basel, 1993; Vol. XII, p 376.
(5) Ito, K.; Kawaguchi, S. *Adv. Polym. Sci.* **1999**, *142*, 129−178.
(6) Ito, K. *Prog. Polym. Sci.* **1998**, *23*, 581−620.
(7) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(8) Gnanou, Y. *Indian J. Chem.* **1993**, *31*, 317−338.
(9) Rempp, P. F.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1−53.
(10) Quirk, R. P.; Gomochak Pickel, D. L.; Schulz, G. O. Macromonomers as Precursors for Thermoplastic Elastomers. In *Thermoplastic Elastomers*, 3rd ed.; Holden, G., Kricheldorf, V. R., Quirk, R. P., Eds.; Hanser: Cincinnati, OH, 2004; pp 323−363.
(11) Peruch, F.; Lahitte, J.-F.; Isel, F.; Lutz, P. J. *Macromol. Symp.* **2002**, *183*, 159−164.
(12) Pantazis, D.; Chalari, I.; Hadjichristidis, N. *Macromolecules* **2003**, *36*, 3783−3785.
(13) Wakefield, B. J. *Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974.
(14) Quirk, R. P.; Han, K.; Lee, Y. *Polym. Int.* **1999**, *48*, 99−108.
(15) Asami, R.; Takaki, M.; Hanahata, H. *Macromolecules* **1983**, *16*, 628−631.
(16) Takaki, M.; Asami, R.; Kuwata, Y. *Macromolecules* **1979**, *12*, 378−382.
(17) Takaki, M.; Asami, R.; Kuwata, Y. *Polym. J.* **1979**, *11*, 425−428.
(18) Schulz, G. O.; Milkovich, R. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 148−152.
(19) Milkovich, R.; Chiang, M. T. 3,786,116, 1974.
(20) Milkovich, R. In *Anionic Polymerization: Kinetics, Mechanisms and Synthesis*; McGrath, J., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; p 41.
(21) Gnanou, Y.; Lutz, P. *Makromol. Chem.* **1989**, *190*, 577−88.
(22) Greber, G.; Balciuna, A. *Makromol. Chem.* **1964**, *79*, 149−160.
(23) Greber, G.; Balciunas, A. *Makromol. Chem.* **1963**, *69*, 193−205.
(24) Greber, G.; Reese, E. *Makromol. Chem.* **1962**, *55*, 96−120.
(25) Hirao, A.; Hayashi, M.; Nakahama, S. *Macromolecules* **1996**, *29*, 3353−3358.
(26) Hayashi, M.; Nakahama, S.; Hirao, A. *Macromolecules* **1999**, *32*, 1325−1331.
(27) Knauss, D. M.; Al-Muallem, H. A. *J. Polym. Chem., Polym. Chem. Ed.* **2000**, *38*, 4289−4298.
(28) Carrot, G.; Hilburn, J.; Knauss, D. M. *Polymer* **1997**, *38*, 6401−6407.
(29) Quirk, R. P.; Ma, J. *Polym. Int.* **1991**, *24*, 197−206.
(30) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447−454.
(31) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359−409.
(32) Ishizone, T.; Kato, R.; Ishino, Y.; Hirao, A.; Nakahama, S. *Macromolecules* **1991**, *24*, 1449−1454.
(33) Hirao, A.; Kitamura, K.; Takenaka, K.; Nakahama, S. *Macromolecules* **1993**, *26*, 4995−5003.
(34) Ishizone, T.; Okamoto, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1999**, *32*, 1453−1462.
(35) Reutenauer, S.; Hurtrez, G.; Dumas, P. *Macromolecules* **2001**, *34*, 755−760.
(36) Meyer, N.; Delaite, C.; Hurtrez, G.; Dumas, P. *Polymer* **2002**, *43*, 7133−7139.
(37) Meyer, N.; Eddine, M. N.; Delaite, C.; Hurtrez, G.; Dumas, P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3329−3335.
(38) Hensley, D. R.; Goodrich, S. D.; Huckstep, A. Y.; Harwood, H. J.; Rinaldi, P. L. *Macromolecules* **1995**, *28*, 1586−1591.
(39) Tochtermann, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 351−371.
(40) Glaze, W.; West, R. *J. Am. Chem. Soc.* **1960**, *82*, 7−4437.
(41) Janata, M.; Lochmann, L. *Makromol. Chem.* **1993**, *1993*, 625−636.
(42) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jerome, R.; Teyssie, P. *Macromolecules* **1990**, *23*, 2618−22.
(43) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, P.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442−1444.
(44) Zune, C.; Jerome, R. *Prog. Polym. Sci.* **1999**, *24*, 631−664.
(45) Quirk, R. P.; Lee, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 145−151.
(46) Hoeg, D. F.; Lusk, D. I. *J. Am. Chem. Soc.* **1964**, *86*, 928−929.
(47) Hoeg, D. F.; Lusk, D. I. *J. Organomet. Chem.* **1966**, *5*, 1−12.
(48) Worsfold, D. J.; Bywater, S. *Makromol. Chem.* **1963**, *65*, 245−247.
(49) Fetters, L. J.; Firer, E. M. *Polymer* **1977**, *18*, 306−307.
(50) Quirk, R. P.; Chen, W. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2993−3000.
(51) Quirk, R. P.; Jiang, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42*, 27−28.
(52) Ashraf, A.; Smith, S. D.; Satkowski, M. M.; Spontak, R. J.; Clarson, S. J.; Lipscomb, G. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 581−582.
(53) Smith, S. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 48−49.
(54) Smith, S. D.; Ashraf, A.; Satkowski, M. M.; Spontak, R. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 651−652.
(55) Smith, S. D.; Ashraf, A.; Satkowski, M. M.; Grothaus, J. T.; Kornfield, J. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37*, 639−640.

MA0511604