Macromolecules **2009**, *42*, 2411−2418

Dendritic Polystyrene with Hydroxyl-Functionalized Branch Points by Convergent Living Anionic Polymerization

Jack T. Bender and Daniel M. Knauss*

Chemistry Department, Colorado School of Mines, Golden, Colorado 80401

Received November 26, 2008; Revised Manuscript Received January 30, 2009

ABSTRACT: Dendritic polystyrene with hydroxyl functional groups at each branch point was synthesized using convergent living anionic polymerization. The polymer samples were formed by the slow addition of a 1/10 molar mixture of 4-vinylstyrene oxide/styrene to living polystyryllithium chains in a benzene/THF solution. The 4-vinylstyrene oxide contains both a vinyl group, which can undergo anionic vinyl addition polymerization, and an epoxide moiety, which can undergo a ring-opening addition reaction to result in an unreactive or terminated lithium alkoxide. The extent of generational growth for the dendritic polymers was calculated by molecular weight analysis and by titration of hydroxyl groups to determine generations as high as 3.8 and polymers with up to 14 hydroxyl groups situated at the branch points. Addition of LiCl to the benzene/THF solutions containing polystyryllithium chains resulted in the highest generational growth of the polymers. The polymers were characterized using gel permeation chromatography coupled with a MALLS detector, ^{1}H NMR spectroscopy, and differential scanning calorimetry.

Introduction

The interest in highly branched polymers has resulted in the development of numerous methods for the synthesis of stars, combs, dendritic polymers, and polymers with more complex architectures.[1−9] Dendritic polymers can be classified as either dendrimers, dendritic polymers, or polymers with a branch-on-branch topology but which also contain a significant molecular weight between branch points. Examples of dendritic polymers with oligomeric chains between branch points include comb-burst polymers,[10] arborescent polymers,[11−18] dendrigraft polymers,[19−23] block-graft polymers,[24] inimer−comonomer polymers,[25−38] dendrimer-like stars[39−46] and other dendritic polymers,[47−51] polymers by TERMINI,[52−54] and, in our own work, polymers produced by convergent living anionic polymerization.[55−60]

Convergent living anionic polymerization is a technique that is based on in-situ chain-end functionalization and polymerization. A coupling agent, or branching monomer, is designed to contain both a terminating group, which can quickly and quantitatively react with the growing polymer chain end, and a polymerizable vinyl group that can add to a growing chain to maintain a living reactive site. For example, in the living anionic polymerization of styrene, a coupling agent such as vinylbenzyl chloride (VBC) or 4-(chlorodimethylsilyl)styrene (CDMSS) can quantitatively react with a living chain end to produce a vinyl-functionalized macromonomer.[57,60] If that macromonomer is formed in the presence of other reactive polymer chains, addition to the vinyl group occurs to result in a branch. The addition of a comonomer along with the coupling agent results in a dendritic polymer with comonomer units between the branch points. We have used this technique to synthesize dendritic polystyrene homopolymers and copolymers as well as other more complex polymer architectures.[55−60]

Continuing to investigate this method of in-situ chain-end functionalization as a route to branched polymers, we have begun the study of coupling agents that can introduce a functional group at the branch point. In this paper, we report the synthesis of dendritic polystyrenes using a coupling agent, 4-vinylstyrene oxide, which contains both a polymerizable vinyl group and an epoxide functional group. The epoxide is proposed to be capable of termination of a living anionic chain through a single ring-opening addition reaction. The ring opening of the vinyl-functionalized styrene oxide results in a lithium alkoxide chain end, which under the reaction conditions is an effectively terminated chain. The vinyl group is available for addition with remaining living anionic chains, and the sequence of macromonomer formation and polymerization with slow addition of coupling agent can be effected. Copolymerization with added styrene and final acidification of the alkoxide groups results in dendritic polystyrene with hydroxyl functional groups at each branch point.

Experimental Section

Materials. All glassware used in reactions was heated in an oven at 150 °C overnight, assembled hot, and flame-dried under argon purge. All solvents, sodium hydroxide, potassium carbonate, and lithium chloride were acquired from Fisher Scientific. 2,6-Di-*tert*-butyl-*p*-cresol was obtained from MCB Chemicals. All other chemicals were obtained from Aldrich. Benzene was washed with concentrated sulfuric acid, then with 1 M sodium hydroxide, and finally with water and dried with CaCl before distillation under argon from blue sodium benzophenone ketyl. HPLC grade THF was distilled under argon from blue sodium benzophenone ketyl. Styrene was washed with 2.5 M sodium hydroxide solution, then washed with water, and dried with $MgSO_4$ before being distilled from CaH_2 under reduced pressure (500 mTorr). Dimethyl sulfoxide (DMSO) was distilled from CaH_2 under reduced pressure (500 mTorr). Styrene oxide was distilled from CaH_2 under reduced pressure (500 mTorr) immediately before use. *sec*-Butyllithium (1.3 M) in cyclohexane from Aldrich was used without further purification. Flasks containing LiCl and *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) were put on a vacuum line in the presence of phosphorus pentoxide at 100 mTorr for 24 h. Pyridine was dried over calcium hydride and distilled under argon. Acetyl chloride was distilled immediately before use. All other chemicals were used as received. Gas-tight syringes were kept in a desiccator under reduced pressure. Immediately before use, the syringes were heated with a heat gun and purged with argon. Metered syringe injections were performed with a Model 100 kd Scientific syringe pump.

4-Vinylbenzaldehyde. 4-Vinylbenzaldehyde was prepared by a Wittig reaction similar to a procedure reported by Le Bigot.[61] Methyltriphenylphosphonium bromide (71.45 g, 0.200 mol) and potassium carbonate (35.0 g, 0.253 mol) were added to a 1 L three-necked flask fitted with a mechanical stirrer, a reflux condenser

---

* To whom correspondence should be addressed.

10.1021/ma802657c CCC: \$40.75

with argon bubbler, and a thermometer. The solids in the reaction vessel were mixed thoroughly. Terephthaldicarboxaldehyde (26.83 g, 0.200 mol) was dissolved in 200 mL of dioxane and 3 mL of water. The solution was added to the reaction flask, and the reaction mixture was refluxed for 4 h with vigorous stirring. The solution was cooled to room temperature and filtered through a coarse frit glass funnel. The filtrate was cooled, and the solvent was removed by rotary evaporation. The resulting solid was extracted with three 100 mL portions of hexane. The hexane volumes were combined, and the solvent was removed by rotary evaporation. Approximately 10 mg of 2,6-di-*tert*-butyl-*p*-cresol (BHT) was added to the resulting yellow oil, which was then distilled at 60−65 °C at 100 mTorr. The resulting colorless liquid (16.5 g, 61.5%) was fractionally vacuum distilled several times (each time from BHT) to remove starting material and any 1,4-divinylbenzene impurity. The pure product (8.2 g, 30.1%) was sealed under argon and stored at −25 °C. ^{1}H NMR: [δ, $CDCl_3$ relative to tetramethylsilane (TMS) at 0 ppm]: 5.41 (d, 1H), 5.88 (d, 1H), 6.73 (dd, 1H), 7.51 (d,2H), 7.81 (d, 2H), 9.95 (s, 1H).

Trimethyloxosulfonium Iodide. Trimethyloxosulfonium iodide was prepared by the procedure of Kuhn and Trischmann.[62] A 250 mL reaction flask containing a stirbar was fitted with a condenser and an argon inlet. DMSO (53.3 g, 0.68 mol) and methyl iodide (100 mL, 1.60 mol) were added to the reaction flask and refluxed under argon for 3 days. The dark brown solution was cooled, and the resulting yellow precipitate was filtered, washed with chloroform, and dried in a vacuum oven. The light yellow solid was recrystallized from water. The resulting white crystals (63.52 g, 42.3%) were crushed and dried in a vacuum oven in the presence of phosphorus pentoxide.

4-Vinylstyrene Oxide. Sodium hydride (1.64 g, 0.068 mol) and trimethyloxosulfonium iodide (12.50 g, 0.0684 mol) were added to a 500 mL three necked round-bottom flask containing a stir bar, a reflux condenser, an addition funnel, and a thermometer. DMSO (100 mL) was added very slowly to the flask with vigorous stirring to minimize the amount of foam generated as the hydrogen gas evolved. After the addition of the DMSO, the reaction was allowed to stir for an additional hour at room temperature. 4-Vinylbenzaldehyde (7.50 g, 0.057 mol) was dissolved in 20 mL of DMSO and was added dropwise to the solution over a 30 min period. The solution was heated to 50 °C for 1 h and then was quenched with 150 mL of water. The solution was extracted with three 100 mL portions of ether. The extracts were combined and dried with $MgSO_4$, and the ether was then removed by rotary evaporation. The resulting light yellow oil was distilled at 45−50 °C at 80 mTorr to yield the product (4.46 g, 53.8%). The product was sealed in a round-bottom flask using a rubber septum. The flask was purged with argon and stored at −25 °C, whereupon the liquid solidified. Elemental Analysis: Calcd for $C_{10}H_{10}O$: C, 82.16%; H, 6.89%; O, 10.94%. Found: C, 82.39%; H, 6.79%; O, 10.82%. ^{1}H NMR: [δ, $CDCl_3$ relative to tetramethylsilane (TMS) at 0 ppm]: 2.79 (dd, 1H), 3.14 (d, 1H), 3.84 (d, 1H), 5.24 (d, 1H), 5.73 (d, 1H), 6.70 (dd, 1H), 7.23 (d,2H), 7.38 (d, 2H).

Synthesis of Linear Polystyryllithium. A 125 mL round-bottom flask containing a stirbar and sealed with a rubber septum was flame-dried and purged with argon for 20 min. To the flask were added 35 mL of benzene and 2.2 mL of styrene (19.2 mmol) using a gas-tight syringe. *sec*-Butyllithium (1.5 mL, 2.0 mmol) was then added using a gas-tight syringe. The solution was allowed to stir for 2−4 h. The desired amount of tetrahydrofuran (either $[THF]/[PS^-Li^+] = 15$ or $[THF]/[PS^-Li^+] = 60$) was then introduced using a gas-tight syringe. A sample of the linear polystyrene (3.5 mL) was subsequently removed for analysis and injected into argon-purged methanol. The polystyryllithium solution was used in subsequent reactions as described below.

LiCl or TMEDA was added in some of the experiments. In these cases the additive was placed into the reaction flask after the flask was removed from the oven and before the addition of solvent or styrene. The flask was placed on a vacuum line for an additional 3 h at 100 mTorr. After purging with argon, the flask was sealed with a rubber septum.

Addition of Styrene Oxide: End-Capping. A stoichiometric amount of styrene oxide (0.24 g, 2.0 mmol) was introduced all at once to the polystyryllithium using a gas-tight syringe. The reaction was allowed to stir for 5 h and was then terminated by adding several drops of argon-purged glacial acetic acid. The polymer was precipitated into methanol, recovered by filtration, and dried in a vacuum oven.

Fast Addition of 4-Vinylstyrene Oxide: End-Capping. 4-Vinylstyrene oxide (0.28 g, 2.0 mmol) was injected into the polystyryllithium solution all at once using a gas-tight syringe, and the solution was allowed to stir for 5 h. The reaction was terminated by adding several drops of argon purged glacial acetic acid. The polymer was precipitated into methanol, recovered by filtration, and was placed in a vacuum oven to remove any residual solvent.

Slow Addition of 4-Vinylstyrene Oxide: Synthesis of Dendritic Polymers. A solution of styrene (2.2 mL, 19.2 mmol), 4-vinylstyrene oxide (0.28 mL, 2.0 mmol), and benzene (3 mL) was transferred to an argon-purged gas-tight syringe. The solution was introduced to the polystyryllithium solution over 4−6 h, using a metering syringe pump. The progress of the reaction was followed qualitatively by the change in color of the solution. The red-orange color typical of polystyryllithium faded with the addition of coupling agent solution to a very pale yellow and eventually became colorless. The reactions were terminated with argon-purged glacial acetic acid, and the polymer was precipitated into methanol. The polymer was isolated by filtration and dried in a vacuum oven.

Characterization. Molecular weights and polydispersity indices were determined by gel permeation chromatography (GPC). The measurements were performed on a HP model 1084B liquid chromatograph equipped with a Waters R401 refractive index detector and a Wyatt Technologies MiniDAWN multiangle laser light (MALLS) detector. The separation was achieved using THF as the eluent (flow rate of 1.0 mL/min) and two HP Plgel mixed D columns. The d*n*/d*c* (refractive index increment) of the polymers was determined to be 0.192 using an ABBE refractometer. ^{1}H NMR spectroscopy was performed on samples dissolved in deuterated chloroform using a Chemagnetics CMX Infinity 400. Glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer Pyris 1 instrument using Pyris software. The samples were scanned twice at 10 °C/min from 50 to 135 °C. The T_g was determined as the midpoint of the slope based on the extrapolation of the baselines from the second heat. Elemental analysis was performed by Huffman Laboratories (Golden, CO).

The average number of hydroxyl groups per polymer molecule was determined by an indirect titration method.[63−67] A weighed amount of the dendritic polymer (∼0.2000 g) was added to 10.0 mL of toluene in a round-bottom flask containing a stir bar. A 0.162 M stock solution of acetyl chloride in pyridine was prepared. 1.50 mL of stock solution was added to the dissolved polymer by graduated pipet, and the solution was allowed to stir overnight. Water (10 mL, 0.56 mol) was added to the solution to hydrolyze any remaining acetyl chloride. The solution was allowed to stir for 2 h. The solution was then titrated with a standardized 1.94×10^{-2} M NaOH solution with phenolphthalein as the indicator. A sample without the polymer was run as a blank. The amount of acetyl chloride consumed, equal to the amount of acetyl chloride titrated from the blank minus the amount titrated from the polymer solution, was used to calculate the hydroxyl concentration. Triplicate titrations were performed for each polymer and for the blank.

Results and Discussion

Our previous work in the development of a one-pot procedure for the synthesis of low-polydispersity dendritic polymers has been previously described.[57,60] In this method, a bifunctional coupling agent and styrene are slowly and continuously added to living polystyryllithium. CDMSS and VBC have been previously used as coupling agents to form dendritic polystyrenes. Both VBC and CDMSS have a vinyl group and a substitutable halide (Figure 1). The addition of the coupling

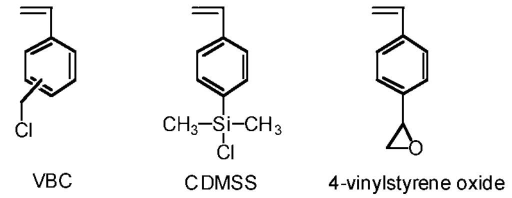


Figure 1. Coupling agents for the synthesis of dendritic polystyrene by convergent living anionic polymerization.

agent to the polystyryllithium results in either a substitution reaction with the halide, resulting in a vinyl-terminated macromonomer, or an addition reaction with the vinyl group, which results in coupling while maintaining a living chain end. The structure of the dendritic polymer is somewhat controlled by the relative rates of the substitution vs addition reactions and the rate of addition of the coupling agent into the reaction mixture. The use of a coupling agent with a faster substitution reaction relative to the addition at the vinyl group results in a macromonomer, while the slow addition of reagent ensures subsequent reaction of the macromonomer with an available living chain to form a coupled polymer. The dendritic polymer is a result of successive coupling reactions, and the termination occurs when the final stoichiometric amount of coupling agent is introduced. Addition of a comonomer, such as styrene, along with the coupling agent results in a dendritic polymer with comonomer units between branch points.

4-Vinylstyrene oxide (Figure 1), a bifunctional coupling agent with an epoxide group and a vinyl group, can also be expected to form dendritic polymers, although by a different mechanism. As the 4-vinylstyrene oxide is added to a solution of polystyryllithium, the living polymer chains can either react at the epoxide functional group of the coupling agent in a ring-opening reaction or react with the available vinyl group of the coupling agent. The addition reaction to the epoxide results in a deactivated polymer chain terminated by a lithium alkoxide, while the addition reaction to the vinyl group results in a living anionic chain capable of further reaction. Because the 4-vinylstyrene oxide is added slowly, successive coupling reactions can lead to a multigenerational branched polymer. By adding styrene along with the 4-vinylstyrene oxide coupling agent, polystyrene blocks can be produced between functionalized branch points (Scheme 1).

The 4-vinylstyrene oxide was synthesized (Scheme 2) in a two-step reaction from terephthaldicarboxaldehyde instead of direct epoxidation of divinylbenzene because all commercially available divinylbenzene is a mixture of the *ortho*, *meta*, and *para* isomers. The terephthaldicarboxaldehyde was converted to the 4-vinylbenzaldehyde by a Wittig reaction.[61] The aldehyde of the 4-vinylbenzaldehyde was then selectively epoxidized using dimethyloxosulfonium methylide formed by the addition of dimethyl sulfoxide to a sodium hydride/trimethyloxosulfonium iodide mixture.[68] The dimethyloxosulfonium methylide was used in favor of dimethylsulfonium methylide which is more commonly used for the epoxidation of aldehydes[69] because the dimethylsulfonium methylide also results in the epoxidation of the vinyl group.[68]

To synthesize a dendritic polymer by the desired process, the reaction of polystyryllithium with the epoxide ring of the 4-vinylstyrene oxide must be quantitative and relatively fast. The addition of styrene oxide to polystyryllithium can be used to model the end functionalization of polystyrene with an epoxide ring and to determine if oligomerization of epoxide groups will occur. The quantitative end functionalization of polystyryllithium with styrene oxide in benzene and benzene/THF solutions was previously investigated by Hasegawa and Quirk.[70,71] The reaction of polystyryllithium with styrene oxide was found to be significantly less than quantitative in purely hydrocarbon solutions.[70,72] The addition of 1.31 equiv of styrene oxide to a polystyryllithium solution in benzene resulted in ω-hydroxy-functionalized polystyrene (85.3%) and unfunctionalized polystyrene homopolymer and dimer (14.7%). The dimer was the result of an electron transfer reaction. The side reactions that led to the formation of unfunctionalized polystyrene were in part attributed to polystyryllithium aggregation. The aggregation of alkyllithium chains in hydrocarbon solutions has been extensively studied and is known to be decreased by the addition of THF.[73−76] The addition of THF to the benzene solution at the concentration of [THF]/[PSLi] = 15 resulted in the quantitative synthesis of ω-hydroxy-functionalized polystyrene.[70]

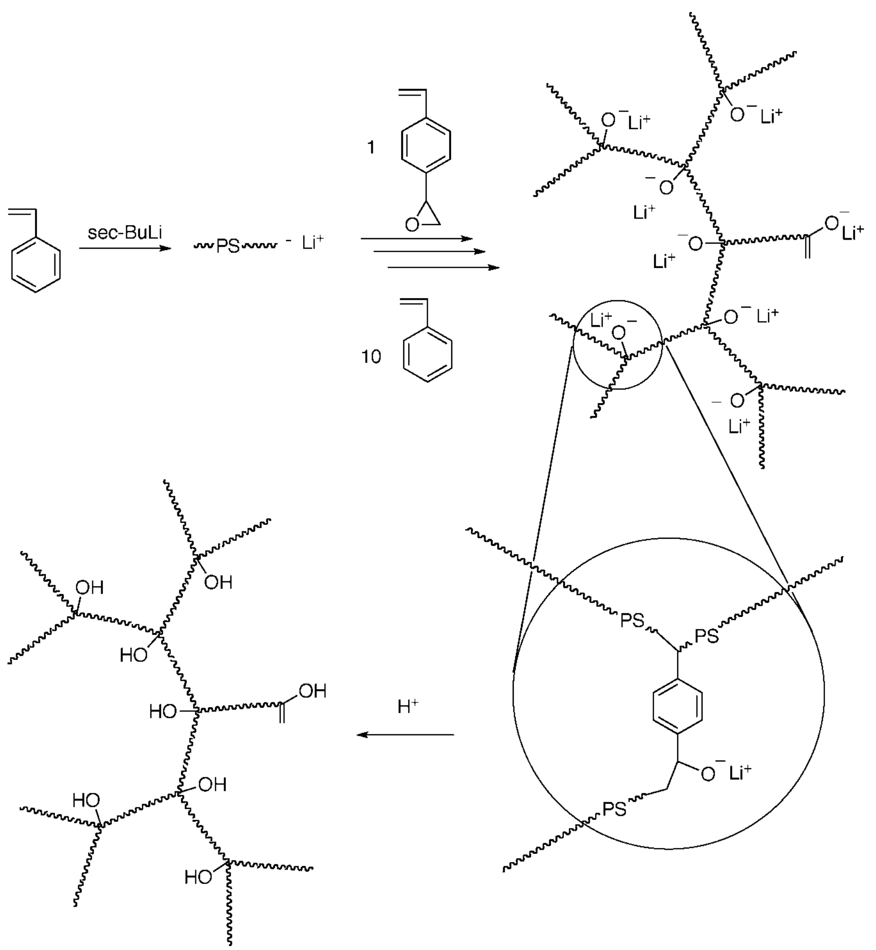
The regioselectivity of attack and epoxide oligomerization in the polystyryllithium reaction with styrene oxide has also been determined by Quirk.[71,77] MALDI-TOF mass spectrometry was used to confirm that no amount of styrene oxide oligomerization occurs in the end functionalization of polystyryllithium in a benzene/THF solution ([THF]/[PSLi] = 15).[71] The relative amounts of primary (47%) and secondary (53%) alcohol, which result from nucleophilic attack of the polystyryllithium on either the least hindered or most hindered carbons of the epoxide ring, were determined by ^{13}C NMR spectroscopy.

In order to further investigate the end-capping reaction of styrene oxide with polystyryllithium, we performed reactions at different THF concentrations. Polystyryllithium chains were synthesized using *sec*-butyllithium in benzene. An amount of THF, corresponding to either [THF]/[PSLi] = 15 or [THF]/[PSLi] = 60, was then added to the polystyryllithium solution. Although conditions exist in which alkyllithium species will react with tetrahydrofuran,[78−81] polystyryllithium has been shown to have negligible side reactions with up to 20% v/v THF in hydrocarbon solvents.[57,60] The addition of the styrene oxide (1.1 equiv to BuLi) to the living polystyryllithium chains was done all at once using a gas-tight syringe. The color of the solution turned immediately from red-orange, the color of polystyryllithium, to a light yellow in both cases. The yellow color continued to fade to colorless for both samples over time. The sample containing the higher concentration of THF faded more quickly, in less than 1 h, versus more than 5 h for the sample with the lower concentration of THF. Samples were terminated with glacial acetic acid, precipitated into methanol, and recovered by filtration.

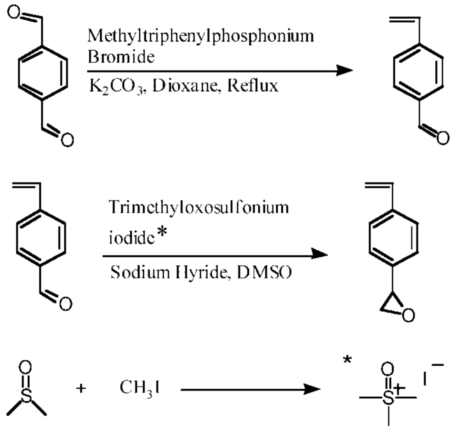
Characterization of the end-functionalized polystyrenes synthesized at both THF concentrations indicated the addition of styrene oxide to the polystyryllithium. The GPC plots of the end-capped polymers synthesized at both concentrations showed no evidence of any high molecular weight shoulder corresponding to dimerization of the initial chains. Figure 2 shows the GPC traces for the linear and end-capped polystyrene for [THF]/[PSLi] = 60. A similar result is observed for the reaction with [THF]/[PSLi] = 15, in agreement with the results of Quirk.[71] ^{1}H NMR spectroscopy was used to confirm that the polystyrene chains are capped with styrene oxide. The spectra for reactions at both concentrations were similar and contained peaks in the region from 2.8 to 4.5 ppm (Figure 3) which correspond to the methylene and methine protons that result from the ring-opening reaction of styrene oxide.[70]

Experiments were designed to determine whether the reaction of 4-vinylstyrene oxide with polystyryllithium is faster at the epoxide than at the vinyl group. Two solutions of polystyryllithium were prepared: one with [THF]/[PSLi] = 15 and a second with [THF]/[PSLi] = 60. 4-Vinylstyrene oxide ([4-vinylstyrene oxide]/[BuLi] = 1.1) was added to the polystyryllithium solutions all at once using a gas-tight syringe, and the reactions were allowed to stir for 2 h. The red-orange color

Scheme 1. Synthesis of Dendritically Branched Polystyrene with Hydroxyl Groups at the Branch Points by the Slow Addition of 4-Vinylstyrene Oxide and Styrene to Polystyryllithium Chains



Scheme 2. Synthesis of 4-Vinylstyrene Oxide



immediately turned yellow for both concentrations and continued to fade to colorless similar to the end-capping with styrene oxide.

The GPC chromatograms of the polymers are presented in Figure 4. The GPC chromatogram of the reaction with the higher concentration of THF, [THF]/[PSLi] = 60 (Figure 4a), displays a small shoulder at lower elution volume, corresponding to a very small amount of higher molecular weight material that is twice the molecular weight of the initial chains. The lack of any significant amount of higher molecular weight material implies that the reaction of the polystyryllithium chains with the epoxide is preferred over the reaction at the double bond. The reaction for the lower concentration of THF, [THF]/[PSLi] = 15 (Figure 4b), led to a multimodal chromatogram containing a considerable amount of higher molecular weight material. In this case, reaction was more competitive at both the vinyl group and the epoxide. ^{1}H NMR spectroscopy was used to examine the integration ratios of the vinyl peaks relative to the aromatic polystyrene peaks and showed that the vinyl content of the polystyrene polymer from the reaction with low THF concentra-

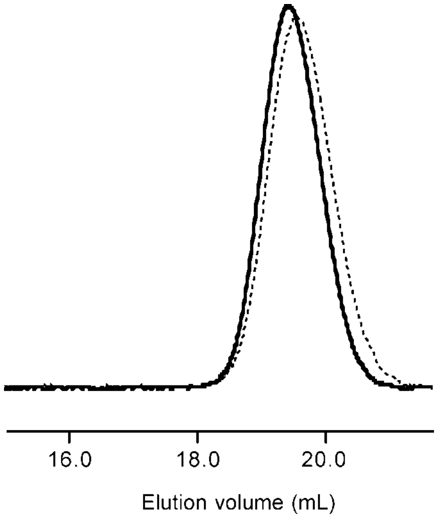


Figure 2. Addition of styrene oxide to polystyryllithium chains with [THF]/[PSLi] = 60. GPC traces for (---) linear polystyrene sample before addition of styrene oxide (—) sample of chains after addition of 1.1 equiv of styrene oxide.

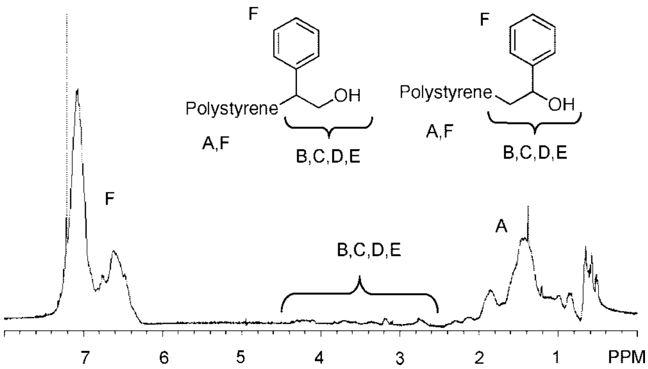


Figure 3. ^{1}H NMR spectrum of polystyrene polymer capped by styrene oxide; addition of styrene oxide all at once for [THF]/[PSLi] = 15.

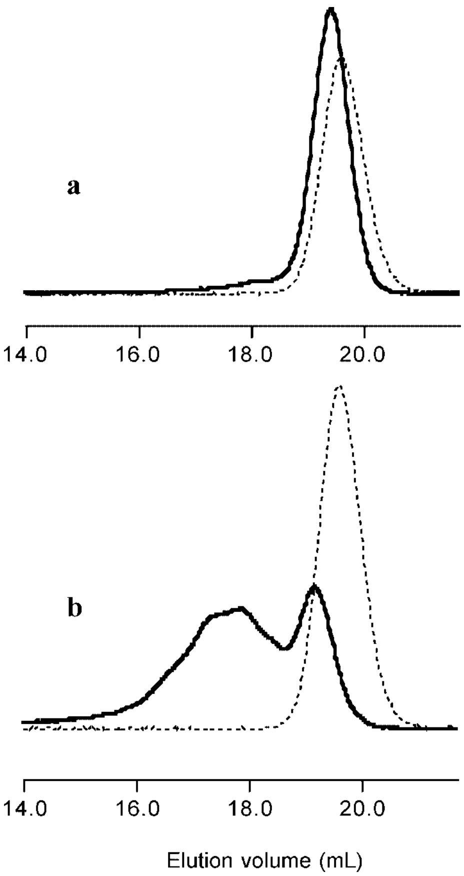


Figure 4. Addition of 4-vinylstyrene oxide all at once to polystyryllithium: (a) GPC traces for [THF]/[PSLi] = 60 (---) linear polystyrene, (—) after addition of coupling agent; (b) GPC traces for [THF]/[PSLi] = 15, (---) linear polystyrene, (—) after addition of coupling agent.

tion was approximately one-fifth that of the polystyrene polymer from the reaction with high THF concentration, demonstrating the reaction of the vinyl group in the low THF concentration reaction. The integration ratio of vinyl protons to aromatic protons in the macromonomer (Figure 5a) is ~92% of the calculated value for complete end-capping using GPC-MALLS determined molecular weights. The deviation from the calculated value is caused by difficulty in integration of the low concentration of vinyl protons and some overlap with the aromatic region.

Dendritic polymers were synthesized by the slow addition of a mixture of styrene and 4-vinylstyrene oxide to polystyryllithium solutions. Reactions were carried out in benzene/THF solutions with [THF]/[PSLi] = 15 or [THF]/[PSLi] = 60. The molar ratio of styrene to 4-vinylstyrene oxide was kept at 10 to 1 for each of the experiments. The styrene/4-vinylstyrene oxide mixture was introduced into the reaction flask by gas-tight syringe using a metering syringe pump to control the rate of addition. The addition time was kept at 4−6 h. Addition over longer periods of time did not demonstrate an increase in the molecular weight of the dendritic polymer. The initial red-orange color of the living chains in the benzene/THF solution initially became a much darker red color with the addition of coupling agent and gradually faded as the addition of coupling agent neared completion. Alkoxide groups were protonated with glacial acetic acid, and the polymers were precipitated into methanol.

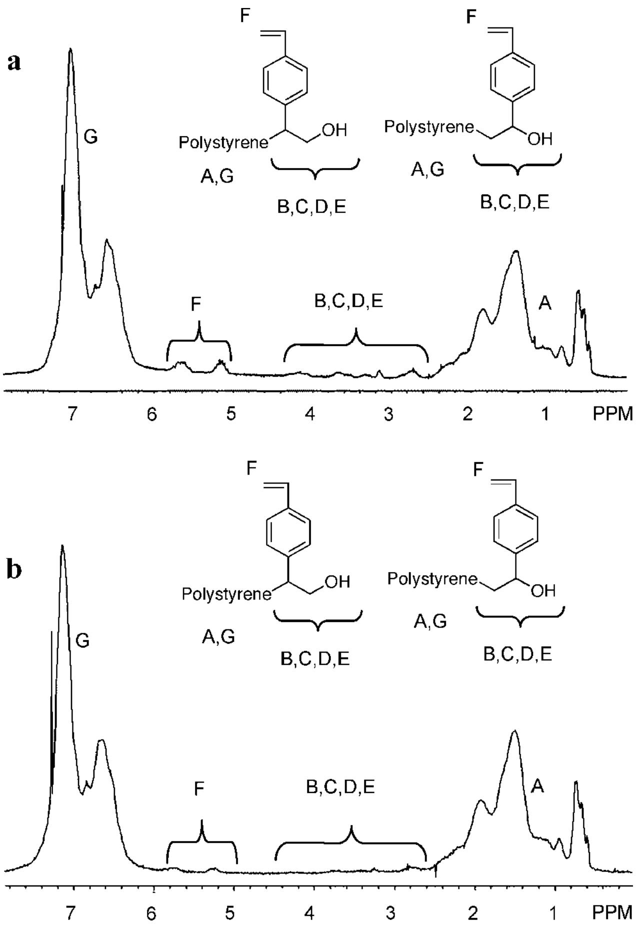


Figure 5. ^{1}H NMR spectra of polymer after the addition of coupling agent all at once for (a) [THF]/[PSLi] = 60 and (b) [THF]/[PSLi] = 15.

Lithium chloride ([LiCl]/[PSLi] = 5) or *N,N,N′,N′*-tetramethylenediamine ([TMEDA]/[PSLi] = 1) was added to some polystyryllithium solutions to determine the effect of additives on the synthesis of the dendritic polymers. The addition of LiCl to low polystyryllithium concentrations in THF is known to reduce the reactivity by shifting the equilibrium toward less reactive ion pairs.[73] However, it has been determined that the addition of lithium chloride, which is dimeric in THF solutions, to high polystyryllithium concentrations (>10^{-3} M) in THF has the effect of increasing the reactivity.[82−84] It was concluded that at high polystyryllithium concentrations the scavenging of Li^{+} ions by dimeric LiCl results in an increase in the amount of free polystyryl anions. TMEDA has also been used to increase the amount of free polystyryl anions by acting as a ligand for lithium ions in living anionic polymerization.[85]

Table 1 summarizes the results obtained for all coupling reactions. GPC coupled with multiangle laser light scattering (GPC-MALLS) was used to calculate molecular weights and molecular weight distributions for all of the polymers synthe-

Table 1. Characterization of Dendritically Branched Polymers

	initial chains (g/mol)[a]				branched polystyrene (g/mol)[a]					
run	[THF]/[PSLi]	additive	M_n	M_w/M_n	M_n	M_w/M_n	M_n PS per OH group (g/mol)[b]	avg gen[c]	avg gen[d]	T_g[e]
1	15	none	1230	1.02	12 900	1.41			2.5	90
2	60	none	1190	1.03	14 500	1.62	1800 ± 20	3.0	2.7	90
3	15	LiCl[f]	1240	1.03	13 300	1.51			2.6	90
4	60	LiCl[f]	1040	1.04	24 800	1.28	1840 ± 20	3.8	3.6	93
5	15	TMEDA[g]	1200	1.02	10 800	1.60			2.3	88
6	60	TMEDA[g]	1110	1.04	12 000	1.74	1710 ± 40	2.8	2.5	90

[a] Determined by GPC-MALLS using THF as the eluent and a d*n*/d*c* of 0.192 mL/g. [b] Determined by an indirect titration method,[63−67] measured in triplicate; only the [THF]/[PSLi] = 60 samples were analyzed. [c] Calculated according to eq 1. [d] Calculated according to eq 2. [e] Determined by DSC at 10 °C/min. [f] [LiCl]/[PSLi] = 5. [g] [TMEDA]/[PSLi] = 1.

sized. The reactions where [THF]/[PSLi] = 60 yielded higher molecular weight polymers than reactions where [THF]/[PSLi] = 15. The addition of LiCl to the polystyryllithium solutions resulted in higher molecular weight polymers than for the reactions without additives. However, the addition of TMEDA to the polystyryllithium solutions resulted in a decrease in molecular weight from reactions without additives.

The extent of coupling, defined by the generational growth of the dendritic polymers, was calculated using two methods. The generational growth was determined experimentally by an indirect titration of the hydroxyl groups and also by calculation using the molecular weight of the initial chains, the molecular weight of the final polymer, and the composition of the coupling agent/styrene mixture.

The molecular weight of polymer per hydroxyl group was determined by an indirect titration method.[63−67] Acetyl chloride was used to acetylate the hydroxyl groups of the dendritic polymer dissolved in a toluene/pyridine solution, and then the excess acetyl chloride was hydrolyzed with water. The solution was titrated in the presence of phenolphthalein with a standardized NaOH solution. The concentration of hydroxyl groups was determined by the consumption of acetyl chloride, and the molecular weight of the polymer per hydroxyl group was determined by dividing the GPC-MALLS molecular weight by the number of hydroxyl groups. The value for the average generation of the polymer was then calculated using eq 1. In eq 1, G equals the average number of generations, M_G is the number-average molecular weight of the final polymer, and M_H is the number-average molecular weight of polymer per hydroxyl group as determined by titration. Table 1 summarizes the results of the titrations.

$$G = \log(M_G/M_H)/\log 2 \qquad (1)$$

The generational growth of the dendritic polymer was also calculated using eq 2. The value for the generational growth is based on the complete consumption of styrene and coupling agent added to the polystyryllithium solution. In eq 2, G equals the average number of generations, M_G is the number-average molecular weight of the final polymer, M_0 is the number-average molecular weight of the initial chains, and M_B is the average molecular weight of the styrene added between branch points plus the molecular weight of one unit of coupling agent. For all of the polymers the value of M_B was equal to 1186 g/mol (styrene to 4-vinylstyrene oxide molar ratio of 10 to 1 added to initial chains). The values for the generational growth are listed in Table 1. Generational growth calculated from the titration data (eq 1) agrees reasonably well with the generational growth calculated from the monomer to coupling agent ratio (eq 2).

$$G = \log(M_G) - \log(M_0+M_B)/\log 2 \qquad (2)$$

The chromatograms for run 4 (Figure 6) illustrate the increase in molecular weight from the initial chains to the dendritic polymer formed by the addition of coupling agent/styrene to the initial chains. A small increase in polydispersity is found in going from the initial chains to the dendritic polymer, although the polydispersities remain rather low compared to other hyperbranching polymerizations. Polydispersities of the branched polymers synthesized from 4-vinylstyrene oxide had a range of 1.28−1.74, which is comparable to previously reported polydispersities for dendritic polymers synthesized from VBC using this method of in-situ chain-end functionalization (M_w/M_n = 1.20−1.88)[57] and slightly higher than dendritic polymers synthesized using CDMSS (M_w/M_n = 1.13−1.45).[60] The polydispersity is somewhat tied to generational growth. The growth is related to the amount of coupling relative to the termination by continuously added coupling agent. If the stoichiometric amount of coupling agent is reached without giving sufficient time for larger macromolecules to couple, low generations will result. Previous modeling of this reaction demonstrates low average generational growth leads to higher polydispersity.[60] The lower generational growth of the hydroxyl-functionalized polymer compared with the previously reported dendritic polymers produced using VBC and CDMSS could be attributed to the hindrance of reaction at the vinyl group with a nearby lithium alkoxide group.

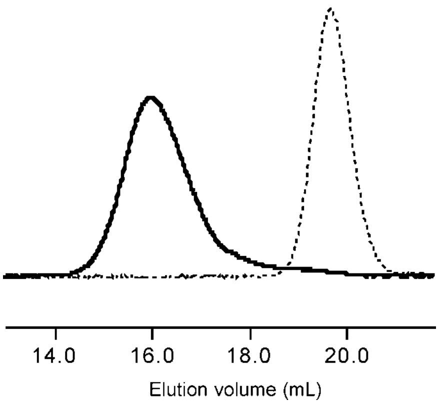


Figure 6. Slow addition of coupling agent to polystyryllithium chains for run 4: (---) GPC traces for linear chains and (—) dendritically branched chains.

Characterization of the molecular weight by GPC-MALLS relative to elution volume was examined for the dendritic polymers and compared with polystyrene standards. For all of the dendritic polymers, a greater elution volume was found for a given molecular weight than for the polystyrene standards, reflecting the more compact structure of the dendritic polymers. Figure 7 displays the log(molecular weight) vs elution volume data for two of the dendritic samples and the behavior of polystyrene standards. The effect, if any, of the hydroxyl groups on the conformation of the polymer is not clear from the data.

The ^{1}H NMR spectrum of the hydroxyl-functionalized polystyrene polymer is shown in Figure 8. Peaks in the region

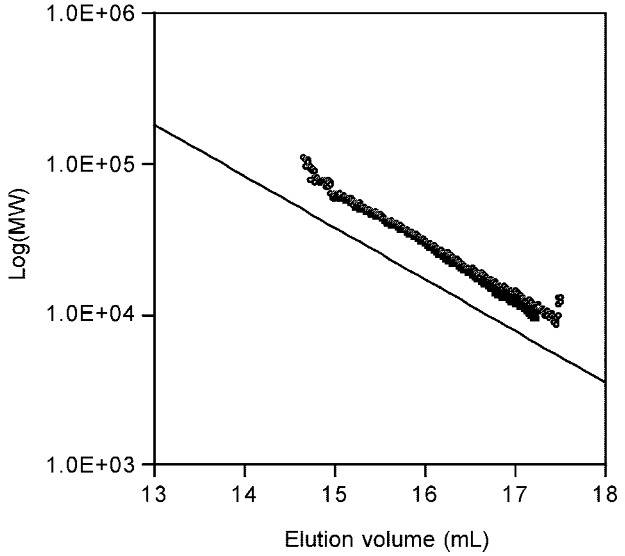


Figure 7. Log(molecular weight) vs elution volume by GPC-MALLS: (—) behavior of linear polystyrene standards, (○) run 3, and (▲) run 4.

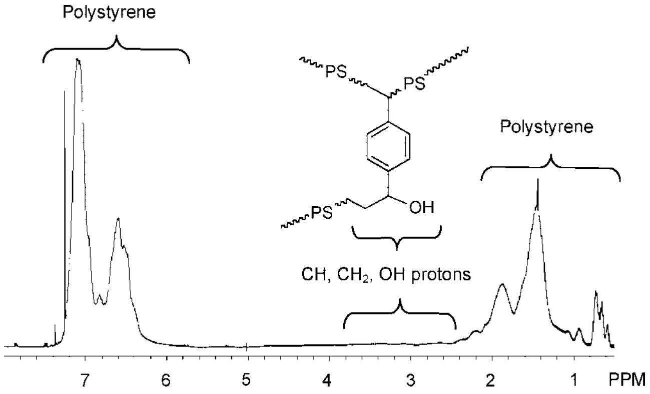


Figure 8. ^1H NMR spectrum of hydroxyl-functionalized dendritic polystyrene polymer for run 4.

δ 2.5−4.5 ppm corresponding to the methine and methylene protons at each branch point are barely visible due to the high relative amount of styrene units.

The glass-transition temperatures for all of the dendritically branched polymers were measured by differential scanning calorimetry. The glass-transition temperature of dendritic polymers can be affected by the molecular weight, composition, and number of chain ends.[86] The polymers synthesized in this study have similar structure, number-average molecular weight of the initial chains, hydroxyl groups at branch points, and ratio of chain ends to molecular weight. The only substantial difference is the total molecular weight of the polymers, as determined by generational growth. The glass transition temperatures were found to increase slightly with molecular weight. The temperatures were 88 °C for the lowest molecular weight sample to 93 °C for the highest molecular weight sample. The T_g of dendritically branched polymers formed by the addition of VBC/styrene to polystyryllithium has also been measured.[57] These dendritic polymers had a structure where the initial chains, end-group functionalization, and length of chains between branch points are roughly equivalent to the polymers in this work. The range of T_g's of the polymers synthesized by VBC with a generational growth of 3.9−4.2 was found to be 83−90 °C. The slightly higher T_g of the hydroxyl-functionalized polymers could be attributed to the presence of hydroxyl groups at the branch points of the dendritic polymer, as increases in T_g are observed in other cases for hydroxyl chain-end functionalization of dendritic polymers over analogous unfunctionalized dendritic polymers, presumably due to hydrogen bonding.[86] However, no conclusive statement can be made here as to the effect of the hydroxyl groups on T_g as the differences could be due to other factors including molecular weight differences, number of branch points, and other variations between the samples.

Conclusions

This work presents modification of the convergent coupling of living chains by CDMSS and VBC, wherein a novel bifunctional coupling agent introduces functionalization into dendritic polymers as a consequence of the coupling reaction. A facile method for the synthesis of well-defined dendritic polystyrenes containing a hydroxyl functional group at each branch point has been developed implementing the slow addition of a bifunctional coupling agent, 4-vinylstyrene oxide and styrene monomer to living polystyrene in a benzene/THF solution. The addition of coupling agent to the polystyryllithium led to a ring-opening reaction at the epoxide, resulting in an unreactive lithium alkoxide followed by an addition reaction at the vinyl moiety. The conditions that gave the highest value of generational growth were obtained with a ratio of [THF]/[PSLi] = 60 and a ratio [LiCl]/[PSLi] = 5. The presence of hydroxyl groups was confirmed by titrimetric analysis. The hydroxyl groups will be exploited to form unique block copolymers that will be reported in a future publication.

Acknowledgment. This work was supported by the National Science Foundation (DMR-9985221) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685–1698.
(2) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453–571.
(3) Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, *143*, 1–34.
(4) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules: Concepts, Synthesis, Perspectives*; Weinheim: New York, 1996.
(5) Newkome, G. R. *Advances in Dendritic Macromolecules*; Jai Press: Greenwich, 2002.
(6) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendrimers and Dendrons*; Wiley-VCH: New York, 2001.
(7) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505–2525.
(8) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.
(9) Kobayashi, S.; Mishra, M. K. *Star and Hyperbranched Polymers*; Marcel Dekker: New York, 1999.
(10) Tomalia, D. A.; Hedstrand, D. M.; Ferritto, M. S. *Macromolecules* **1991**, *24*, 1435–8.
(11) Gauthier, M.; Moeller, M. *Macromolecules* **1991**, *24*, 4548–53.
(12) Gauthier, M.; Li, W.; Tichagwa, L. *Polymer* **1997**, *38*, 6363–6370.
(13) Li, J.; Gauthier, M. *Macromolecules* **2001**, *34*, 8918–8924.
(14) Li, J.; Gauthier, M.; Teertstra, S. J.; Xu, H.; Sheiko, S. S. *Macromolecules* **2004**, *37*, 795–802.
(15) Hempenius, M. A.; Michelberger, W.; Moeller, M. *Macromolecules* **1997**, *30*, 5602–5605.
(16) Walach, W.; Kowalczuk, A.; Trzebicka, B.; Dworak, A. *Macromol. Rapid Commun.* **2001**, *22*, 1272–1277.
(17) Walach, W.; Trzebicka, B.; Justynska, J.; Dworak, A. *Polymer* **2004**, *45*, 1755–1762.
(18) Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36*, 7446–7452.
(19) Schappacher, M.; Bernard, J.; Deffieux, A. *Macromol. Chem. Phys.* **2003**, *204*, 762–769.
(20) Schappacher, M.; Deffieux, A. *Macromolecules* **2000**, *33*, 7371–7377.
(21) Muchtar, Z.; Schappacher, M.; Deffieux, A. *Macromolecules* **2001**, *34*, 7595–7600.
(22) Grubbs, R. B.; Hawker, C. J.; Dao, J.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **1997**, *36*, 270–272.
(23) Bernard, J.; Schappacher, M.; Ammannati, E.; Kuhn, A.; Deffieux, A. *Macromolecules* **2002**, *35*, 8994–9000.

(24) Ishizu, K.; Takahashi, D.; Takeda, H. *Macromol. Rapid Commun.* **2000**, *21*, 660–664.
(25) Paulo, C.; Puskas, J. E. *Macromolecules* **2001**, *34*, 734–739.
(26) Litvinenko, G. I.; Mueller, A. H. E. *Macromolecules* **2002**, *35*, 4577–4583.
(27) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079–81.
(28) Simon, P. F. W.; Mueller, A. H. E. *Macromolecules* **2001**, *34*, 6206–6213.
(29) Litvinenko, G. I.; Simon, P. F. W.; Mueller, A. H. E. *Macromolecules* **2001**, *34*, 2418–2426.
(30) Litvinenko, G. I.; Simon, P. F. W.; Mueller, A. H. E. *Macromolecules* **1999**, *32*, 2410–2419.
(31) Trollsås, M.; Hedrick, J. L. *Macromolecules* **1998**, *31*, 4390–4395.
(32) Mori, H.; Walther, A.; Andre, X.; Lanzendoerfer, M. G.; Mueller, A. H. E. *Macromolecules* **2004**, *37*, 2054–2066.
(33) Mori, H.; Seng, D. C.; Lechner, H.; Zhang, M.; Mueller, A. H. E. *Macromolecules* **2002**, *35*, 9270–9281.
(34) Simon, P. F. W.; Mueller, A. H. E.; Pakula, T. *Macromolecules* **2001**, *34*, 1677–1684.
(35) Simon, P. F. W.; Radke, W.; Muller, A. H. E. *Macromol. Rapid Commun.* **1997**, *18*, 865–873.
(36) Mecerreyes, D.; Trollsås, M.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 8753–8759.
(37) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763–4.
(38) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441–53.
(39) Hedrick, J. L.; Trollsås, M.; Hawker, C. J.; Atthoff, B.; Claesson, H.; Heise, A.; Miller, R. D.; Mecerreyes, D.; Jerome, R.; Dubois, P. *Macromolecules* **1998**, *31*, 8691–8705.
(40) Trollsaas, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 4644–4651.
(41) Trollsaas, M.; Loewenhielm, P.; Lee, V. Y.; Moeller, M.; Miller, R. D.; Hedrick, J. L. *Macromolecules* **1999**, *32*, 9062–9066.
(42) Feng, X.-S.; Taton, D.; Chaikof, E. L.; Gnanou, Y. *J. Am. Chem. Soc.* **2005**, *127*, 10956–10966.
(43) Feng, X.; Taton, D.; Chaikof, E. L.; Gnanou, Y. *Biomacromolecules* **2007**, *8*, 2374–2378.
(44) Matmour, R.; Lepoittevin, B.; Joncheray, T. J.; El-khouri, R. J.; Taton, D.; Duran, R. S.; Gnanou, Y. *Macromolecules* **2005**, *38*, 5459–5467.
(45) Feng, X.; Taton, D.; Ibarboure, E.; Chaikof, E. L.; Gnanou, Y. *J. Am. Chem. Soc.* **2008**, *130*, 11662–11676.
(46) Lepoittevin, B.; Matmour, R.; Francis, R.; Taton, D.; Gnanou, Y. *Macromolecules* **2005**, *38*, 3120–3128.
(47) Orfanou, K.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *Macromolecules* **2006**, *39*, 4361–4365.
(48) Chalari, I.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1519–1526.
(49) Matsuo, A.; Watanabe, T.; Hirao, A. *Macromolecules* **2004**, *37*, 6283–6290.
(50) Hirao, A.; Matsuo, A.; Watanabe, T. *Macromolecules* **2005**, *38*, 8701–8711.
(51) Hutchings, L. R.; Roberts-Bleming, S. J. *Macromolecules* **2006**, *39*, 2144–2152.
(52) Percec, V.; Barboiu, B.; Grigoras, C.; Bera, T. K. *J. Am. Chem. Soc.* **2003**, *125*, 6503–6516.
(53) Percec, V.; Grigoras, C.; Kim, H.-J. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 505–513.
(54) Matmour, R.; Gnanou, Y. *J. Am. Chem. Soc.* **2008**, *130*, 1350–1361.
(55) Knauss, D. M.; Huang, T. *Macromolecules* **2003**, *36*, 6036–6042.
(56) Knauss, D. M.; Huang, T. *Macromolecules* **2002**, *35*, 2055–2062.
(57) Knauss, D. M.; Al-Muallem, H. A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4289–4298.
(58) Knauss, D. M.; Al-Muallem, H. A.; Huang, T. *Polym. Mater. Sci. Eng.* **1999**, *80*, 153–154.
(59) Al-Muallem, H. A.; Knauss, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *39*, 152–161.
(60) Knauss, D. M.; Al-Muallem, H. A.; Huang, T.; Wu, D. T. *Macromolecules* **2000**, *33*, 3557–3568.
(61) Le Bigot, Y.; Delmas, M.; Gaset, A. *Synth. Commun.* **1983**, *13*, 177–82.
(62) Kuhn, R.; Trischmann, H. *Liebigs Ann. Chem.* **1958**, *611*, 117–21.
(63) Gyenes, I. *Titration in Non-aqueous Media*; Van Nostrand: Princeton, NJ, 1967.
(64) Veibel, S. *The Determination of Hydroxy Groups*; Academic Press: New York, 1972.
(65) Kaufmann, H. P.; Funke, S. *Ber.* **1937**, *70B*, 2549–54.
(66) Smith, D. M.; Bryant, W. M. D. *J. Am. Chem. Soc.* **1935**, *57*, 61–5.
(67) Choi, Y. K.; Bae, Y. H.; Kim, S. W. *Macromolecules* **1998**, *31*, 8766–8774.
(68) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353–64.
(69) Tanimoto, S.; Oda, R. *Kyoto Daigaku Nippon Kagaku Sen'i Kenkyusho Koenshu* **1968**, *25*, 51–8.
(70) Hasegawa, H. Functionalization Reactions of Polymeric Organolithium Compounds with Styrene Oxide. Ph.D. Thesis, University of Akron, **1994**.
(71) Quirk, R. P.; Hasegawa, H.; Gomochak, D. L.; Wesdemiotis, C.; Wollyung, K. *Macromolecules* **2004**, *37*, 7146–7155.
(72) Quirk, R. P.; Kuang, J. J.; Hasegawa, H.; Han, K. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1994**, *53*, 15–27.
(73) Szwarc, M.; Beylen, M. V. *Ionic Polymerization and Living Polymers*; Chapman & Hall: New York, 1993.
(74) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(75) Fetters, L. J.; Balsara, N. P.; Huang, J. S.; Jeon, H. S.; Almdal, K.; Lin, M. Y. *Macromolecules* **1995**, *28*, 4996–5005.
(76) Bywater, S.; Worsfold, D. J. *Can. J. Chem.* **1962**, *40*, 1564–70.
(77) Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2002**, *35*, 2912–2918.
(78) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560–2.
(79) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133–95.
(80) Honeycutt, S. C. *J. Organomet. Chem.* **1971**, *29*, 1–5.
(81) Ogle, C. A.; Strickler, F. H.; Gordon, B. *Macromolecules* **1993**, *26*, 5803–5.
(82) Verheyden, H.; Van Lierde, P.; Szwarc, M.; Litvinenko, G.; Van Beylen, M. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2148–2157.
(83) Smid, J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2101–2107.
(84) Van Beylen, M.; Van Lierde, P.; Zimm, B. H.; Szwarc, M. *Macromol. Rapid Commun.* **1997**, *18*, 113–115.
(85) Collum, D. B. *Acc. Chem. Res.* **1992**, *25*, 448–54.
(86) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J. *Macromolecules* **1993**, *26*, 1514–19.

MA802657C