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High-Yield Synthesis of Functionalized Alkoxyamine Initiators and Approach to Well-Controlled Block Copolymers Using Them

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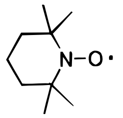
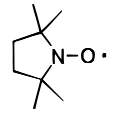
ABSTRACT: Reaction of ethylbenzene, 4-bromo-, 4-(ethoxycarbonyl)-, and 4-methoxyethylbenzenes with di-*tert*-butyl diperoxyoxalate at 35 °C in the presence of stable nitroxide radicals gave alkoxyamines in 50−91% yields. Lithiation of the 4-bromophenylalkoxyamine and subsequent treatment with DMF gave 4-formylphenylalkoxyamine in 95% yield, and the reduction of the 4-formylphenylalkoxyamine with $NaBH_4$ yielded 4-(hydroxymethyl)phenylalkoxyamine in 89% yield. Anionic polymerization of butadiene (BD) with *sec*-BuLi and subsequent termination with 4-formylphenylalkoxyamine gave an end-functionalized poly(butadiene) [poly(BD)]. "Living" radical polymerization of styrene (St) initiated by the functionalized poly(BD) at 120 °C gave a poly(BD)-*block*-poly(St) with a M_w/M_n of 1.30. Anionic polymerization of hexamethylcyclotrisiloxane (D_3) with 4-lithiophenylalkoxyamine gave poly(D_3) with an alkoxyamine moiety at a polymer end. "Living" radical polymerization of St initiated by the functionalized poly(D_3) gave poly(D_3)-*block*-poly(St) with M_w/M_n's of 1.73−1.80.

Introduction

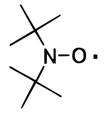
Since the initial report by Georges et al. in 1993 on the stable free radical (SFR)-mediated "living" radical polymerization of styrene (St),[1] much attention has been paid to this controlled polymerization process. SFR-mediated "living" radical polymerization has also been utilized to make a variety of well-defined block and graft copolymers, including star and dendritic polymers, which are difficult to make by other methods.[2−6] Nitroxides including 2,2,6,6-tetramethylpiperidinyl-1-oxyl (**1a**, TEMPO), 2,2,5,5-tetramethylpyrrolidinyl-1-oxyl (**1b**), and di-*tert*-butyl nitroxide (**1c**) are typical SFR that simply do not react with double bonds under standard conditions[1,7−9] After the pioneering works by Rizzardo et al.,[10] subsequent developments in this area have shown that the key initiators are alkoxyamines having a weak C−O bond.[11] Syntheses of alkoxyamines have widely been studied, and many procedures based on the radical trapping technique[9,12−17] or nucleophilic method[13,18] have been developed. Alkoxyamines carrying a functional group such as aldehyde and ester can be used for preparation of controlled macromolecular architectures by combination of "living" free radical polymerization and other types of polymerization (e.g., anionic and cationic) using functionalized alkoxyamines. Hawker et al. reported the synthesis of a functionalized alkoxyamine **2** by hydrolysis of the benzoyloxy−styrene−TEMPO adduct, and a variety of controlled macromolecular architectures have been prepared using **2**.[3,4,6] However, it is difficult to synthesize alkoxyamines with a variety of functional groups from **2**. It is therefore important to establish convenient and widely applicable synthetic routes for functionalized alkoxyamines. We have found that the reaction of ethylbenzenes with di-*tert*-butyl diperoxyoxalate (**4**) in the presence of nitroxides at 35 °C gives alkoxyamines including 4-bromo (**3d**), 4-ethoxycarbonyl (**3e**), and 4-methoxy derivatives (**3f**) in good to excellent yields. Of particular interest is **3d**, from which a variety of functionalized alkoxyamines can be derived via the corresponding lithio or Grignard reagent. After our preliminary publication on the preparation of functionalized alkoxyamines,[19] other procedures have been reported.[20,21]



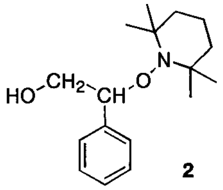
1a (TEMPO)



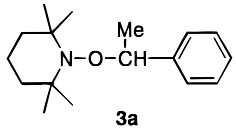
1b



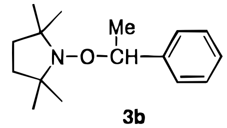
1c



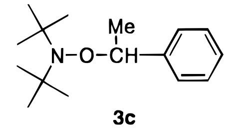
2



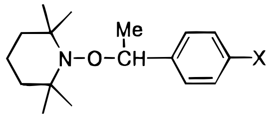
3a



3b



3c



3d: X = Br
3e: X = COOEt
3f: X = OMe

Using functionalized alkoxyamines as a tool for syntheses of well-controlled polymer architectures, poly(butadiene) [poly(BD)]-*block*-poly(styrene) [poly(St)] and poly(hexamethylcyclotrisiloxane) [poly(D_3)]-*block*-poly(St) copolymers have been prepared. For the preparation of former copolymer the procedure of Priddy and Kobatake was traced:[22,23] anionic polymerization of BD with *sec*-butyllithium, termination of the poly(butadienyl)lithium with **3h**, and "living" radical polymerization of St with the end-functionalized poly(BD). On the other hand, the latter copolymer was prepared by anionic polymerization of D_3 with 4-lithiophenylalkoxyamine and subsequent "living" radical polymer-

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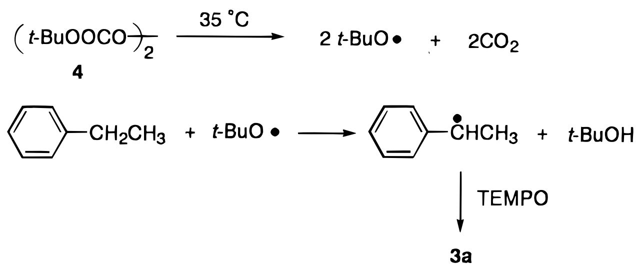
Scheme 1



ization of St with the end-functionalized poly(D_3). Herein we wish to report the synthesis of functionalized alkoxyamines and an approach to well-controlled block copolymers using such functionalized alkoxyamines.

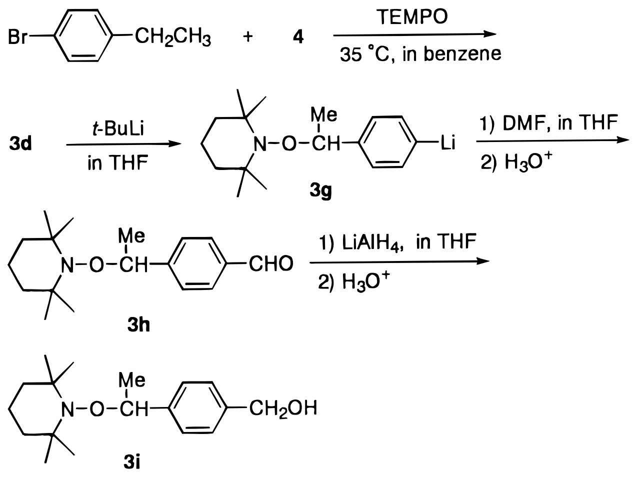
Results and Discussion

Synthesis of Alkoxyamines by Reaction of Di-*tert*-butyl Diperoxyoxalate with Ethylbenzene in the Presence of Nitroxide Radicals. The preparation of **3a** is outlined in Scheme 1. Perester **4** decomposes at a moderate rate in hydrocarbon solvents such as benzene at room temperature to give two *tert*-butoxyl radicals.[24] Since the homolytic decomposition is very clean, **4** has served as a good source of *tert*-butoxyl radicals under mild conditions. Furthermore, since this perester can be stored in a freezer (−20 °C) for at least 1 year without decomposition, it is not necessary to prepare it each time in the preparation of alkoxyamines.

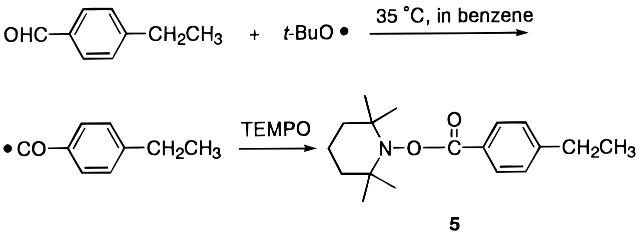
The reaction of ethylbenzene with **4** in the presence of TEMPO was carried out at 35 °C in benzene under nitrogen using 1.0 equiv of **4** for TEMPO and using ethylbenzene as the solvent. After 3 h, the characteristic red color due to TEMPO disappeared, and the solution showed a pale yellow color. An excess of ethylbenzene was removed, and the residue was chromatographed on silica gel to give almost pure **3a** in 90% yield (based on TEMPO). In the same manner the reaction of ethylbenzene with **4** in the presence of **1b** or **1c** was carried out, and alkoxyamines **3b** and **3c** were obtained in 89 and 90% yields, respectively, as a colorless oil after column chromatography.

Synthesis of Functionalized Alkoxyamines. Alkoxyamines **3d**, **3e**, and **3f** were prepared in benzene using small amounts of the corresponding ethylbenzenes to avoid wasting the expensive ethylbenzenes. In addition, since the ethylbenzenes have high boiling points,[25] it is difficult to remove them at room temperature if they are used in a large amount as the solvent. When the reaction of 4-ethylbromobenzene with **4** was carried out in benzene (10 mL) using 8.0 equiv of the ethylbenzene (16.9 mmol) and 1.6 equiv of **4** (∼3.4 mmol) for TEMPO (2.11 mmol), **3d** was obtained in 88% yield (based on TEMPO) after column chromatography. When 4.0, 2.0, and 1.0 equiv of the ethylbenzene were employed (the amounts of **4** and TEMPO are constant), the yields were reduced to 77, 56, and 36%, respectively. Reaction of 4.0 equiv of ethyl 4-ethylbenzoate with 1.6 equiv of **4** in the presence of 1.0 equiv of TEMPO gave **3e** in 50% yield, and reaction of 4.0 equiv of 4-ethylanisole with 1.6 equiv of **4** in the presence of 1.0 equiv of TEMPO gave **3f** in 91% yield. Accordingly, it can be said that the reaction of **4** with ethylbenzenes carrying an electron-donating group gives alkoxyamines in high yields.

Scheme 2



Scheme 3



Although preparation of **3d** was previously carried out by heating a mixture of di-*tert*-butyl peroxide and TEMPO in ethylbenzene at 125 °C, the product was obtained as a colorless oil in a low yield (32%).[13] No crystallization of the product suggests that it is contaminated with impurities.

According to Scheme 2, functionalized alkoxyamines **3h** and **3i** were prepared from **3d**. Treatment of **3d** with *t*-BuLi in ether at −78 °C and subsequent reaction with DMF afforded **3h** in 95% yield. The high yield of **3h** suggests that the alkoxyamine group is stable to strong bases such as alkyllithiums.[22] Reduction of **3h** with $NaBH_4$ in MeOH−THF afforded **3i** in 89% yield, and reduction with $LiAlH_4$ in anhydrous THF at room temperature gave **3i** in 82% yield.

An alternating method for preparation of **3h** is hydrogen abstraction from 4-formylethylbenzene and subsequent trapping by **1a** (Scheme 3). A mixture of 3.0 equiv of 4-formylethylbenzene, 1.6 equiv of **4**, and 1.0 equiv of TEMPO in benzene was stirred at 35 °C for 3 h under nitrogen. TLC inspection showed two spots; one was due to 4-formylethylbenzene, and the other was due to a product. Chromatography of the reaction mixture gave the product **5** in 60% yield. In the ^1H NMR spectrum the presence of TEMPO moiety was shown by two singlets at 1.12 and 1.272 ppm due to the four methyl groups at the 2- and 6-positions of the piperidine ring. No disappearance of the quartet due to $CH_3C\mathbf{H}_2$ at 2.72 ppm indicated no reaction of the ethyl group. On the other hand, disappearance of the singlet due to the formyl proton at 10.00 ppm showed that the *tert*-butoxyl radicals abstracted preferentially the formyl hydrogen. On the basis of the ^1H NMR results, the structure was determined to be **5**. It was previously reported that the formyl hydrogen is 8.6 times more reactive than the phenetyl α-hydrogens for hydrogen abstraction by *tert*-butylperoxyl radicals.[26] Taking this fact into account, the above result seems to be quite reasonable.

Bulk Polymerization of St by Functionalized Alkoxyamines. Bulk polymerization of St initiated by

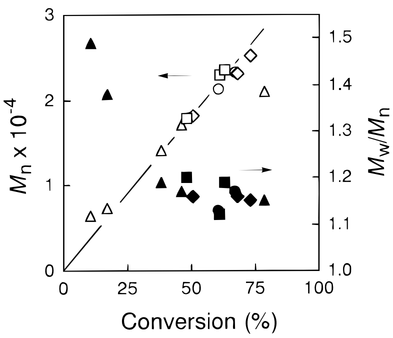
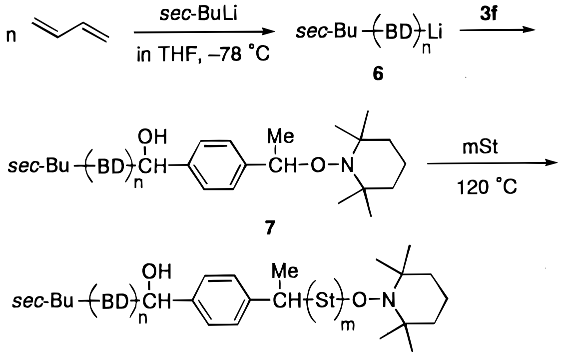


Figure 1. M_n vs conversion and M_w/M_n vs conversion plots for the functionalized alkoxiamine-mediated bulk polymerization of St at 120 °C: **3d** (○, ●); **3e** (△, ▲); **3f** (□, ■); **3h** (◇, ◆).

Scheme 4



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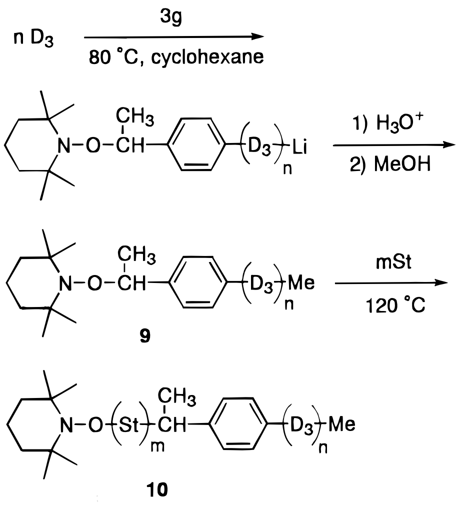
alkoxyamines **3d**−**f** and **3h** (20 mM) was carried out at 120 °C. The number-average molecular weights (M_n) and polydispersities (M_w/M_n) were determined by size exclusion chromatography (SEC) using polystyrene standards as the reference. In all cases first-order plots were observed for St, up to high conversion, and M_n values were increased linearly with conversion (see, Figure 1). Furthermore, M_w/M_n values were decreased with conversion and became below 1.2 at 50% conversion. On the basis of the observations, it is concluded that bulk polymerization of St initiated with the functionalized alkoxyamines proceeds in the "living" manner and that the functional groups give no effect for homolysis of the C−O bond.

Synthesis of Poly(BD)-*block*-poly(St) Copolymer. Using **3h** as a tool for syntheses of well-controlled block copolymers, poly(BD)-*block*-poly(St) copolymer was synthesized according to Scheme 4. Previously, Priddy and Kobatake et al. reported a synthesis of end-fuctionalized poly(BD)s by treatment of poly(butadienyl)lithium (**6**) with alkoxyamines carrying an epoxide or alkyl halide group.[22,23] However, epoxide and alkyl halide groups are less reactive for nucleopheric attack by carbanions than formyl groups.

Anionic polymerization of BD was carried out in toluene using *sec*-butyllithium. After 24 h at room temperature, the poly(butadienyl)lithium obtained was allowed to react with **3h** at room temperature. The mixture was then allowed to stand for 24 h and poured into methanol to give an end-functionalized poly(BD) **7** as a light yellow viscous oil in ~100% yield.

The ^{1}H NMR spectrum of **7** is shown in Figure 2. The 1,4-unit content estimated from Figure 2 was 89%,[22,27] which is a typical value (~90%) for poly(BD) prepared in hydrocarbon solvents.

Scheme 5



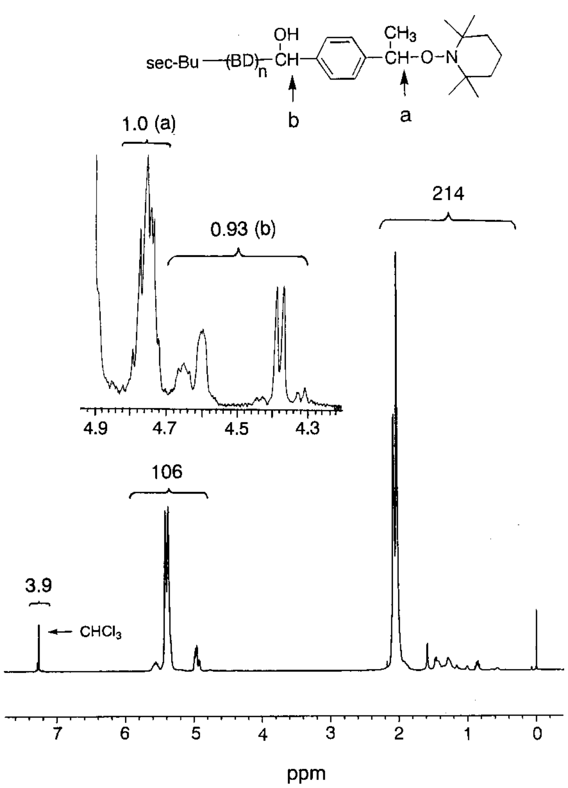


Figure 2. ^{1}H NMR spectrum of **7** in $CDCl_3$.

Upon recording at high gain, the two methine protons, −C**H**(Me)− (a) and −C**H**(OH)− (b), were detected in δ = 4.72−4.79 and 4.31−4.67 ppm, respectively, as multiplets. By comparing the relative intensity of the peaks due to −C**H**(Me)− with those of the olefinic protons in the 1,2- and 1,4-structures, the M_n value of **7** was estimated to be 5660.[28] On the other hand, the M_n value determined by SEC using poly(St) standards was 7980, which was much higher than that determined by ^{1}H NMR. Since SEC tends to give a higher M_n value for poly(BD), the M_n value was also measured by vapor pressure osmometry (BPO) using toluene as the solvent and benzil as the reference, and a value of 5970 was obtained. This magnitude agrees with that determined by ^{1}H NMR, and the end-functionality for the poly(BD) obtained was indicated to be ~100%.

Bulk polymerization of St with **7** was carried out at 120 °C for 20 h, giving block copolymer **8** in 46% yield.

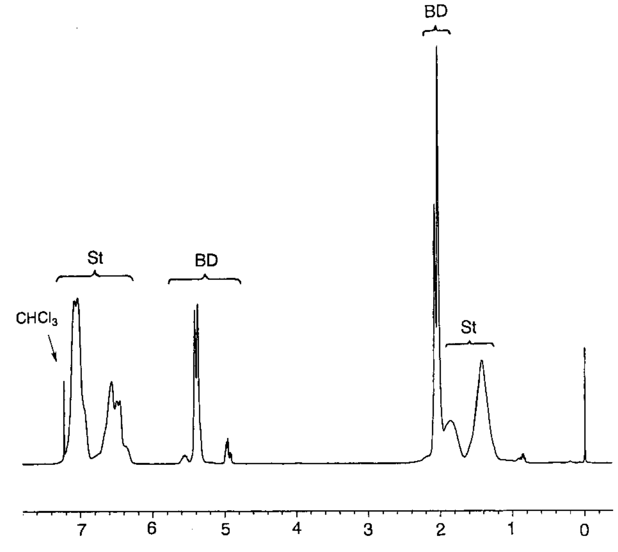


Figure 3. ^{1}H NMR spectrum of **8** in $CDCl_3$. BD and St refer to the BD and St units, respectively.

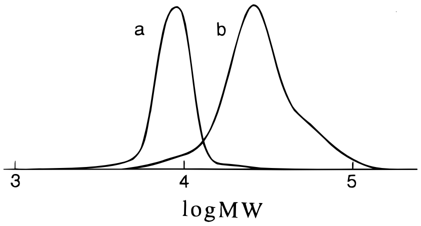


Figure 4. SEC elution curves of **7** (a) and **8** (b).

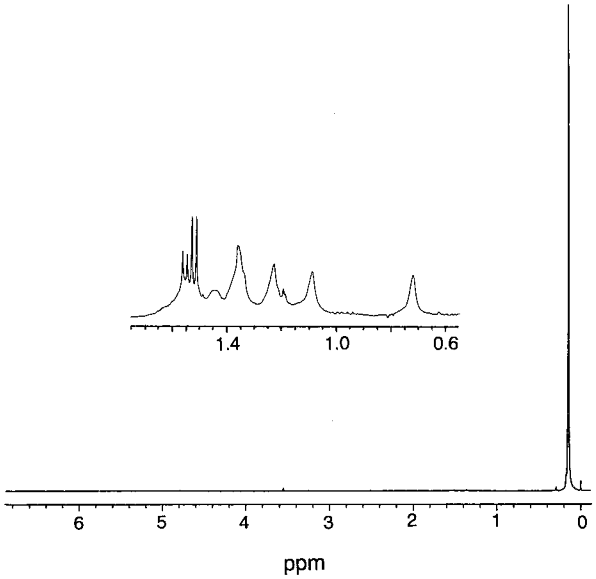


Figure 5. ^{1}H NMR spectrum of **9** in $CDCl_3$.

The ^{1}H NMR spectrum of **8** is shown in Figure 3. The peaks due to $-C\mathbf{H}_2-C\mathbf{H}Ph-$ are observed at $\delta = 1.43$ and 1.86 ppm, and peaks due to the aromatic protons are observed in 6.37−7.08 ppm. On the other hand, peaks due to the BD units are observed at $\delta = 2.03$, 2.07, 4.92−5.00, 5.37−5.42, and 5.54−5.62 ppm. From the ratio of the relative intensity of the peaks due to the olefinic protons in the BD units to that of the peaks due to $-C\mathbf{H}_2-CHPh-$, the ratio of the BD units to the St units was estimated to be 1.63, which was in good agreement with that (1.58) calculated from the M_n values of **7** and **8**.

The SEC elution curves of **7** and **8** are shown in Figure 4. A narrow peak of **7** with a small M_w/M_n value of 1.11 is observed at log MW (MW: molecular weight) = 3.9 ($M_n = 7980$). On the other hand, a peak of **8** is observed at log MW = 4.4 ($M_n = 24300$), indicating that polymerization of St was initiated with **7**. The peak of the block copolymer is still narrow ($M_w/M_n = 1.30$) but has a shoulder at log MW = 4.7 (MW = 55 000). This shoulder is not attributable to poly(St) formed by autopolymerization because its M_n ($\sim 10^5$) is much higher than 55 000. We assume that the shoulder is due to a poly(BD)-*block*-poly(St)-*block*-poly(BD) copolymer formed by coupling reaction between poly(BD)-*block*-poly(St)· propagating radicals.

Poly(D_3)-*block*-poly(St) Copolymers. An alternative method for preparation of block copolymers is the use of multifunctionalized alkoxyamine initiators. Since 4-lithiophenylalkoxyamine (**3g**) has a carbanion site, along with the alkoxyamine group, it functions as not only a radical initiator but also an anionic initiator. Although multifunctionalized alkoxyamines were recently reported,[29,30] alkoxyamines possessing both anionic and “living” radical initiating sites have not yet been reported.

In the present study poly(D_3)-*block*-poly(St) copolymer was prepared by anionic polymerization of D_3 with **3g** and subsequent “living” radical polymerization of St with the resulting end-functionalized poly(D_3). Poly(siloxane)-*block*-poly(St) copolymers were previously prepared by anionic polymerization of St and subsequent anionic polymerization of D_3[31,32] or by nitroxide-mediated “living” radical polymerization of St initiated with an azo macroinitiator containing dimethylsiloxane units.[33]

As described above, **3d** can be easily converted to **3g** in a high yield by reaction with *tert*-butyllithium. However, use of an excess of *tert*-butyllithium may leave unreacted *tert*-butyllithium which may initiate D_3 to give unfunctionalized poly(D_3). On the other hand, use of a smaller amount of *tert*-butyllithium leaves unreacted **3d** which may disturb the anionic polymerization of D_3. Accordingly, lithiation of **3d** was accomplished by treating **3d** with lithium metal in anhydrous THF at 80 °C. An almost quantitative conversion of **3d** to **3g** was confirmed by the ^{1}H NMR spectrum of **3a** obtained by quenching **3g** in THF with aqueous NH_4Cl.

Anionic polymerization of D_3 by **3g** was carried out in cyclohexane at 80 °C. After 4 h, the mixture was poured into methanol, and an end-functionalized poly(D_3) **9** was obtained as a colorless oil in 67% yield. The ^{1}H NMR spectrum is shown in Figure 5. A strong singlet due to the dimethylsilyl groups is observed at $\delta = 0.07$ ppm, and a weak singlet due to $-OMe$ at a terminal end is observed at 3.48 ppm. The $-OMe$ group is formed by the reaction of the terminal $-Si(Me_2)OH$ with MeOH used as the precipitant. Upon recording at high gain many peaks due to the phenylalkoxyamine group were observed at 0.72−1.44, 1.52, and 1.55 (d, $J = 6.8$ Hz), 4.81 and 4.85 (d, $J = 6.8$ Hz), and 7.26 and 7.50 ppm (d, $J = 7.4$ Hz). The M_n and M_w/M_n values determined by SEC were 7600 and 1.33, respectively.

Bulk polymerization of St initiated with **9** was carried out at 120 °C for 16 h. At ~8 h (~20% conversion) the polymerization mixture became heterogeneous, and the copolymer formed began to separate.

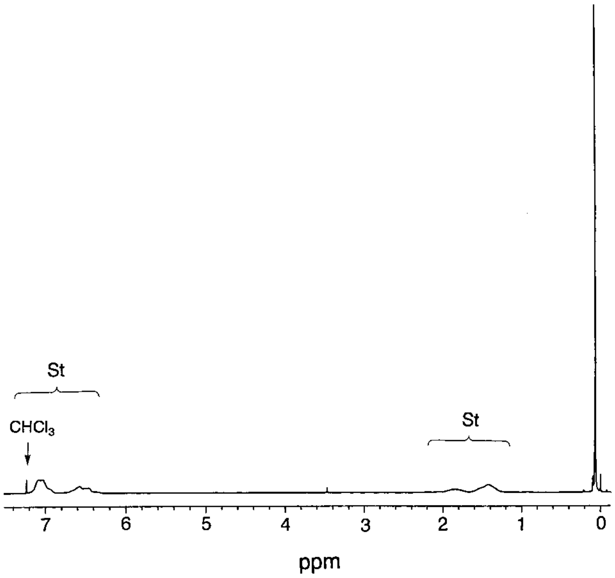


Figure 6. ^{1}H NMR spectrum of **10** in CDCl$_3$. St refers to the St units.

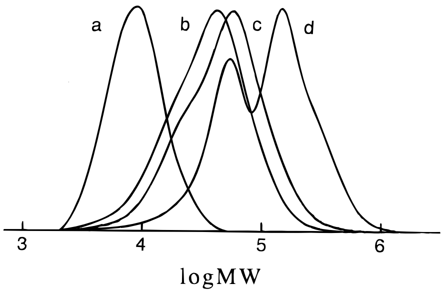


Figure 7. SEC elution curves of **9** (a) and **10** (b−d); b, c, and d refer to those of the block copolymers obtained at 17, 21, and 53% conversions of St, respectively.

The ^{1}H NMR spectrum of poly(D$_3$)-*block*-poly(St) copolymer **10** is shown in Figure 6. A singlet due to the dimethylsilyl groups is observed at $\delta = 0.07$ ppm, and a broad singlet due to $-\mathrm{C}\mathbf{H}_2-\mathrm{CHPh}-$, a broad singlet due to $-\mathrm{CH}_2-\mathrm{C}\mathbf{H}\mathrm{Ph}-$, and multiplets due to the aromatic protons are observed at $\delta = 1.43$, 1.84, and 6.33−7.25 ppm, respectively. The ratios of the D$_3$ units to the St units determined from the ratios of the relative intensity of the peaks due to the $-\mathrm{Si(CH_3)_2}-$ to that of the peaks due to $-\mathrm{C}\mathbf{H}_2-\mathrm{C}\mathbf{H}\mathrm{Ph}-$ were 5.40 (17% conversion) and 8.33 (21% conversion), which were in good agreement with those determined from the molecular weights (5.43 and 8.00 at 17 and 21% conversions, respectively).

The SEC elution curves of **9** and **10** are shown in Figure 7. While the M_n value of **9** is 7600 (peak a), the M_n values of the block copolymers obtained at 17% (peak b) and 21% conversions (peak c) are 26 300 ($M_w/M_n = 1.73$) and 35 100 (1.80), respectively, indicating that polymerization of St was initiated with the functionalized poly(D$_3$). However, the copolymer obtained at 53% conversion gave a bimodal SEC elution curve. The M_n for the lower molecular weight component is almost the same as that of the copolymer at 21% conversion, and that of the higher molecular weight component is equal to that (1.1×10^5) of poly(St) formed by autopolymerization. We assume that the nitroxide-mediated living radical polymerization of St no longer occurs above ~21% conversion of St. Above 21% conversion autopolymerization of St only occurs, giving uncontrolled poly(St) with a high MW.

Experimental Section

IR spectra were obtained on a JASCO FT/IR-230 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL α-400 spectrometer using TMS as the internal standard. SEC was performed on a Tosoh 8020 series equipped with TSK-gel columns G5000HHR, GMultiporeHXL-M, and GMHHR-L using polystyrene standards as the references and using THF as the eluant. Vapor pressure osmometry was carried out with a Knauer vapor pressure osmometer (model 1100) using toluene as the solvent and benzil as the reference. Column chromatographic purification was carried out on silica gel (Fuji Silysia Co., Ltd., BW-127ZH). 2,2,6,6-Tetramethylpiperidinyl-1-oxyl (TEMPO), di-*tert*-butyl nitroxide, ethylbenzene, 4-ethylbromobenzene, and 4-ethylanisole were commercially available and used without any further purification. 2,2,5,5-Tetramethylpyrrolidinyl-1-oxyl was prepared according to the reported methods and purified by column chromatography on silica gel before use.[34] Di-*tert*-butyl diperoxyoxalate was obtained by the reported method and stored at −25 °C.[24]

General Procedure for Preparation of Alkoxyamines 3a−c. A solution of a nitroxide radical (3.14 mmol), **4** (~0.77 g, ~3.3 mmol) (caution! *do not scrape the crystals*), in ethylbenzene (20 mL) was stirred at 35 °C under a nitrogen atmosphere until the characteristic red color of nitroxide disappeared (ca. 3 h). The reaction mixture was then concentrated to ca. 1 mL by evaporation under reduced pressure at room temperature, and the residue was chromatographed on silica gel using 1:10 ethyl acetate−hexane to give almost pure compounds of **3a**−**c** as a colorless oil. Crystallization of **3a** from pentane or ethanol and subsequent cooling to −20 °C gave colorless needles.

***N*-(α-Methylbenzyloxy)-2,2,6,6-tetramethylpiperidine (3a):**[12,13] Yield 90%; mp 44−45 °C (lit.[12] 44.5−45 °C).

***N*-(α-Methylbenzyloxy)-2,2,5,5-tetramethylpyrrolidine (3b):** Yield 89%; colorless oil. ^{1}H NMR (CDCl$_3$): δ 0.64 (s, Me, 3 H), 1.03 (s, Me, 3 H), 1.17 (s, CH$_3$, 3 H), 1.26 (s, CH$_3$, 3 H), 1.49 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 1.40−1.63 (br m, (CH$_2$)$_2$, 4 H), 4.66 (q, $J = 6.8$ Hz, C**H**-CH$_3$, 1 H), 7.22−7.35 (m, aromatic, 5 H).

***N*-(α-Methylbenzyloxy)-di-*tert*-butylamine (3c):**[9] Yield 90%; colorless oil. ^{1}H NMR (CDCl$_3$): δ 1.04 (s, *t*-Bu, 9 H), 1.31 (s, *t*-Bu, 9 H), 1.46 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 4.82 (q, $J = 6.8$ Hz, C**H**−CH$_3$, 1 H), 7.21−7.33 (m, aromatic, 5H).

General Procedure for Preparation of Alkoxyamines 3d−f. A solution of TEMPO (0.33 g, 2.11 mmol), **4** (~0.77 g, ~3.4 mmol), and ethylbenzene (8.45 mmol) in benzene (10 mL) was stirred at 35 °C under a nitrogen atmosphere until the characteristic red color due to TEMPO disappeared (ca. 2 h). The mixture was then concentrated to ca. 1 mL by evaporation under reduced pressure at room temperature, and the residue was chromatographed on silica gel using benzene to give pure compounds of **3d**−**f**. Crystallization from pentane or methanol gave colorless plates.

***N*-(α-Methyl-4-bromobenzyloxy)-2,2,6,6-tetramethylpiperidine (3d):**[13] Yield 88%; mp 57−59 °C (methanol). ^{1}H NMR (CDCl$_3$): δ 0.64 (s, CH$_3$, 3 H), 1.01 (s, CH$_3$, 3 H), 1.15 (s, CH$_3$, 3 H), 1.27 (s, CH$_3$, 3 H), 1.44 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 1.35−1.6 (br m, (CH$_2$)$_3$, 6 H), 4.73 (q, $J = 6.8$ Hz, C**H**-CH$_3$, 1 H), 7.19 (d, $J = 8.3$ Hz, aromatic, 2 H), 7.43 (d, $J = 8.3$ Hz, aromatic, 2 H). Calcd for $\mathrm{C_{17}H_{26}BrNO}$: C, 60.00; H, 7.70; N, 4.12. Found: C, 59.93; H, 7.68; N, 3.82.

***N*-[α-Methyl-4-(ethoxycarbonyl)benzyloxy]-2,2,6,6-tetramethylpiperidine (3e):** Yield 50%; mp 62−64 °C (pentane). IR (KBr): 1715 (C═O) and 1280 cm^{-1} (ester). ^{1}H NMR (CDCl$_3$): δ 0.62 (s, CH$_3$, 3 H), 1.02 (s, CH$_3$, 3 H), 1.17 (s, CH$_3$, 3 H), 1.29 (s, CH$_3$, 3 H), 1.39 (t, $J = 6.8$ Hz, CH$_2$C**H**$_3$, 3 H), 1.48 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 1.34−1.58 (br m, (CH$_2$)$_3$, 6 H), 4.37 (q, $J = 6.8$ Hz, C**H**$_2$CH$_3$, 2 H), 4.82 (q, $J = 6.8$ Hz, C**H**-CH$_3$, 1 H), 7.38 (d, $J = 8.3$ Hz, aromatic, 2 H), 7.99 (d, J

= 8.3 Hz, aromatic, 2 H). Calcd for $C_{20}H_{31}NO_3$: C, 71.82; H, 9.34; N, 4.19. Found: C, 72.03; H, 9.22; N, 3.87.

***N*-(α-Methyl-4-methoxybenzyloxy)-2,2,6,6-tetramethylpiperidine (3f):** Yield 91%; mp 73−74 °C (pentane). ^1H NMR ($CDCl_3$): δ 0.65 (s, CH_3, 3 H), 1.01 (s, CH_3, 3 H), 1.15 (s, CH_3, 3 H), 1.28 (s, CH_3, 3 H), 1.2−1.6 (br m, $(CH_2)_3$, 6 H), 1.46 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 3.80 (s, OCH_3, 3 H), 4.73 (q, $J = 6.8$ Hz, C**H**-CH_3, 1 H), 6.85 (d, $J = 8.8$ Hz, aromatic, 2 H), 7.24 (d, $J = 8.8$ Hz, aromatic, 2 H). Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.32; H, 9.77; N, 4.52.

***N*-(α-Methyl-4-formylbenzyloxy)-2,2,6,6-tetramethylpiperidine (3h):** A stirred solution of 1.55 g (4.6 mmol) of **3d** in 40 mL of dry ether under nitrogen was cooled in a dry ice MeOH bath, and a pentane solution of *t*-BuLi (1.64 M) (5.8 mL, 9.5 mmol) was added. The resulting mixture was stirred for 1 h at the same temperature, and dry DMF (2.0 mL, 26 mmol) was added. After the mixture was gradually raised to 0 °C, aqueous NH_4Cl was added at 0 °C, and the mixture was extracted with CH_2Cl_2. The extract was washed with brine, dried ($MgSO_4$), evaporated, and chromatographed on silica gel using 1:4 hexanes−ethyl acetate to give an almost pure compound of **3h** in 95% yield. Crystallization from pentane gave colorless plates. Mp 92−93 °C. IR (KBr): 1700 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 0.63 (s, CH_3, 3 H), 1.03 (s, CH_3, 3 H), 1.18 (s, CH_3, 3 H), 1.30 (s, CH_3, 3 H), 1.49 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 1.35−1.6 (br m, $(CH_2)_3$, 6 H), 4.85 (q, $J = 6.8$ Hz, C**H**−CH_3, 1 H), 7.48 (d, $J = 8.3$ Hz, aromatic, 2 H), 7.84 (d, $J = 8.3$ Hz, aromatic, 2 H), 10.00 (s, CHO, 1 H). Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.59; H, 9.37; N, 4.60.

Reduction of 3h to 3i with $NaBH_4$. To a stirred solution of 310 mg (1.07 mmol) of **3h** in EtOH (12)−THF (4 mL) was added 0.20 g (4.3 mmol) of $NaBH_4$ at room temperature. After the mixture was stirred for 2 h, the usual workup and subsequent chromatography (silica gel, 1:1 benzene−ethyl acetate) gave **3i** as an colorless oil in 89% yield (0.278 g, 0.953 mmol).

***N*-[α-Methyl-4-(hydroxymethyl)benzyloxy]-2,2,6,6-tetramethylpiperidine (3i):** IR (neat): 3400 cm^{-1} (OH). ^1H NMR ($CDCl_3$): δ 0.67 (s, CH_3, 3 H), 1.02 (s, CH_3, 3 H), 1.16 (s, CH_3, 3 H), 1.29 (s, CH_3, 3 H), 1.47 (d, $J = 6.8$ Hz, CH−C**H**$_3$, 3 H), 1.35−1.6 (br m, $(CH_2)_3$, 6 H), 4.69 (s, C**H**$_2$OH, 2 H), 4.79 (q, $J = 6.8$ Hz, C**H**−CH_3, 1 H), 7.32 (s, aromatic, 4 H).

Reduction of 3h to 3i with $LiAlH_4$. A solution of 304 mg (1.05 mmol) of **3h** in 5 mL of anhydrous THF was added dropwise to a stirred suspension of 63 mg (1.66 mmol) of $LiAlH_4$ in 10 mL of anhydrous THF. After the resulting suspension was stirred for 2 h, the usual workup and subsequent chromatography (silica gel, 1:1 ethyl acetate−hexane) gave **3i** in 82% yield (241 mg, 0.86 mmol) as a colorless oil.

Reaction of 4-Formylethylbenzene with 4 in the Presence of TEMPO. A solution of TEMPO (0.386 g, 2.47 mmol), **4** (∼0.94 g, ∼4.0 mmol), and 4-formylethylbenzene (1.03 g, 7.65 mmol) in benzene (10 mL) was stirred at 35 °C for 3 h under a nitrogen atmosphere. After the reaction mixture was concentrated to ca. 1 mL by evaporation under reduced pressure at room temperature, the residue was chromatographed on silica gel using benzene as eluant to give almost pure compounds of **5** in 60% yield as a colorless oil.

***N*-(4-Ethylphenylcarbonyloxy)-2,2,6,6-tetramethylpiperidine (5).** IR (neat): 1750 (C=O), 1260 cm^{-1} (ester). ^1H NMR ($CDCl_3$): δ 1.12 (s, CH_3, 6 H), 1.267 (t, $J = 7.3$ Hz, CH_2C**H**$_3$, 3 H), 1.272 (s, CH_3, 6 H), 1.4−1.8 (br m, $(CH_2)_3$, 6 H), 2.72 (q, $J = 7.3$ Hz, C**H**$_2$$CH_3$, 2 H), 7.29 (d, $J = 8.3$ Hz, aromatic, 2 H), 8.00 (d, $J = 8.3$ Hz, aromatic, 2 H).

Polymerization of St with Alkoxyamines 3d−f and 3h. St (1.0 mL, 0.909 g) and an alkoxyamine (0.020 mmol) were placed in a glass tube, and the tube was degassed by three freeze−pump−thaw cycles and sealed off. After the tube was heated to 120 °C for 15−30 h, the reaction mixture was poured into a large excess of methanol, and poly(St) precipitated was collected by filtration and dried in vacuo. Conversion was determined by weight, and M_n and M_w/M_n were determined by SEC.

Anionic Polymerization of BD and Termination by 3h. In one leg of an H-shaped glass tube was placed 0.15 g (0.52 mmol) of **3h**, and in the other leg 2 mL of BD and 7.5 mL of dry toluene were placed. After the tube was charged with nitrogen, 0.43 mL (0.43 mmol) of *sec*-butyllithium (1.01 M in pentane) was added to the toluene solution with a syringe through a double septum, and the tube was sealed off from the vacuum system. After 24 h at room temperature, the toluene solution was mixed with **3h** by shaking the tube, and it was allowed to stand for 24 h at room temperature. The reaction mixture was then poured into a large excess of methanol to give **7** as a yellowish oil in ∼100% yield. M_n = 7980 (SEC), 5970 (VPO); M_w/M_n = 1.11 (SEC).

Polymerization of St with 7. Functionalized poly(BD) **7** (0.262 g) and St (1.35 g, 12.9 mmol) were placed in a glass tube, the content was degassed by three freeze−pump−thaw cycles, and the tube was sealed off. It was then heated to 120 °C for 20 h, and the reaction mixture was poured into a large excess of methanol. The resulting polymeric material was filtered and dried in a vacuum. Yield 0.88 g (46%); M_n = 24 300; M_w/M_n = 1.30.

Lithiation of 3d with Lithium Metal. To a solution of 0.50 g (1.5 mmol) of **3d** in 2 mL of anhydrous THF was added 41 mg (5.90 g atom) of Li, and the mixture was gently refluxed for 3 h. After cooling to temperature, aqueous NH_4Cl (2.0 mL) was added, and the mixture was stirred for 1 h at room temperature. After extraction with ether, drying ($MgSO_4$), and evaporation, the residue was subjected to ^1H NMR measurements using $CDCl_3$ as the solvent.

Anionic Polymerization of D_3 with 3g. A solution of 10.0 g (45.0 mmol) of D_3 in 8.0 mL of dry cyclohexane was refluxed over CaH_2 for 3 h, and 4.0 mL of the supernatant was taken with a syringe and placed in a two-necked round flask charged with nitrogen. A solution of **3g** in anhydrous THF (ca. 2 mL) was added to the cyclohexane solution with a syringe through a double septum. The mixture was heated to 80 °C for 4 h under nitrogen with stirring and poured into a large excess of methanol to give poly(D_3) as an colorless biscous oil in 67% yield. M_n = 7600, M_w/M_n = 1.33.

Polymerization of St with 9. The poly(D_3) macroinitiator **9** (30 mg) and St (0.28 g, 2.7 mmol) were placed in a glass tube, the content was degassed by three freeze−pump−thaw cycles, and the tube was sealed off. It was then heated to 120 °C for 4, 8, and16 h, and the reaction mixture was poured into a large excess of methanol. The resulting polymeric material was filtered and dried in vacuo.

References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66.
(3) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183.
(4) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373.
(5) Colombani, D. *Prog. Polym. Sci.* **1997**, *22*, 1649.
(6) Malmström, E. E.; Hawker, C. J. *Macromol. Chem. Phys.* **1998**, *199*, 923.
(7) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323.
(8) Yamada, B.; Miura, Y.; Nobukane, Y.; Aota, M. *Controlled Radical Polymerization;* Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998; p 200.
(9) Catala, J.-M.; Bubel, F.; Mammouch, S. O. *Macromolecules* **1995**, *28*, 8441. Hammouch, S. O.; Catala, J.-M. *Macromol. Rapid Commun.* **1996**, *17*, 683.
(10) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US Pat 4581429, 1986; *Chem. Abstr.* **1985**, *102*, 221335.
(11) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.
(12) Howell, B. A.; Priddy, D. B.; Li, I. Q.; Smith, P. B.; Kastl, P. E. *Polym. Bull.* **1996**, *37*, 451.
(13) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245.
(14) Connolly, T. J.; Baldoví, M. V.; Mohtat, N.; Scaiano, J. C. *Tetrahedron Lett.* **1996**, *37*, 4919.
(15) Nagashima, T.; Curran, D. P. *Synlett* **1996**, 330.
(16) Braslau, R.; Burrill, L. C.; Siano, M.; Naik, N.; Howden, R. K.; Mahal, L. K. *Macromolecules* **1997**, *30*, 6445.

(17) Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2555.

(18) Wang, D.; Wu, Z. *Macromolecules* **1998**, *31*, 6727.

(19) Miura, Y.; Hirota, K.; Moto, H.; Yamada, B. *Macromolecules* **1998**, *31*, 4659.

(20) Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z. *Macromolecules* **1998**, *31*, 5955.

(21) Dao J.; Benoit, D.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2161.

(22) Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1997**, *30*, 4238. Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1998**, *31*, 3735.

(23) Kobatake, S.; Harwood, H. J.; Quirk, R. P.; Priddy, D. B. *Macromolecules* **1999**, *32*, 10.

(24) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

(25) Boiling points are 204 (4-ethylbromobenzene), 213 (ethyl 4-ethylbenzoate), and 195 °C (4-ethylanisole).

(26) Howard, J. A.; Korcek, S. *Can. J. Chem.* **1970**, *48*, 2165. Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, p 78.

(27) 4.92−5.00 ($C\mathbf{H}_2{=}CH-$ of the 1,2-BD units), 5.54−5.62 ($CH_2{=}C\mathbf{H}-$ of the 1,2-BD units), 5.37−5.42 ppm (two olefinic protons of the 1,4-BD units).

(28) The end-terminal groups are taken into account in determination of M_n by ^{1}H NMR.

(29) Weimer, M. W.; Scherman, O. A.; Sogah, D. Y. *Macromolecules* **1998**, *31*, 8425.

(30) Mecerreyes, D.; Moineau, G.; Dubois, P.; Jérôme, R.; Hedrick, J. L.; Hawker, C. J.; Malmström, E. E.; Trollsas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1274.

(31) Saam, J. C.; Gordon, D. J.; Lindsey, S. *Macromolecules* **1970**, *3*, 1.

(32) Zilliox, J. G.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1975**, *8*, 573.

(33) Yoshida, E.; Tanimoto, S. *Macromolecules* **1997**, *30*, 4018.

(34) Hankovszky, H. O.; Hideg, K.; Lovas, M. J.; Jerkovich, G.; Rockenbauer, A.; Györ, M.; Sohár, P. *Can. J. Chem.* **1989**, *67*, 1392.

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