Universal Multifunctional Initiator Containing Orthogonal Reactive Sites. Synthesis of Macromonomers and Comb Polymers Using Consecutive Controlled Free Radical and Cationic Ring-Opening Polymerizations

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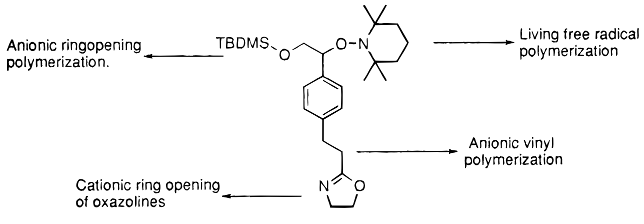
ABSTRACT: A multifunctional reagent (**1**) containing orthogonal reactive sites that could serve as an initiator for multiple living polymerizations, namely, controlled free radical, anionic, and cationic polymerizations, and a source for a variety of macromonomers, including those for condensation polymerization and functional polymers, has been designed and synthesized in three steps in good yields. The reagent contained an alkoxyamine derived from 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO), an oxazoline, and a protected hydroxyl group. Thus, initiation of controlled free radical polymerization of styrene at the alkoxyamine terminal gave a polystyrene (PS) macromonomer with low polydispersity ($M_w/M_n = 1.06-1.16$). Cationic ring-opening polymerization of the oxazoline group gave an amphiphilic comb polymer with a hydrophilic poly(ethyleneimine) backbone and a hydrophobic PS side chain. The polymers were characterized by GPC, ^{1}H and ^{13}C NMR, and MALDI−TOF mass spectroscopy. The versatility of the structure is such that different types of macromonomers and macroinitiators suitable for many of the major methods of polymer synthesis can be made, making **1** a "universal" initiator.

Introduction and Rationale

Synthesis of functional polymers and materials of controlled architectures is of current interest in both industrial and academic research. Furthermore, there is an increasing tendency, especially in industry, to add value to existing products through modifications. These challenges are being met partly through the use of living polymerizations that lead to materials having a variety of functional groups.[1−5] In our continued effort toward design and synthesis of functional polymers of controlled architectures, we have designed and prepared a single compound which can serve as a "universal" multifunctional initiator (**1**, Scheme 1) and a polymer modification agent. The overall goal is to obtain a compound capable of initiating the major polymerizations. This requires that the species has characteristics that will enable reactive sites to be independently accessed in such a way that when only one initiating site is used, for example, the resulting polymer will be both a macromonomer and a multifunctional macroinitiator. The critical requirement is that the necessary reactive groups survive each of the different polymerization processes. Compound **1** fulfills these requirements, and its design is based on the following: (1) alkyl adducts of nitroxyl radicals initiate controlled free radical polymerization;[3−5] (2) oxazolines are excellent protective groups for carboxylic acids and are readily removed;[6] (3) neutral oxazolines are stable toward free radical and anionic reactions;[6−7] (4) the α-position with respect to the oxazoline group is relatively acidic and can serve as a carbanion source;[8] and (5) cationic ring opening polymerization of oxazoline,[9] alkoxide-initiated anionic polymerization of heterocycles,[10] and carbanion-initiated polymerizations living/controlled polymerization methods.[2,11] The possibilities are indicated in Scheme 1.

Scheme 1



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It can be seen from the structure of **1** that initiation and propagation of controlled free radical polymerization using the alkoxyamine functional group, for example, will give a polymer with oxazoline and protected hydroxyl groups both at the same terminus of the chain. The oxazoline-containing macromonomer may be polymerized to give a graft polymer. Alternatively, the protective groups may be removed to provide an AB-type macromonomer that contains one hydroxyl and one carboxylic acid group, which, in turn, may be readily converted into an AA-type macromonomer by reduction of the acid. Thus, several novel materials can be made available for incorporation into several step-growth polymers, such as polyesters, polyamides, polyether polyurethanes, and polyimides, if desired. Initiation of polymerization of different types of monomers from each of the initiating sites to give what could be called a *heteromultiarmed* star is also possible. The versatility of the structure is such that different types of macromonomers suitable for any of the major methods of polymer synthesis (with, perhaps, the single exception of metathesis polymerization) can be made. Hence, faced with the above attractive potential, we set out to synthesize **1** and demonstrate its utility as a universal initiator. Star polymers via tris(alkoxyamine) unimolecular initiators,[4a,b] various kinds of alkoxyamine-terminated polymers,[5] and a polyimide-*graft*-polystyrene copolymer[12] have been reported, but none of these examples has the versatility presented by **1**. In this paper we report the synthesis of **1** and our preliminary results of its use in controlled stable free radical-mediated and cationic ring-opening polymerizations in a sequential fashion. The use of **1** in the synthesis of

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graft copolymers and double comb polymers will be described in a future publication.

Experimental Details

General. Common reagents were purchased from Aldrich, and solvents, from Fisher Scientific. THF was distilled from Na under N_2. *o*-Dichlorobenzene (ODCB, 99%, anhydrous grade) was fractionally distilled twice under vacuum from CaH_2 and stored in a drybox. 2-Methyl-2-oxazoline and diisopropylamine were distilled from CaH_2 under nitrogen. *n*-Butyllithium was titrated with *sec*-butanol and 1,10-phenanthroline indicator. Styrene was distilled under vacuum. Methyl triflate was received in ampules, which were opened and stored in a drybox. ^{1}H NMR spectra were recorded on either a Varian XL-200 spectrometer operating at 200.057 MHz or a Varian XL-400 spectrometer operating at 399.952 MHz with TMS or chloroform as internal standards. ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 100.577 MHz with TMS or $CDCl_3$ as an internal standard. IR spectra were recorded on a Perkin Elmer 16PC FT-IR spectrophotometer using KBr pellets. Gel permeation chromatography was carried out on a Viscotek GPC system with a 222c HPLC pump, a model 200 Differential Refractometer/Viscometer, and two linear mixed bed and one 500 Å American Polymer Standards 10 μm columns. Matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) mass spectroscopy was carried out on a Finigan Lasermat 2000 with *trans*-indoleacrylic acid or 2,5-dihydroxybenzoic acid as matrix. Elemental analysis was carried out by Oneida Research Labs, Inc., New York. Electron ionization (low-resolution (EI) and high-resolution (HREI)) mass spectroscopy was carried out by University of Illinois Mass Spectroscopy facility. All evaporations were performed in vacuo using a Büchi rotatory evaporator.

Benzoic Acid 2-(4-(Chloromethyl)phenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl Ester (2). Benzoyl peroxide (2.0 g, 8.3 mmol) and TEMPO (2.84 g, 18.2 mmol) were dissolved in 4-vinylbenzyl chloride (80 mL). The mixture was heated for 24 h at 80 °C. The reaction mixture was cooled to room temperature and evaporated with a rotatory evaporator under high vacuum. The recovered 4-vinylbenzyl chloride had a reddish color due to some codistilled TEMPO. The crude dark-colored residue was chromatographed over silica gel using a gradient elution which was started with 30% CH_2Cl_2 in hexanes and gradually increased to 100% CH_2Cl_2. Pure **2** (1.5 g) was isolated as a clear oil. ^{1}H NMR ($CDCl_3$) δ: 1.8 (s, 3H), 1.1 (s, 3H), 1.2 (s, 3H), 1.4 (s, 3H), 1.2−1.6 (m, 6H), 4.5 (dd, J = 11, 6.4 Hz, 1H), 4.6 (s, 2H), 4.8 (dd, J = 11, 4.6, 1H), 5.0 (dd, J = 5.2, 5.2 Hz, 1H), 7.3−7.6 (m, 7H), 7.9 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 17.1, 20.3, 34.0, 40.3, 46.1, 60.1, 66.6, 83.5, 126.7, 127.8, 128.3, 128.3, 128.5, 130.1, 132.8, 132.8, 136.7, 141.0, 166.2. IR (KBr): 1722, 1271 cm^{-1}. Anal. Calcd for $C_{25}H_{32}ClNO_3$: C, 69.83; H, 7.50; N, 3.26. Found: C, 69.94; H, 7.29; N, 3.13.

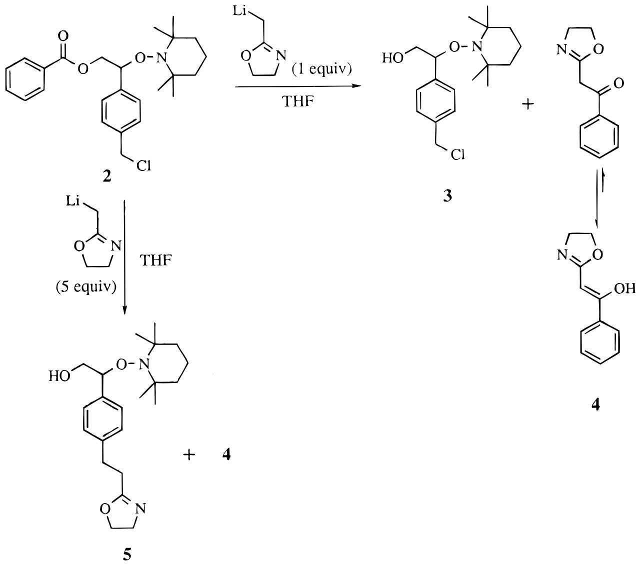
2-(4-(Chloromethyl)phenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanol (3). Lithium diisopropylamide (LDA) was prepared by adding *n*-BuLi (1.67 mL, 1.53 M solution in hexanes, 2.55 mmol) to diisopropylamine (0.36 mL, 2.57 mmol) in THF (5 mL) at 0 °C. After 30 min the solution was cooled to −78 °C and transferred via a cannula to a precooled solution of 2-methyl-2-oxazoline (0.22 mL, 2.59 mmol) in THF (5 mL) at −78 °C. The mixture was stirred for 30 min at −78 °C, after which a precooled solution of **2** (1.13 g, 2.56 mmol) in THF (30 mL) at −78 °C was added via a cannula. After 90 min the reaction was quenched with MeOH, and the reaction mixture was allowed to warm up to room temperature and evaporated. The residue was dissolved in CH_2Cl_2, washed with water and brine, and dried over Na_2SO_4. The crude product was purified by column chromatography over silica gel using gradient elution, which was started with 10% EtOAc in hexanes and increased gradually to 100% EtOAc. The first fraction yielded 0.56 g (67%) of **3**, which slowly solidified to a white solid. A second fraction contained 0.49 g (>99%) of **4** (reddish solid). **3**: Mp: 58−60 °C. ^{1}H NMR ($CDCl_3$) δ: 1−1.7 (m, 18H), 3.7 (d, J = 13 Hz, 1H), 4.2 (dd, J = 12.2, 9.5 Hz, 1H), 4.6 (s, 2H), 5.3 (dd, J = 2.4, 9.5 Hz, 1H), 5.8 (s, 1H), 7.4 (s, 4H). ^{13}C NMR ($CDCl_3$) δ: 17.1, 20.4, 20.7, 32.8, 34.6, 40.2, 40.4, 45.9, 60.4, 61.7, 83.2, 127.1, 128.6, 137.0, 139.2. IR (KBr): 3375, 2932, 1456, 1363 cm^{-1}. HRMS: calcd for $C_{18}H_{28}ClNO_2$ (M$^+$), 325.1809; found, 325.1808. Anal. Calcd for $C_{18}H_{28}ClNO_2$: C, 66.34; H, 8.66; N, 4.39. Found: C, 66.19; H, 8.82; N, 4.09. **4**: Mp: 65−75 °C. ^{1}H NMR ($CDCl_3$) δ: 3.8 (t, J = 8 Hz, 2H), 4.5 (t, J = 8 Hz, 2H), 5.6 (s, 1H), 7.4 (m, 3H), 7.8 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 43.0, 67.4, 74.2, 126.8, 128.1, 130.5, 139.9, 170.1, 187.5. IR (KBr): 3307, 1627, 1498 cm^{-1}. MS (EI): 189 (M$^+$, 30%), 188 (M − 1, 75%). HRMS(EI): calcd for $C_{11}H_{11}NO_2$ (M$^+$), 189.0712; found, 189.0709.

2-{4-[2-(4,5-Dihydrooxazol-2-yl)ethyl]phenyl}-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanol (5). To a solution of 2-(lithiomethyl)-2-oxazoline (7.17 mmol) in THF (20 mL), prepared as described for **3**, was added dropwise a solution of **2** (0.69 g, 1.6 mmol) in THF (100 mL) at −78 °C via a cannula. After 30 min the reaction was quenched with MeOH, and the reaction mixture was allowed to warm up to room temperature and evaporated. The residue was dissolved in CH_2Cl_2, washed with water and brine, and dried over Na_2SO_4. The crude product was purified by column chromatography over silica gel using gradient elution, which started with 20% EtOAc in hexanes and increased gradually to 100% EtOAc. One fraction containing both **5** and **4** (total weight, 0.31 g) in a 1:1 molar ratio (by NMR) was used for characterization. (**4** has been characterized spectroscopically earlier.) **5**: ^{1}H NMR ($CDCl_3$) δ: 1−1.7 (m, 18H), 2.5 (dd, J = 8, 8 Hz, 2H), 2.93 (dd, J = 8, 8 Hz, 2H), 3.75 (m, 4H), 4.2 (m, 2H), 5.3 (dd, J = 3, 9.5 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 16.7, 20.1, 20.4, 29.3, 31.5, 32.5, 34.3, 39.9, 40.1, 54.1, 60.0, 61.3, 69.2, 83.2, 126.5, 127.9, 136.6, 140.1, 167.4. IR (KBr): 3248, 2926, 1670 cm^{-1}. MS(CI): 375 (M$^+$), 218 (M − TEMPO). HRMS: calcd for $C_{22}H_{35}N_2O_3$ (M$^+$), 375.2648; found, 375.2633.

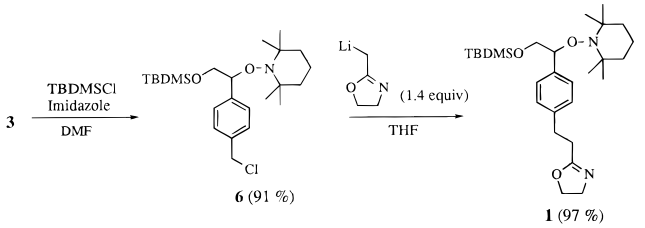
1-[2-((*tert*-Butyldimethylsilanyl)oxy)-1-(4-(chloromethyl)phenyl)ethoxy]-2,2,6,6-tetramethylpiperidine (6). Alcohol **3** (0.25 g, 0.77 mmol) was reacted with TBDMSCl (0.14 g, 0.93 mmol) in DMF (1.0 mL) in the presence of imidazole (0.13 g, 1.9 mmol). The mixture was stirred overnight at room temperature, quenched with a 5% aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, and dried over $MgSO_4$. Evaporation followed by chromatography over silica gel with 10% EtOAc in hexanes afforded 0.31 g (91%) of a colorless oil. ^{1}H NMR ($CDCl_3$) δ: −0.174 (s, 3H), −0.165 (s, 3H), 0.72 (s, 3H), 0.77 (s, 9H), 1−1.7 (m, 15H), 3.7 (dd, J = 10.1, 6.7 Hz, 1H), 4.0 (dd, J = 10.1, 5 Hz, 1H), 4.6 (s, 2H), 4.7 (dd, J = 6.7, 5 Hz, 1H), 7.3 (m, 4H). ^{13}C NMR ($CDCl_3$) δ: −5.72, −5.68, 17.2, 18.2, 20.4, 25.7, 40.4, 46.4, 60.0, 65.6, 86.5, 127.8, 128.2, 136.0, 142.5. IR (KBr): 2931, 1466, 1362 cm^{-1}. Anal. Calcd for $C_{24}H_{42}ClNO_2Si$: C, 65.49; H, 9.62; N, 3.18. Found: C, 66.01; H, 9.30; N, 3.13.

1-{2-((*tert*-Butyldimethylsilanyl)oxy)-1-{4-[2-(4,5-dihydrooxazol-2-yl)ethyl]phenyl}ethoxy}-2,2,6,6-tetramethylpiperidine (1). LDA was prepared as described above with *n*-BuLi (0.75 mL, 1.53 M in hexanes, 1.15 mmol), diisopropylamine (0.17 mL, 1.21 mmol), and THF (4 mL). The solution was cooled to −78 °C and transferred via a cannula to a precooled solution of 2-methyl-2-oxazoline (0.10 mL, 1.18 mmol) in THF (4 mL) at −78 °C. The mixture was stirred for 30 min at −78 °C, after which a precooled solution of **6** (0.31 g, 0.71 mmol) in THF (8 mL) at −78 °C was added via a cannula. After 1 h, the reaction was quenched with MeOH, and the reaction mixture was allowed to warm up to room temperature and evaporated. The crude mixture (0.34 g, 97%) was purified by column chromatography over silica gel using 50% EtOAc in hexanes to yield 0.28 g (82%) of analytically pure **1** as an oil that slowly solidified to form soft white crystals. Mp: 69−72 °C. ^{1}H NMR ($CDCl_3$) δ: −0.17 (s, 3H), −0.18 (s, 3H), 0.7 (s, 3H), 0.8 (s, 9H), 1−1.6 (m, 15H), 2.55 (dd, J = 8.1, 8.1 Hz, 2H), 2.93 (dd, J = 8.1, 8.1 Hz, 2H), 3.7 (dd, J = 9.9, 6.7 Hz, 1H), 3.81 (dd, J = 9.5, 9.5 Hz, 2H), 4.05 (dd, J = 9.9, 5.4 Hz, 1H), 4.2 (dd, J = 9.5, 9.5 Hz, 2H), 4.68 (dd, J = 7.0, 5.1 Hz, 1H), 7.1 (d, J = 8.1, 2H), 7.2 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: −5.67, −5.72, 17.2, 18.2, 20.4, 25.8, 29.9, 31.9, 34.3, 40.5, 54.4, 59.9, 65.8, 67.2, 86.5, 127.4,

Scheme 2



Scheme 3



128.0, 139.3, 140.0, 167.8. IR (KBr): 1669, 836 cm^{-1}. MS (EI): 488.8 (M$^+$, 2%), 332.2 (M − TEMPO, 100%). Anal. Calcd for $C_{24}H_{42}ClNO_2Si$: C, 68.80; H, 9.90; N, 5.73. Found: C, 68.75; H, 10.04; N, 5.71.

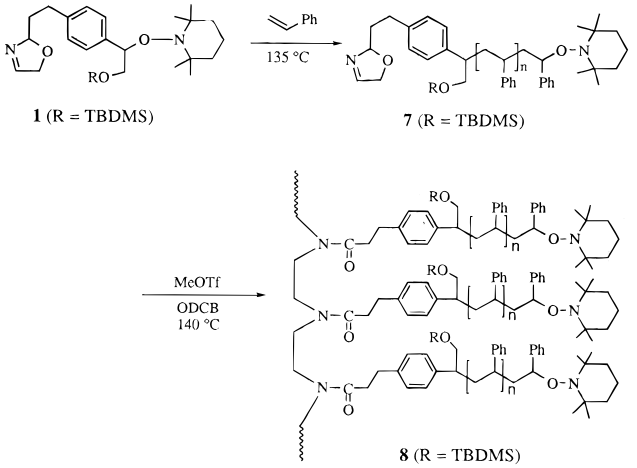
Polystyrene Macromonomer (7). A 5 mL round bottom flask equipped with a reflux condenser and a magnetic stirring bar was charged with **1** (0.05 g, 0.10 mmol) and styrene (1.0 mL, 8.70 mmol). The mixture was heated at 135 °C for 3 days. The viscous solution was dissolved in CH_2Cl_2 (5 mL) and precipitated from MeOH (100 mL). Filtration through a fritted glass filter (porosity 25−50 μm) yielded 0.50 g (52%) of a white polymer. M_n (calc) 5000 (corrected for conversion). GPC: M_n 5000, M_w 5800, PDI 1.16. ^{1}H NMR: M_n 6000. MALDI-TOF: M_n 5000, M_w 5300, PDI 1.06.

Polymerization of Macromonomer 7 to Form 8. Inside a drybox, macromonomer **7** (0.41 g) was dissolved in ODCB (0.40 mL) in a 25 mL round bottom flask equipped with a Rotaflo stopcock. A solution of methyl triflate (0.10 mL, 0.10 g, 0.63 mmol) in 9.1 mL ODCB was added, and the flask was sealed, taken out of the drybox, and heated at 140 °C for 21 days. After cooling to room temperature, CH_2Cl_2 was added, and the polymer was precipitated from MeOH to yield 0.32 g (78%) of an off-white powder. GPC: Peak MW M_p 40 000. See the text for ^{1}H NMR and ^{13}C NMR spectra.

Results and Discussion

Synthesis of 1. Schemes 2 and 3 outline the synthesis of initiator **1** from readily available materials. Alkoxyamine adduct **2** was synthesized from 4-vinylbenzyl chloride by modification of published procedures for the corresponding alkoxyamine from styrene.[4c] We have previously shown that carbanions derived from 2-methyl-2-oxazolines could be readily alkylated.[8] However, addition of 1 equiv of 2-(lithiomethyl)-2-oxazoline (LiOXZ) to **2** following our earlier procedures led to products resulting from exclusive attack at the ester carbonyl group by LiOXZ to give **3** and **4** without any of the desired product. Efforts to prepare **5** directly by treatment of **2** with excess LiOXZ (5 equiv) gave the desired product. However, excessive contamination by **4** rendered purification by chromatography extremely difficult (both compounds have almost the same R_f values in the solvent systems tried). Hence, **3** was prepared by treatment of **2** with only 1 equiv of LiOXZ and separated from **4** by column chromatography in 67% yield. It was then protected with TBDMSCl to give **6** in 91% yield (Scheme 3). Subsequent treatment of **6** with LiOXZ (1.4 equiv) gave the desired product **1** in 97% yield (62% overall, 3 steps from **2**). In principle, LiOXZ in the first step could be replaced by other organolithium or similar bases to give **3**. However, direct saponification of **2** failed to give acceptable yields of **3**.

Scheme 4



Polymerizations. The stable free radical-mediated polymerization of styrene using **1** as initiator (Scheme 4) was carried out at 135 °C to give the expected oxazoline-ended polystyrene macromonomer/macroinitiator **7** in 52% isolated yield. Figure 1 shows both GPC (a) and MALDI−TOF (b) plots. The GPC analysis gave $M_n = 5000$ and $M_w/M_n = 1.16$. This, remarkably, is the same as the calculated molecular weight based upon the molar ratio of styrene to **1** and corrected for yield. The M_n determined by MALDI−TOF mass spectroscopy was 5000, which coincidentally is the same as the molecular weight at the peak maximum (M_m, vertical line in Figure 1) due to the approximate Gaussian shape of the plot. However, the polydispersity index $M_w/M_n = 1.06$ obtained by MALDI−TOF is slightly less than that from GPC, which is evident from the shapes of the plots in Figure 1. That the two methods can give slightly different MW characteristics has been observed previously.[13] For example, Thomson *et al.* found that a PMMA sample with the peak molecular weight $M_p = 1680$ and $M_w/M_n = 1.15$ determined by GPC gave $M_n = 1515$ and $M_w/M_n = 1.08$ by MALDI.[13c] Our findings were further corroborated by integration of the appropriate peaks in the ^{1}H NMR spectrum, which gave $M_n = 6000$.

Figure 2 shows the ^{1}H NMR spectra of **1** (a) and product **7** (b). If the reaction occurred as shown in Scheme 4, then the benzylic methine proton (H-3) attached to the tertiary carbon of the alkoxyamine and the α-methylene hydrogens (H-2,2′) adjacent to the siloxy group should be most affected. However, the methylene hydrogens removed from the reaction center, H-8 and H-9, and the oxazoline methylene protons, H-11 and H-12, should be least affected. Examination of the spectra revealed that the H-3 signal at δ 4.7 and the

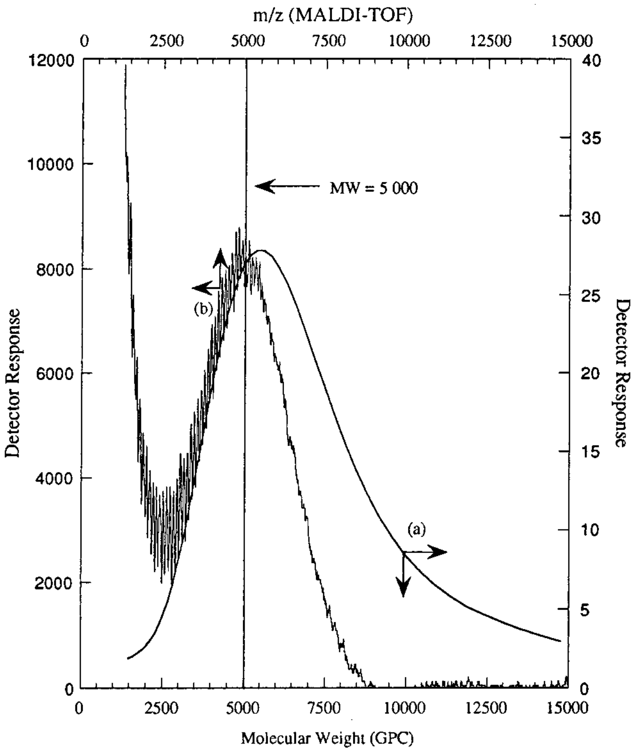


Figure 1. Gel permeation chromatogram (a) and matrix-assisted laser desorption–time of flight spectrum (b) of polystyrene macromonomer **7**. The detector responses were arbitrarily scaled, and GPC was converted to a number average molecular weight scale for proper comparison with the MALDI–TOF spectrum. The latter was performed using nitrophenyl octyl ether and silver trifluoroacetate as matrix.

diastereotopic methylene protons (H-2,2′) of **1** (Figure 2a) shifted upfield to 3.0 and 3.4 ppm, respectively, in the spectrum of polymer **7** (Figure 2b). The chemical shifts of the characteristic signals of the oxazoline methylenes H-11 and H-12 (δ 3.7 and 4.3) and those of H-8 and H-9 and the TBDMS group (H-1) remained essentially the same in both spectra. That the oxazoline moiety and the relatively acidic H-3, H-8, and H-9 survived the reaction conditions suggests that chain transfer involving these hydrogens did not occur to any appreciable extent (if at all). Examination of CPK molecular models of **1** suggests that H-3 is sterically shielded by the bulky (tetramethylpiperidinyl)oxy group.

The above findings were further confirmed by ^{13}C NMR (Figure 3a and b) spectroscopy. Comparison of the two spectra (Figure 3a vs b) reveals that the signals of C-3 of **1**, which occurred at 86.5 ppm, could no longer be seen in that position in the spectrum of the macromonomer. This is a clear indication that the initiation occurred from that carbon. The signal probably shifted upfield and overlapped those of the tertiary carbons of polystyrene. The chemical shifts of C-8, C-9, C-11, C-12, and C-10 (29.9, 31.9, 54.4, 67.2, and 167.8 ppm, respectively) remained unchanged. The above results demonstrate that **1** is effective in initiating controlled stable free radical-mediated polymerization of styrene to give a novel macromonomer which, at same time, is a polymeric initiator and that the oxazoline moiety is stable to the reaction conditions. The small peaks between δ 6.0 and 6.2 in the ^{1}H NMR spectrum and that at 108 ppm in the ^{13}C spectrum of **7** might be due to an alkene end group resulting from low level thermal decomposition of the alkoxyamine end group of the polymer. This has been reported to be one of the principal side reactions in the controlled stable free radical-mediated polymerizations.[14]

Cationic ring-opening polymerization of the oxazoline group of macromonomer **7**, initiated by methyl triflate, was carried out in ODCB at 140 °C. As expected for a homopolymerization of a macromonomer, the reaction

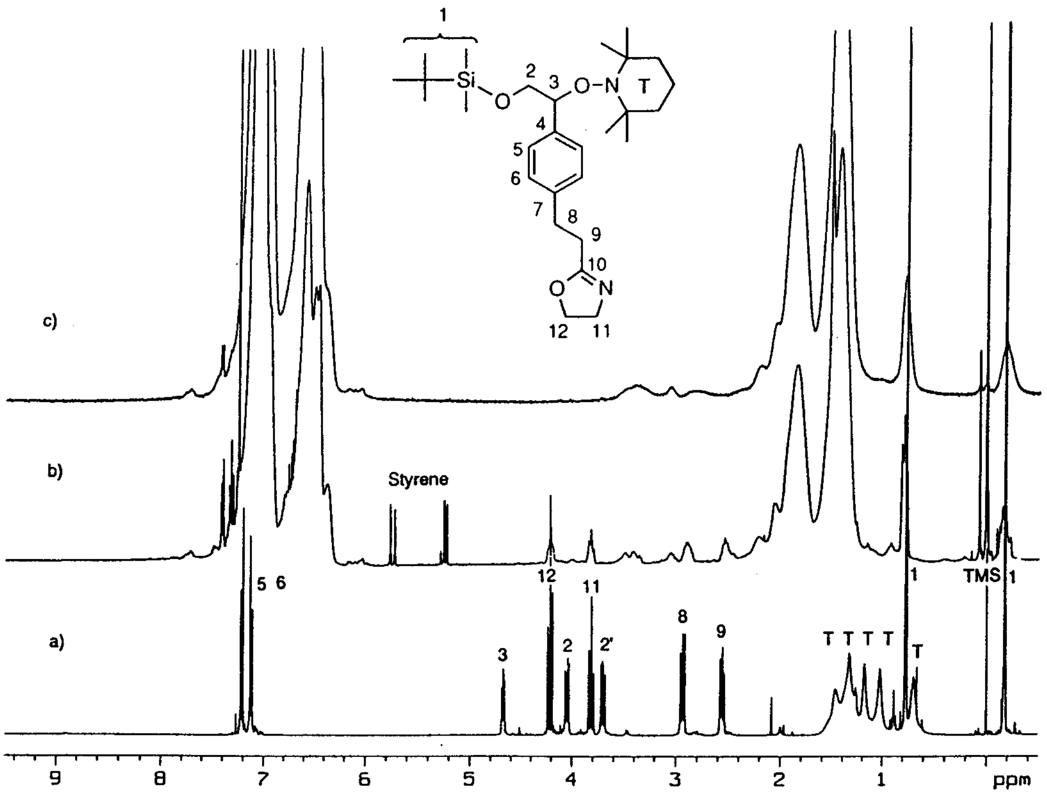


Figure 2. ^{1}H NMR (400 MHz) spectra of the multifunctional initiator **1** (a), macromonomer **7** (b), and comb polymer **8** (c) recorded using a Varian XL-400 spectrometer.

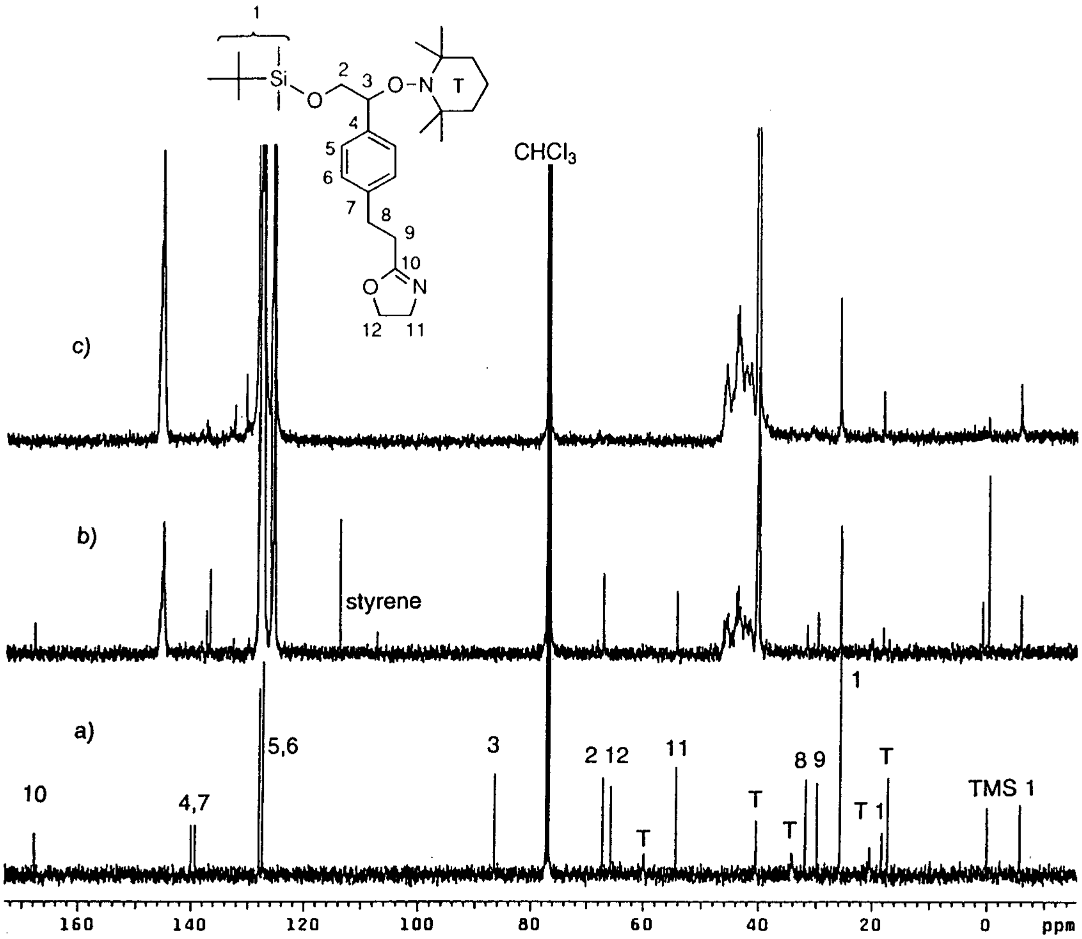


Figure 3. ^{13}C NMR (100 MHz) spectra of the multifunctional initiator **1** (a), macromonomer **7** (b), and comb polymer **8** (c) recorded using a Varian XL-400 spectrometer.

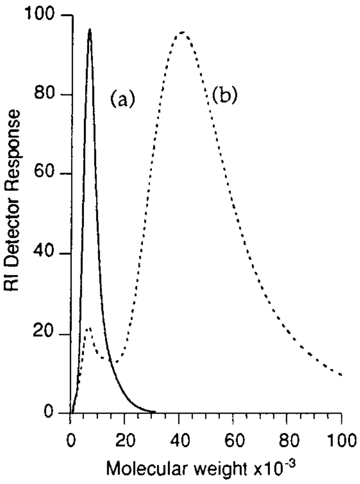


Figure 4. Gel permeation chromatograms of macromonomer **7** (a) and comb polymer **8** (b).

was slow and took several days.[15] The polymerization was monitored by GPC (Figure 4). The chromatograms revealed that as the reaction progressed, the peak corresponding to the starting macromonomer **7** (M_p 5500) disappeared while a new peak grew with M_p = 40 000. This appreciable homopolymerization of **7** to form **8** should be contrasted with homopolymerization of vinyl-ended macromonomers which tend to be not only sluggish but also inefficient, possibly due to steric congestion.[15] Apparently, in the case of **7**, steric congestion is relieved upon opening the oxazoline ring, and molecular weight build up is less hindered. Saegusa and co-workers have made similar observations. They used the alkoxide of 2-(4-hydroxyphenyl)-2-oxazoline to initiate polymerization of ethylene oxide and obtained oligomers (M_n = 1000−1900). Homopolymerization of the resulting oligomeric macromonomers gave comb polymers with M_n = 5000−10 000 while copolymerization with phenyl-2-oxazoline gave comb copolymers with M_n = 8000.[16]

Examination of the ^{1}H NMR spectra in Figure 2 revealed that the characteristic oxazoline methylene signals (H-11 and H-12) observed at δ 3.7 and 4.3 in the spectra of **1** and **7** (Figure 2a and b) shifted upfield to δ 3.2−3.6 (Figure 2c) and broadened, which is consistent with the oxazoline ring being opened. The ^{1}H NMR further showed that the TBDMS group (−0.2 and 0.75 ppm) survived both polymerization stages. These deductions were further confirmed by ^{13}C NMR (Figure 3) spectroscopy. Thus, the signals corresponding to C-8 and C-9 became very broad and were barely discernible at 30 and 26 ppm (overlapped with the peak from the alkoxyamine group), respectively. Those corresponding to C-11 and C-12 shifted upfield and overlapped with styrene peaks. These were assigned by comparison with the ^{13}C NMR spectrum of an authentic polyoxazoline, which gave C-11 and C-12 peaks between 42 and 44 ppm. The peak corresponding to C-10 (which becomes amide carbonyl upon ring opening), which occurred at 172 ppm in an authentic polyoxazoline spectrum, was not seen, probably due to excessive broadening in the spectrum of comb polymer **8** (Figure 3c). Additional corroboration for our interpretation can be seen in the FTIR spectra, which showed that the

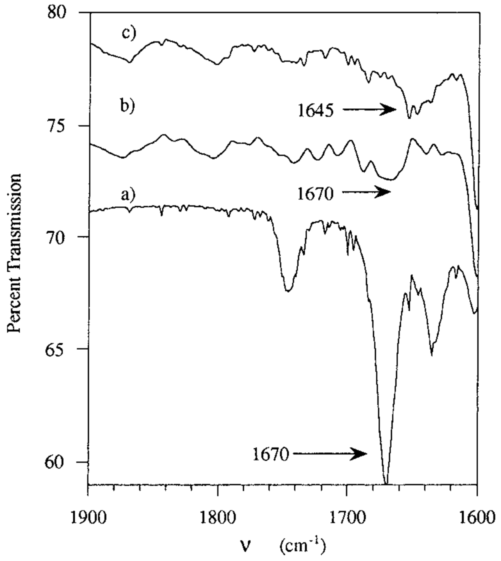


Figure 5. FTIR spectra of multifunctional initiator **1** (a), macromonomer **7** (b), and comb polymer **8** (c) performed on a Perkin Elmer 16PC FTIR spectrometer.

C═N stretching at 1670 cm^{-1} observed in both **1** (Figure 5a) and **7** (Figure 5b) shifted to lower frequency (1645 cm^{-1}). This is consistent with formation of an amide carbonyl group and demonstrates the viability of **1** as a multifunctional initiator for comb polymer synthesis. Polymer **8** is amphiphilic in that it possesses a hydrophilic polyoxazoline backbone with hydrophobic polystyrene side chains. Hence, it is expected to have unique surface properties. We have earlier shown that similar polymers with hydrophobic perfluoroalkyl side chains formed extremely stable monolayers in a Langmuir−Blodgett trough.[17] Studies regarding formation of multilayers and use of such polymers as compatibilizing agents are currently in progress. An alternative approach to the sequence of polymerizations described herein is to first cationically homopolymerize **1** or copolymerize it with another oxazoline monomer followed by the controlled stable free radical-mediated polymerization of styrene. Even though this approach is likely to give a higher MW polymer, it will also lead to a graft polymer whose side chains will not necessarily be of uniform chain length, which is the advantage offered by the use of macromonomers. These efforts are also in progress.

Summary and Conclusions

We have shown that through an appropriate design a single species can serve as a multifunctional initiator for different types of polymerization reactions. In the example demonstrated above comb polymer **8** still possesses protected alcohol groups that can be readily converted to initiator sites for polymerization of such monomers as lactones, lactides, and epoxides or be used as hydrophilic sites for increased water solubility, if desired. It should also be noted that the polymerization conditions used (temperatures ≥ 130 °C, high boiling solvents, such as ODCB) are compatible with both cationic ring-opening and nitroxide-mediated free radical polymerizations. Since cationic polymerization of styrene is not expected to occur under those conditions to any appreciable extent, the two types of polymerizations, in principle, could be carried out concurrently. Preliminary one-pot polymerization results from our laboratories using **6** as a dual initiator for polymerization of oxazoline and styrene monomers suggest that this is feasible. Furthermore, our results show that both the oxazoline and the TBDMS-protected hydroxyl groups are stable under the free radical conditions employed and that each initiating site of **1** can be addressed selectively and independently, thus providing the possibility to develop a one-pot synthesis for a variety of complex functional polymers. Results of such studies together with the use of **1** to form double comb polymers with side chains of very well controlled hydrophobic/hydrophilic balance will be described in a future publication.

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