Macromolecules

Volume 29, Number 16 July 29, 1996

Initiating Systems for Nitroxide-Mediated "Living" Free Radical Polymerizations: Synthesis and Evaluation

Craig J. Hawker,*,† George G. Barclay,*,‡ Arturo Orellana,‡ Julian Dao,† and Wayne Devonport†

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099, and Shipley Company, 455 Forest Street, Marlborough, Massachusetts 01752-3092

Received December 26, 1995; Revised Manuscript Received May 8, 1996[⊗]

ABSTRACT: A variety of initiating systems for the preparation of macromolecules by nitroxide-mediated "living" free radical procedures have been prepared and evaluated. The systems can be divided into two classes, unimolecular initiators in which alkylated TEMPO (2,2,6,6-tetramethylpiperidinyloxy) derivatives dissociate to provide both the initiating radical and the stable radical, and bimolecular systems in which a traditional free radical initiator, such as BPO or AIBN, is used in conjunction with TEMPO. For the unimolecular initiators it was found that an α-methyl group is essential for "living" character, while a variety of substituents could be placed on the phenyl ring or the β-carbon atom without affecting the efficiency of the unimolecular initiator. It was also found that the rate of polymerization is approximately the same for both the unimolecular and corresponding bimolecular systems; however, the unimolecular initiators afforded better control over molecular weight and polydispersity.

Introduction

The ability to synthesize macromolecules with complex and controlled architectures is becoming an increasingly important aspect of polymer science. Traditionally, control of macromolecular architecture has been achieved using living polymerization techniques such as anionic,[1] cationic,[2] or group transfer procedures.[3] To expand the scope of complex macromolecular architectures, the concept of a "living", or pseudoliving, free radical polymerization process has long been a goal of synthetic polymer chemists. Initial attempts at producing a "living" system based on free radical chemistry involved the "iniferter" concept, which takes advantage of sulfur-centered radicals.[4] These sulfur-centered free radicals react reversibly with the growing polymer chain ends, thereby controlling the radical concentration; however, they also initiate new polymer chains, which leads to uncontrolled growth. As a result, the macromolecules obtained from such a system were found to have polydispersities similar to traditional free radical processes. While this leads to facile block copolymer formation, these systems cannot be considered to be truly "living" in nature and do not permit control of macromolecular architecture.

To overcome these deficiencies, a nitroxide-mediated free radical polymerization having the characteristics of a living polymerization has recently been developed. It should be noted that while this process may not strictly obey the definition of a living polymerization, it does satisfy many of the requirements, hence the use of "living", or pseudoliving. While the genesis of this field can be traced back to the pioneering work of Moad and Rizzardo,[5] the stimulus for the current interest is the seminal report of Georges[6] that low-polydispersity polystyrene can be prepared using a mixture of benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as an initiating system. Subsequently a large number of publications[7] have appeared confirming the "living" nature of this novel procedure and demonstrating the usefulness of this approach to the preparation of a variety of well-defined and complex macromolecular architectures, a number of which cannot be prepared using traditional methods.

The success of this approach can be related to the ability of stable nitroxide free radicals, such as TEMPO, to react at near diffusion controlled rates with the carbon-centered free radical of the growing polymer chain end in a thermally reversible process. This dramatically lowers the concentration of free radicals in the polymerization system and, coupled with the inability of the nitroxide free radicals to initiate new chain growth, leads to controlled polymerization. These

† IBM Almaden Research Center.
‡ Shipley Co.
[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

S0024-9297(95)01905-X CCC: $12.00

features have been exploited in the preparation star and graft polymers,[8] hyperbranched systems,[9] and low-polydispersity random[10] and block copolymers.[11,12] The living nature of this process also permits the molecular weight[12] and chain ends[13] of the macromolecules to be accurately controlled. Saban[14] has also shown that living free radical polymerizations do not suffer from a gel effect, which may have significant benefit for industrial-scale production. The preparation of well-defined polymers from reactive monomers has also been demonstrated in a number of cases.[15] For example, Keoshkerian[16] has reported the living free radical polymerization of the sodium salt of styrenesulfonic acid in aqueous ethylene glycol leads to narrow-polydispersity water-soluble macromolecules in a single step.

These reports, coupled with the development by Matyjaszewski[17] of an alternate living free radical polymerization process using a copper(I)-catalyzed atom transfer process, have demonstrated the usefulness and potential of a living polymerization process based on free radical chemistry. For any living polymerization procedure, a critical feature is the nature and efficiency of the initiating system. In this report, we describe the synthesis of a variety of unimolecular initiators, a number containing reactive functional groups, suitable for living free radical polymerization procedures. The efficiency of these initiators was evaluated in terms of conversion, molecular weight control, and polydispersity. Comparison of these initiators and the corresponding bimolecular systems allowed insight into the structural variations possible and the advantages and disadvantages of each system.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer as thin films on NaCl. ^{1}H NMR spectra were recorded in solution with a Bruker AM 250 (250 MHz) spectrometer, with TMS proton signal as an internal standard. ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer with the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 with EI ionization. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica gel for flash chromatography was Merck Kieselgel 60 (230−400 mesh). Size exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. Four 5 μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6 Å) were used with THF as solvent. UV−vis absorption spectra were taken on a Perkin-Elmer UV/VIS Lambda 2 spectrometer. Glass transition temperatures (T_g) were recorded on a Perkin-Elmer DSC 7.

((2′,2′,6′,6′-Tetramethyl-1′-piperidinyloxy)methyl)benzene (2). A solution of TEMPO (5.00 g, 32.1 mmol) in dry tetrahydrofuran (20 mL) was cooled with stirring to −78 °C under argon. Benzylmagnesium chloride (6.4 mL of a 1 M solution in THF, 6.4 mmol) was added dropwise, and the reaction mixture was stirred at −78 °C for 2 h. Then the mixture was allowed to warm to room temperature, and stirring was continued for 3 h. The reaction mixture was then evaporated to dryness and purified by flash chromatography eluting with 2:8 hexane/dichloromethane. This gave the benzyl derivative **2** as a slightly yellow oil (1.36 g, 86%): IR (neat) 2950, 1500, 1380, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.11, 1.24 (each br s, 12H, CH_3), 1.30−1.65 (m, 6H, CH_2), 4.79 (s, 2H, CH_2), 7.25−7.35 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.14, 20.31, 33.10, 39.73, 60.02, 78.74, 127.30, 127.46, 128.23, 138.33; mass spectrum (EI) m/z 247. The TEMPO derivative **2** was also prepared from toluene using the same procedure as for **3** and from benzyl bromide using the same procedure as for **19**. The yields were 38 and 71%, respectively.

1-Phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-ethane (3). To ethylbenzene (100 mL) was added di-*tert*-butyl peroxide (5.0 g, 33.0 mmol) followed by TEMPO (10.5 g, 66.0 mmol). The reaction mixture was then heated at reflux under argon for 16 h and evaporated to dryness. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to 1:1 hexane/dichloromethane. This gave the TEMPO derivative **3** as a crystalline white solid which could be recrystallized from cold ethanol (−78 °C) (7.20 g, 42%): mp 46−47 °C; IR (neat) 2950, 1490, 1390, 1375, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.64, 1.05, 1.16, 1.36 (each br s, 12H, CH_3), 1.23−1.58 (m, 6H, CH_2), 1.44 (d, J = 7 Hz, 3H, CH(CH_3)), 4.76 (q, J = 7 Hz, 1H, CH(CH$_3$)), 7.25−7.35 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.22, 20.34, 23.55, 31.59, 34.49, 40.37, 59.66, 83.10, 126.59, 126.74, 127.97, 145.84; mass spectrum (EI) m/z 261.

1-(4′-Bromophenyl)-1-(2″,2″,6″,6″-tetramethyl-1″-piperidinyloxy)ethane (6). To 1-bromo-4-ethylbenzene (25 mL, 33.57 g, 181 mmol) was added di-*tert*-butyl peroxide (1.67 g, 11.0 mmol) followed by TEMPO (3.5 g, 22.0 mmol). The reaction mixture was then heated at 125 °C under argon for 16 h and evaporated to dryness. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to 1:1 hexane/dichloromethane. This gave the TEMPO derivative **6** as a colorless oil (2.44 g, 32%): IR (neat) 2950, 1510, 1380, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.63, 0.98, 1.10, 1.24 (each br s, 12H, CH_3), 1.23−1.58 (m, 6H, CH_2), 1.43 (d, J = 7 Hz, 3H, CH(CH_3)), 4.69 (q, J = 7 Hz, 1H, CH(CH$_3$)), 7.15 and 7.38 (ABq, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.40, 20.51, 23.45, 31.30, 34.72, 40.09, 60.99, 82.97, 125.89, 127.36, 128.85, 144.27; mass spectrum (EI) m/z 339 and 341 (1:1).

1-Naphthyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-ethane (7). To 2-ethylnaphthalene (20 mL, 19.84 g, 127 mmol) was added di-*tert*-butyl peroxide (1.00 g, 6.59 mmol) followed by TEMPO (2.10 g, 13.2 mmol). The reaction mixture was then heated at 125 °C under argon for 16 h and evaporated to dryness. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to 1:1 hexane/dichloromethane. This gave the TEMPO derivative **7** as a colorless oil (1.09 g, 27%): IR (neat) 3020, 2950, 1505, 1380, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.56, 0.98, 1.15, 1.29 (each br s, 12H, CH_3), 1.12−1.45 (m, 6H, CH_2), 1.49 (d, J = 7 Hz, 3H, CH(CH_3)), 4.88 (q, J = 7 Hz, 1H, CH(CH$_3$)), 7.38−7.47 (m, 3H, ArH), 7.66−7.78 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.34, 20.49, 23.79, 34.47, 40.46, 59.79, 83.54, 125.07, 125.24, 125.50, 125.91, 127.76, 127.91, 128.03, 132.78, 133.37, 143.37; mass spectrum (EI) m/z 311.

1-Phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-propane (8). This was prepared from propylbenzene using the same procedure as for **3**. The crude product was purified by flash chromatography eluting with hexane, gradually increasing to 1:1 hexane/dichloromethane to give the TEMPO derivative **8** as an oil (34%): IR (neat) 2950, 1490, 1380, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.56, 1.08, 1.26, 1.67 (each br s, 12H, CH_3), 0.64 (t, J = 6 Hz, 3H, CH_3), 1.10−1.35 (m, 6H, CH_2), 1.70 and 2.05 (each complex m, 1H, CHH), 4.54 (ABq, J = 3 Hz, 1H, CH), 7.25−7.35 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 9.68, 17.21, 20.32, 28.77, 34.08, 40.44, 59.79, 88.65, 126.81, 127.74, 129.62, 143.56; mass spectrum (EI) m/z 275.

1-(Benzyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (12). To a solution of benzoyl peroxide (4.0 g, 12.4 mmol) in distilled styrene (160 mL) was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (5.68 g, 36.4 mmol), and the solution was heated at 80 °C under nitrogen for 20 h. After cooling, the solution was evaporated to dryness and purified by flash chromatography eluting with 1:1 hexane/dichloromethane, gradually increasing to 1:9 hexane/dichloromethane to give the modified TEMPO initiator **12** as a pale yellow oil (2.64 g, 42%): IR (neat) 3100−2850, 1720, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.75, 1.07, 1.21, 1.37 (each br s, 12H, CH_3), 1.38−1.52 (m, 6H, CH_2), 4.53 (ABq, J = 6 Hz, 1H, CHH), 4.83 (ABq, J = 6 Hz, 1H, CHH), 5.06 (ABq, J = 3 Hz, 1H, CH), 7.25−7.56 (m, 8H, ArH), 7.91 (B of ABq, J = 6 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 17.09, 20.31, 34.00, 40.36, 60.01, 66.68, 83.90, 127.54, 127.97, 128.18, 129.48, 130.14, 132.72, 140.61, 166.20; mass spectrum (EI) m/z 381. Anal. Calcd for $C_{24}H_{31}NO_3$: C, 75.6; H, 8.19; N, 3.67. Found: C, 76.0; H, 7.97; N, 3.86.

1-Hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (13). To a solution of the benzyl ester **12** (3.2 g, 8.4 mmol) in ethanol (100 mL) was added aqueous sodium hydroxide (10 mL of a 1 N solution, 10.0 mmol), and the solution was heated at reflux under nitrogen for 2 h. After cooling, the solution was evaporated to dryness and partitioned between water (200 mL) and dichloromethane (200 mL). Then the aqueous layer was extracted with dichloromethane (2 × 100 mL), and the combined organic layers were dried with magnesium sulfate and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:4 hexane/dichloromethane, gradually increasing to 1:9 hexane/dichloromethane to give the hydroxy derivative **13** as a pale yellow oil (2.01 g, 87%): ^{1}H NMR ($CDCl_3$) δ 1.14, 1.21, 1.33, 1.50 (each br s, 12H, CH_3), 1.38−1.72 (m, 6H, CH_2), 3.71 (br d, J = 9 Hz, 1H, C*H*H), 4.21 (d of d, J = 2 and 6 Hz, 1H, CH*H*), 5.29 (d of d, J = 2 and 3 Hz, 1H, C*H*), 5.88 (br s, O*H*), 7.25−7.56 (m, 5 H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 17.15, 20.41, 20.73, 32.76, 34.61, 40.23, 40.41, 60.38, 61.69, 69.73, 83.59, 126.20, 127.89, 128.34, 138.92; mass spectrum (EI) *m*/*z* 277. Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.6; H, 9.81; N, 5.05. Found: C, 73.8; H, 10.05; N, 5.08.

Diphenyl 4-Azobis(4-cyanopentanoate) (15). The diacid chloride **14** (2.00 g, 6.30 mmol) was dissolved in dry tetrahydrofuran (20 mL), and phenol (1.31 g, 13.9 mmol) was added. To the reaction mixture, stirred at room temperature under nitrogen, was added pyridine (1.22 g, 15.5 mmol), and stirring was continued for 2 h. The reaction mixture was then evaporated to dryness, redissolved in dichloromethane (100 mL), washed with aqueous sodium hydroxide (0.5 N, 3 × 50 mL), and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:2 hexane/dichloromethane, gradually increasing to dichloromethane to give the diester **15** as a white solid which decomposed without melting (1.69 g, 62%): IR (neat) 2950, 1720, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75, 1.80 (each s, 6H), 2.48−2.85 (complex m, 8H), 7.10−7.43 (complex m, 10H); ^{13}C NMR ($CDCl_3$) δ 23.73, 23.95, 29.13, 29.22, 32.95, 71.69, 71.81, 117.34, 117.42, 121.28, 125.97, 129.39, 150.30, 169.79; mass spectrum (EI) *m*/*z* 202 (−N_2).

Phenyl 4-Cyano-4-(2′,2′,6′,6′-tetramethylpiperidinyloxy)-pentanoate (17). To a degassed solution of the azo diester **15** (4.32 g, 10.0 mmol) in ethyl acetate (120 mL) was added TEMPO (3.12 g, 20.0 mmol), and the reaction mixture was heated at reflux under argon for 2 h. After cooling, the reaction mixture was evaporated to dryness and the crude product purified by flash chromatography eluting with 1:3 hexane/dichloromethane, gradually increasing to dichloromethane to give the TEMPO derivative **17** as a white solid which decomposed without melting, (1.62 g, 23%): IR (neat) 2950, 1720, 1490, 1370, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.11, 1.13, 1.17, 1.33 (each s, 12H), 1.45−1.56 (br m, 6H), 1.72 (s, 3H), 2.22−2.41 (complex m, 2H), 2.81−2.97 (complex m, 2H), 7.10−7.43 (complex m, 10H); ^{13}C NMR ($CDCl_3$) δ 16.95, 20.62, 21.05, 23.82, 29.61, 32.88, 34.12, 36.56, 40.37, 40.68, 60.04, 60.36, 121.49, 125.95, 129.48, 150.12, 170.87; mass spectrum (EI) *m*/*z* 358.

Bis(pentafluorophenyl) 4-Azobis(4-cyanopentanoate) (16). The bisacid chloride **14** (8.00 g, 25.2 mmol) was dissolved in dry tetrahydrofuran (100 mL), and pentafluorophenol (11.1 g, 60.0 mmol) was added. To the reaction mixture, stirred at room temperature under nitrogen, was added pyridine (4.88 g, 62.0 mmol), and stirring was continued for 2 h. The reaction mixture was then evaporated to dryness, redissolved in dichloromethane (300 mL), washed with aqueous sodium hydroxide (0.5 N, 3 × 150 mL), and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:2 hexane/dichloromethane, gradually increasing to dichloromethane to give the diester **16** as a white solid which decomposed without melting (10.95 g, 71%): IR (neat) 2950, 1720, 1480, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.72, 1.81 (each s, 6H), 2.41−2.92 (complex m, 8H); ^{13}C NMR ($CDCl_3$) δ 23.84, 29.05, 29.21, 32.88, 71.77, 121.24, 135.6−143.2 (complex set of peaks), 168.54; mass spectrum (EI) *m*/*z* 292 (−N_2).

Pentafluorophenyl 4-Cyano-4-(2′,2′,6′,6′-tetramethylpiperidinyloxy)pentanoate (18). To a degassed solution of the azo diester **16** (6.12 g, 10.0 mmol) in ethyl acetate (120 mL) was added TEMPO (3.12 g, 20.0 mmol), and the reaction mixture was heated at reflux under argon for 2 h. After cooling, the reaction mixture was evaporated to dryness and the crude product purified by flash chromatography eluting with 1:3 hexane/dichloromethane, gradually increasing to dichloromethane to give the TEMPO derivative **18** as a white solid which decomposed without melting, (3.10 g, 35%): IR (neat) 2950, 1720, 1490, 1370, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10, 1.12, 1.25, 1.41 (each s, 12H), 1.43−1.58 (br m, 6H), 1.80 (s, 3H), 2.212−2.48 (complex m, 2H), 2.95−3.21 (complex m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.90, 20.57, 20.98, 23.69, 28.59, 34.06, 34.14, 36.41, 40.34, 40.65, 60.05, 60.41, 121.21, 135.9−143.1 (complex set of peaks), 168.59; mass spectrum (EI) *m*/*z* 448.

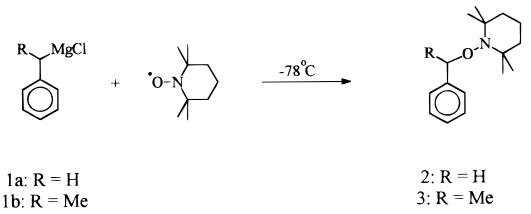
3-Phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-propane (19). To a suspension of TEMPO (2.50 g, 16.0 mmol) in water (25 mL) was added sodium ascorbate (2.98 g, 16.0 mmol) in water (25 mL). The reaction mixture was then stirred for 5 min and the resulting solution extracted with diethyl ether (3 × 75 mL). The combined organic layers were dried and evaporated to dryness. The crude reduced form of TEMPO was redissolved in dry THF (50 mL), and sodium hydride (700 mg of a 60% dispersion in oil, 17.5 mmol) was added. The reaction mixture was stirred for 20 min under argon, and 1-bromo-3-phenylpropane (3.48 g, 17.5 mmol) dissolved in dry THF (10 mL) was added dropwise. The reaction was then heated at reflux under argon for 16 h, cooled, and evaporated to dryness. The residue was partitioned between water (100 mL) and diethyl ether (100 mL), and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were dried and evaporated to dryness, and the crude product was purified by flash chromatography eluting with 1:1 hexane/dichloromethane, gradually increasing to dichloromethane to give the alkyl-TEMPO derivative **19** as a colorless oil (57%): IR (neat) 2950, 1490, 1380, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10, 1.12 (each br s, 12H, CH_3), 1.20−1.65 (m, 6H, CH_2), 1.86 (complex m, 2H, CH_2), 2.69 (ABq, J = 5 Hz, 2H, CH_2), 3.76 (t, J = 5 Hz, 2H, CH_2), 7.25−7.35 (m, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 17.16, 20.18, 30.52, 32.75, 33.08, 39.62, 59.67, 76.11, 125.67, 128.26, 128.37, 142.44; mass spectrum (EI) *m*/*z* 275.

1-((2′,2′,6′,6′-Tetramethyl-1′-piperidinyloxy)methyl)-4-(trifluoromethyl)benzene (20). This was prepared from 4-(trifluoromethyl)benzyl bromide using the same procedure as for **19**. The crude product was purified by flash chromatography eluting with 1:1 hexane/dichloromethane, gradually increasing to dichloromethane to give the TEMPO derivative **20** as a colorless oil (61%): IR (neat) 2950, 1495, 1390, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08, 1.14 (each s, 12H, CH_3), 1.22−1.69 (m, 6H, CH_2), 4.79 (s, 2H, CH_2), 7.35 and 7.51 (ABq, J = 7 Hz, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 17.08, 20.25, 33.02, 39.71, 60.08, 77.94, 125.67, 127.33, 128.10, 129.66 (q), 142.43.

General Procedure for Polymerization Reactions. To a round-bottom flask were added the initiator, or initiating system, and the required amount of styrene. The polymerization mixture was then heated at the desired temperature, typically 123 °C, under argon, with samples being withdrawn at intervals. Molecular weights and polydispersities were evaluated by size exclusion chromatography, with the excess styrene being removed by evaporation; no precipitation or fractionation techniques were employed. For determination of the extent of conversion, the samples were transferred directly from the polymerization reaction to an NMR tube and dissolved in $CDCl_3$. The relative percentages of polystyrene and styrene monomer were determined by integration of the relevant peaks. For all conversion studies, 100 equiv of styrene per mol of initiator was used; this gives a theoretical molecular weight, in each case, of 10 400.

NMR Analysis of Initiator Conversion. A mixture of the initiator **3** (93 mg, 0.36 mmol) and styrene-d_8 (1.0 g, 8.9 mmol) was sealed in an NMR tube under argon and placed in a probe which had been preheated to 123 °C. ^{1}H NMR spectra were then taken at 1 min intervals (total acquisition time per spectra = 24 s) for 60 min. The relative percentage of initiator **3**, remaining at the various polymerization times was calcu-

Scheme 1



1a: R = H
1b: R = Me

2: R = H
3: R = Me

lated by comparing the integration value for the benzylic proton of **3** at 4.70 ppm to the integration value for the aromatic protons. The aromatic protons are due to both the initiator **3** and the polymer formed by the reaction of **3** with styrene-d_8.

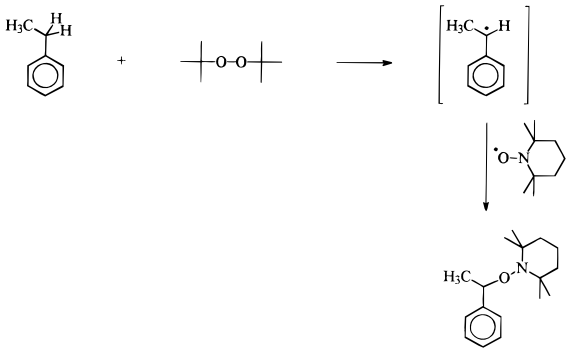
Results and Discussion

Synthetic Studies. A variety of different unimolecular initiators were employed in this study, and they can conveniently be divided into two distinct families, those based on a benzylic, or substituted benzylic, moiety and those derived from AIBN (2,2′-azobis(isobutyronitrile)). The synthesis of the benzylic derivatives was accomplished by three distinct pathways. The first methodology involved coupling of TEMPO with organometallic reagents, the second relied on the effective capture of carbon-centered free radicals by TEMPO, and the final method involved the reaction of the sodium salt of the reduced form of TEMPO with benzylic and alkyl halides.[18]

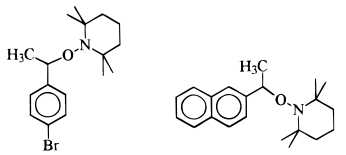
Previously, the reaction of anionically prepared living polystyrene with TEMPO has been employed as a method for the introduction of a TEMPO-functionalized chain end for the synthesis of block copolymers.[11] Presumably this reaction occurs by an electron transfer process between the anionic chain end and a TEMPO molecule to generate a radical which is then captured by another TEMPO molecule. To examine this reaction as a method for the synthesis of unimolecular initiators, the reaction of benzylmagnesium chloride (**1a**) with TEMPO was studied in detail (Scheme 1). It was found that the optimum reaction conditions consisted of addition of the Grignard reagent to 5.0 equiv of TEMPO at −78 °C. This gave the benzylic derivative **2** in 86% yield after purification. Higher reaction temperatures, inverse addition, or lower molar ratios of TEMPO were found to result in decreased yields of **2**. Extension of this synthetic strategy to (1-phenylethyl)magnesium chloride (**1b**) resulted in a lower yield of **3** (45%). The incompatibility of Grignard reagents with many functional groups and the poor yields obtain with **3** prompted the examination of alternate methods for the synthesis of **3** and more complex derivatives.

While this work was in progress, Priddy and Howell reported the synthesis of **3** by the reaction of ethylbenzene with *tert*-butyl peroxide in the presence of TEMPO.[19] In this case, a large excess of ethylbenzene, which is used as solvent, is employed to maximize the efficiency of hydrogen abstraction by the *tert*-butyloxy radical to generate the benzyl radical, which is then trapped by TEMPO to give **3** in 42% yield (Scheme 2). The mild nature of this procedure, coupled with the satisfactory yields, permitted us to examine the synthesis of a number of functionalized derivatives of **3** as unimolecular initiators. Reaction of 1-bromo-4-ethylbenzene and 2-ethylnaphthalene with *tert*-butyl peroxide under the same conditions as for ethylbenzene was found to give the desired TEMPO derivatives, **6** and **7**,in 32 and 27% yield, respectively, after purification. The use of propylbenzene as a starting material in the above reaction was also found to give the 1-substituted product, **8**, in 34% yield. However, **8** was contaminated by a small (ca. 5%) amount of the 2-substituted product, **9**, which could not be easily separated from the desired TEMPO derivative, **8** (Scheme 3). Presumably the introduction of an additional methylene group leads to regioselective abstraction of a hydrogen atom by *tert*-butyl peroxide, with 95% abstraction occurring at the more stable benzylic, or 1-position, and 5% occurring at the 2-position. The 2-substituted product was found to have no discernible effect on the use of **8** as a unimolecular initiator, with accurate molecular weight control and low polydispersities (1.10−1.20) being observed. However, this side reaction potentially limits the use of propyl and higher analog derivatives as starting materials for the synthesis of unimolecular initiators. In all of the above experiments, the yield of the TEMPO adduct was observed to decrease significantly on the addition of a cosolvent. Further, the reaction failed with 4-ethylbenzaldehyde, 4-ethylpyridine, methyl 4-ethylbenzoate, 1,2-diphenylethane, and isopropylbenzene as starting materials, possibly due to thermal decomposition of the TEMPO derivatives. The elevated temperatures at which the above reactions are performed can be circumvented by the use of an initiator that decomposes at a lower temperature[5] or by a photochemical route.[20] Scaiano[21] has reported improved yields of **3** and other derivatives by irradiation of alkylbenzenes in the presence of TEMPO and di-*tert*-butyl peroxide at 300 nm; the advantage of this approach is that the reaction is performed at room temperature and no thermal decomposition of the products therefore occurs.

Scheme 2



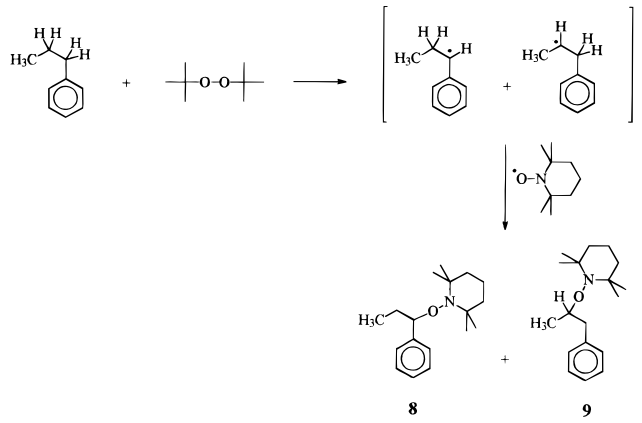
3



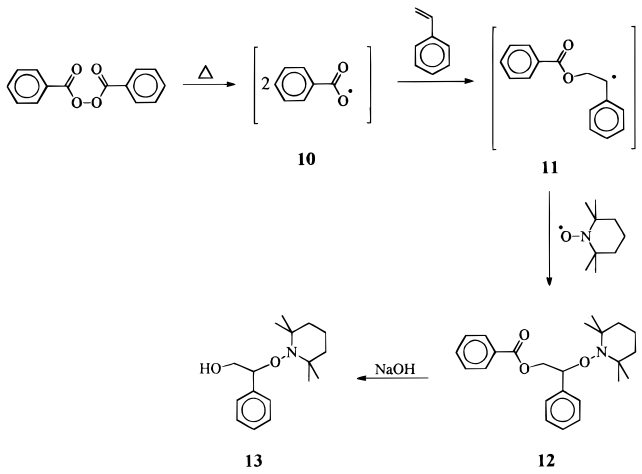
6 **7**

Another approach to functionalized unimolecular initiators involves the reaction of benzoyl peroxide with an excess of styrene in the presence of TEMPO at 80−90 °C. At this temperature, the benzoyl peroxide undergoes decomposition to give benzyloxy radicals, **10**, as the primary product. Due to the low reactivity of oxygen-centered free radicals with TEMPO, **10** can undergo addition with styrene to give a carbon-centered free radical, **11**, which is trapped by TEMPO to give the desired product, **12**, in 42% yield after purification (Scheme 4). This synthetic methodology gives a unimolecular initiator containing an ester functionality

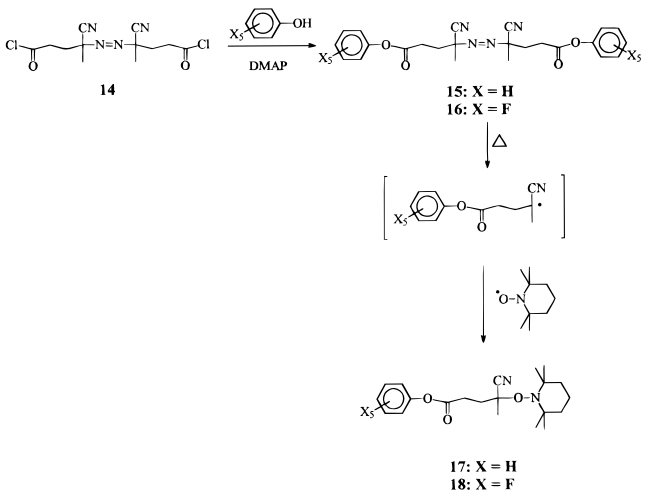
Scheme 3



Scheme 4



Scheme 5



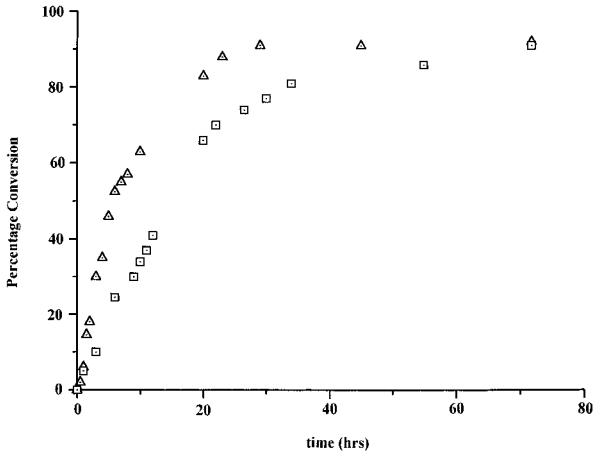


Figure 1. Percentage conversion as a function of time for the polymerization of styrene at 120 °C using the unimolecular initiators **2** (Δ) and **3** (□).

which can undergo a variety of transformation reactions to give a range of functionalized unimolecular initiators. For example, cleavage of **12** with aqueous sodium hydroxide gives the hydroxyl derivative, **13**, in 87% yield, which can undergo further transformation reactions.[13]

Functionalized derivatives of AIBN were prepared from the diacid chloride, **14**, of 4,4′-azobis(4-cyanopentanoic acid) by reaction with either phenol or pentafluorophenol in the presence of pyridine. This gave the diesters **15** and **16** in 62 and 71% yield, respectively, which could then be converted to the corresponding TEMPO derivatives **17** and **18** by reaction with TEMPO in refluxing ethyl acetate for 2 h. In this case, decomposition of the initiator gives a carbon-centered radical which undergoes reaction with TEMPO and therefore eliminates the necessity of using a vinyl monomer as the solvent (Scheme 5). A variety of functional groups can be introduced into the initiating system by reaction of **14** with the appropriately substituted phenols, alcohols, amines, etc.

Polymerization Reactions. Conversion Studies. A fundamental reason for the synthesis of a variety of TEMPO-based derivatives was to examine the effect of structural variation on the efficiency and usefulness of these derivatives as unimolecular initiators in nitroxide-mediated "living" free radical polymerizations. It was also envisaged that comparison with the corresponding bimolecular systems, consisting of a traditional free radical initiator and TEMPO, would permit insight into the advantages and disadvantages of either system.

Initially the effect of structural variation on the rate of polymerization, evolution of molecular weight (M_n), and polydispersity was examined. Figure 1 shows a plot of conversion versus time for the polymerization of styrene at 120 °C in the presence of the benzyl-TEMPO initiator, **2**, and the ethylbenzene derivative, **3**. It can be seen that the absence of the α-methyl substituent in **2** leads to a substantial increase in the polymerization rate. However, the most significant difference between the two initiators is the evolution of molecular weight with conversion (Figure 2). For the benzyl derivative, **2**, a rapid increase in molecular weight occurs at low conversion and a constant value for M_n is obtained at conversions above 30%. This behavior is characteristic of traditional free radical polymerizations and is dramatically different from the behavior observed for **3**, where the molecular weight evolves in a nearly linear fashion with increasing conversion. This linear relationship is characteristic of living polymerizations and has been detailed previously by Georges for nitroxide-mediated free radical polymerizations.[6] The polydispersities of the polymers obtained from either **2** or **3** were also found to be significantly different. As can be seen in Figure 3, the polydispersity of the polymer obtained from the benzyl derivative, **2**, increases dramatically as the conversion increases, with a value of 2.2−2.3 at high conversions. In contrast, the polydispersity of the polymer prepared using **3** decreases as the conversion increases, and values in the range 1.10−1.20 are obtained for conversions greater than 30%. The above results suggest that the stability of the initiating

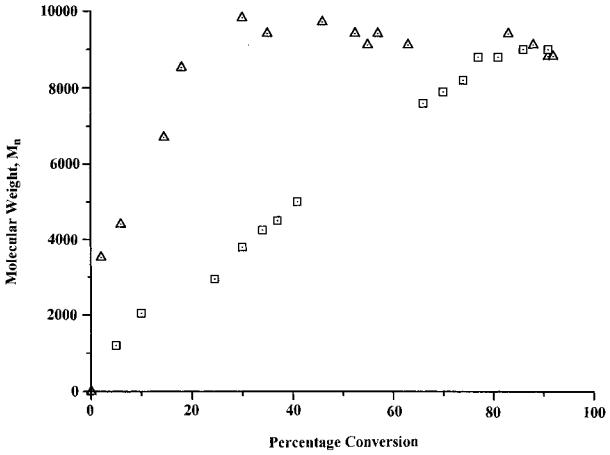


Figure 2. Evolution of molecular weight, M_n, with the percentage conversion for the polymerization of styrene at 120 °C using the unimolecular initiators **2** (Δ) and **3** (□).

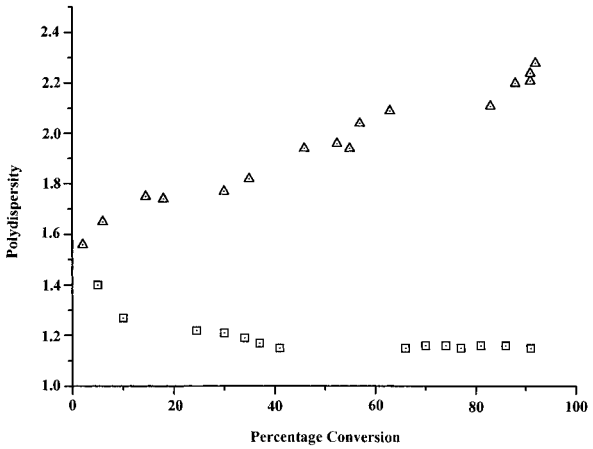


Figure 3. Polydispersity of the macromolecules obtained as a function of conversion for the polymerization of styrene at 120 °C using the unimolecular initiators **2** (Δ) and **3** (□).

radical has a dramatic effect on the overall polymerization and the α-methyl substituent is necessary for benzylic derivatives to act as unimolecular initiators in nitroxide-mediated living free radical polymerizations.

To investigate this point in greater detail, the polymerization of deuterated styrene with either **2** or **3** was studied by NMR spectroscopy in a temperature-controlled probe (123 °C). The use of deuterated styrene permitted the rate of initiator consumption to be followed by ^{1}H NMR spectroscopy since the chemical shifts of the benzylic proton(s) of **2** and **3** undergo a dramatic shift on reaction with monomer. For example, the benzylic protons of the initiator **2** appear as a sharp singlet at 4.79 ppm, which on reaction with deuterated styrene undergo an upfield shift to 2.50 ppm. This upfield shift is a result of the replacement of the electron-withdrawing TEMPO group by one or more deuterated styrene units. The relative percentage of initiator remaining at various times during the polymerization can then be determined by integration of the resonance at 4.79 ppm and comparison of this value with the values for other resonances in the spectrum. From this analysis, the initiation rate for both **2** and **3** can be determined under actual polymerization conditions. A plot of relative initiation concentration with time for the α-methyl initiator, **3**, is shown in Figure 4. From this it can be seen that **3** has a half-life of approximately 5−10 min and essentially all the initiator is consumed within the first hour. Since the conversion

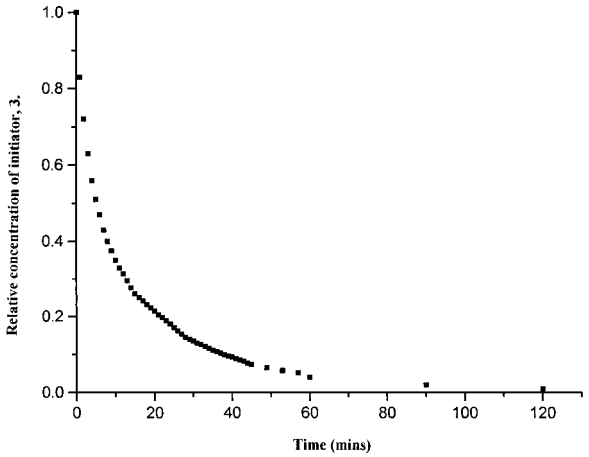
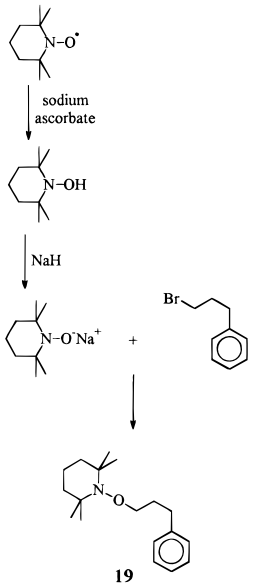


Figure 4. Relative concentration of initiator **3** as a function of time during the polymerization of deuterated styrene at 123 °C.

of monomer during this period is less than 5%, the rate of initiation is actually fast on the polymerization time scale and a living polymerization with low polydispersities is observed. In contrast, the benzyl initiator, **2**, has a half-life of ca. 150 min at 123 °C and a substantial amount of **2** remains after 12 h, at which time the polymerization has reached 70% completion. Significant initiation is therefore occurring during the whole course of the polymerization and this leads to a nonliving polymerization, with high polydispersities being obtained.

To further probe the effect of initiator structure, and hence stability of the initiating radical, on nitroxide-mediated living free radical polymerizations, the synthesis of an alkyl-substituted TEMPO derivative was conducted. Since the decomposition of such an initiator will lead to an even more unstable radical, it is expected that the half-life will be increased and the polymerization will have even less of a living nature. The initiator of choice, **19**, was derived from 1-bromo-3-phenylpropane, and it was synthesized by a variation of method of Anderson[18] which has recently been used to Catala[18] for the preparation of unimolecular initiators based on di-*tert*-butyl nitroxide. In this procedure, the nitroxide (TEMPO) is reduced with sodium ascorbate to give the *N*-hydroxy derivative, which is then deprotonated followed by reaction with 1-bromo-3-phenylpropane. Using this procedure, the desired alkylated TEMPO derivative, **19**, was obtained in 57% yield after purification (Scheme 6). Significantly, polymerization of styrene with **19** gave a polymer with a polydispersity of 3.5, while NMR analysis of the initiation rate revealed a half-life approximately double that of **2**. This is in agreement with the increased stability of alkyl-TEMPO derivatives when compared to the corresponding benzyl derivatives. An attempt was then made to decrease the stability of the benzyl-TEMPO derivative, **2**, by the introduction of a trifluoromethyl group in the para position. The synthesis of the initiator, **20**, was accomplished using the same procedure as for **19** except *p*-(trifluoromethyl)benzyl bromide was employed as the alkylating agent. In this case, polymerization of styrene using **20** as a unimolecular initiator resulted in a polymer with a polydispersity of 1.65. This value is intermediate between the α-methyl initiator, **3**, and the benzyl initiator, **2**, and is in agreement with the NMR analysis, which revealed an initiation rate intermediate between **3** and **2**. This stabilization of a benzylic radical by a *p*-(trifluoromethyl) group leading to enhanced

Scheme 6



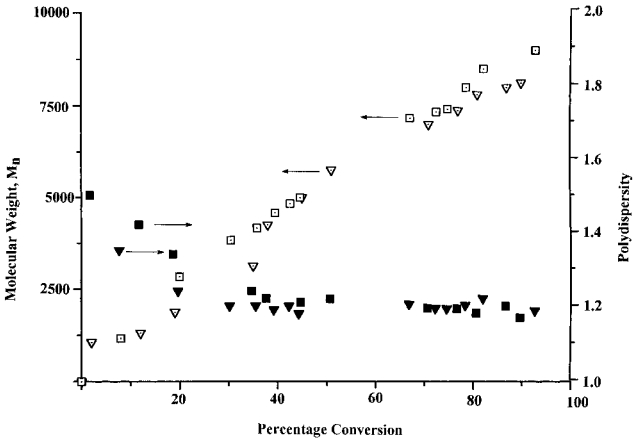


Figure 5. Evolution of molecular weight, M_n, and polydispersity with the percentage conversion for the polymerization of styrene at 123 °C using the unimolecular initiators **6** (▽) and **7** (□).

cleavage of the C−TEMPO bond has also been observed by the Xerox group in an analysis of the rate of polymerization of various substituted styrene derivatives.[22]

The effect of substituents attached to the phenyl ring of **3** was then investigated by the preparation of unimolecular initiators having a bromo group in the para position, **6**, and where the phenyl ring is replaced by a naphthalene ring, **7**. In these cases, the rate of polymerization is approximately the same for both initiators and a linear relationship between molecular weight and conversion is again observed (Figure 5). Interestingly, the polymers obtained from either **6** or **7** were found to have low polydispersities (1.10−1.20), which demonstrates that the electronic character of the phenyl ring in unimolecular initiators based on ethylbenzene can be varied without disrupting the living character of the polymerization.

In a similar way, the effect of substituents introduced at the β-carbon was investigated by the synthesis of the hydroxy derivative, **13**, benzyloxy derivative, **12**, and the methyl derivative, **8**. In each case, living free radical behavior was observed, with the rate of polymerization and polydispersity being approximately the same for each substituent. These experiments suggest

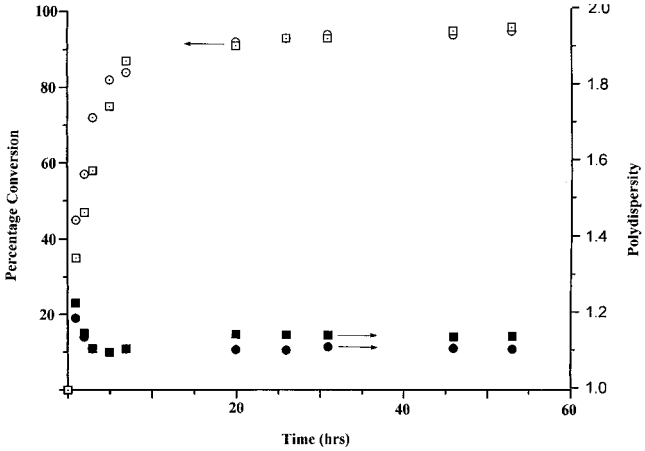


Figure 6. Comparison of the percentage conversion and polydispersity as a function of time for the polymerization of styrene (100 equiv) at 130 °C using the unimolecular initiator **3** (○) and a bimolecular system [1:1.3 molar mixture of BPO and TEMPO] (box).

that, while the β-carbon atom is essential, a variety of different functional groups can be substituted at that position without affecting the ability of the unimolecular initiator to afford accurately controlled macromolecules. This feature is especially important for the preparation of well-defined chain end functionalized macromolecules.[10,13]

By analogy with benzyl-based unimolecular initiators, such as **3**, homolytic cleavage of the C−O bond in the functionalized AIBN derivatives **17** and **18** also leads to TEMPO and a resonance-stabilized carbon-centered free radical. It was therefore envisaged that either **17** or **18** could function as unimolecular initiators. The polymerization of styrene with varying amounts of **17** or **18** was studied in detail, and the results demonstrated that the nature of the ester group had little, if any effect on the polymerization characteristics of AIBN-based unimolecular initiators. Also the results were similar to those observed for α-methylbenzyl-based systems, with a linear relationship between molecular weight and conversion being observed, while the polymers obtained were found to have low polydispersities (1.10−1.20).

It was instructive to compare the unimolecular initiators prepared above with the corresponding bimolecular initiating species such as BPO/TEMPO. Figure 6 shows monomer conversion for the polymerization of styrene at 130 °C in the presence of either **3** or a 1:1.3 mixture of benzoyl peroxide and TEMPO. Both systems display similar polymerization rates, and it should be noted that this rate is increased compared to the previous study of **3** which was conducted at 120 °C. The molecular weight of the polymers was found to increase in an approximately linear fashion with conversion, which is in agreement with the earlier results of Georges for the BPO/TEMPO system, while low polydispersities (1.10−1.20) are maintained throughout the polymerization for both systems (Figure 6). It should be noted that the theoretical molecular weights for both polymerizations is 10 400, which is in the molecular weight region for which the minimum polydispersity is obtained for both systems (see Figure 8). When the functionalized unimolecular initiators derived from AIBN were compared to a bimolecular initiating system consisting of AIBN and TEMPO (1:2 molar ratio), similar results to those observed above were found for a theoretical molecular weight of 10 400. This suggests that the initiating

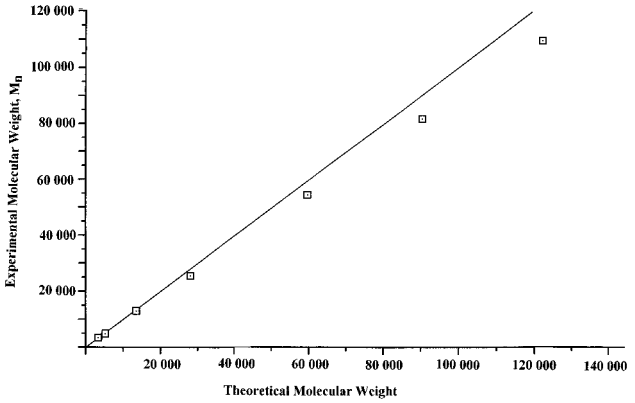


Figure 7. Variation in experimentally determined molecular weight, M_n, and the theoretical molecular weights for the polymerization of styrene at 125 °C using varying amounts of the unimolecular initiator **12** (□).

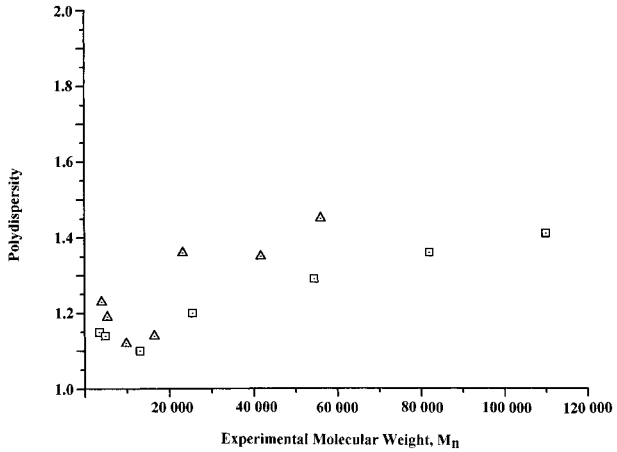


Figure 8. Variation in polydispersity with experimentally determined molecular weight, M_n, for the polymerization of styrene at 125 °C using varying amounts of the unimolecular initiator, **12** (□) and a bimolecular system consisting of a 1:1.3 molar mixture of BPO and TEMPO (△).

characteristics of unimolecular initiators are similar to those of the corresponding bimolecular systems in this molecular weight range. One observed difference between the two systems was that colored polymers were produced with the bimolecular systems at low molecular weights (M_n = 5000−10000) while the unimolecular systems gave colorless materials. This color could not be removed by repeated precipitations and may be detrimental for certain applications where optical clarity is important, such as photoresists for microlithography.[23]

While nitroxide-mediated living free radical polymerizations have been primarily employed in the controlled polymerization of styrene, a number of groups have extended this procedure to the preparation of well-defined random copolymers of styrene with acrylates, methacrylates,[10] butadiene,[25] acrylonitrile,[26] etc. In examining the polymerization of an 8:2 mixture of styrene and *tert*-butyl acrylate using the above initiating systems, similar results were obtained. The molecular weight increases in an approximately linear fashion with conversion while low-polydispersity materials are obtained with **3**, **12**, **13**, or a 1:1.3 mixture of BPO and TEMPO. The use of the benzyl initiator **2** was again observed to give polymers with polydispersities greater than 2.0 with a nonlinear relationship between M_n and conversion.

Molecular Weight Control. Previously[12] we reported that the molecular weight of macromolecules can be accurately controlled by the use of unimolecular initiators, such as **12**. The reason for this high degree of control is the same as for living anionic or cationic polymerizations; each molecule of **12** initiates a signal polymer chain which then undergoes controlled growth with little termination. To investigate this novel aspect of nitroxide-mediated living free radical polymerizations in greater detail and to compare the molecular weight control for unimolecular initiators to that obtained with the corresponding bimolecular systems, the polymerization of styrene with varying molar ratios of initiator was studied at 125 °C.

Initially the benzyloxy-substituted unimolecular initiator **12** and a 1:1.3 mixture of BPO/TEMPO were investigated as initiating systems. As can be seen in Figure 7, the experimental molecular weights of the polymers prepared using **12** are close to the theoretical molecular weights calculated from the feed ratio of styrene to **12**. At molecular weights below 30 000 amu, the agreement is excellent, and as the molecular weight increases, this difference increases only slightly, with the experimental value still within 10% at molecular weights above 100 000. For the bimolecular system, an approximately linear relationship is still maintained between the amount of initiator and the experimental molecular weight. However, the calculation of theoretical molecular weight is complicated by the actual number of initiating species that are generated from a 1:1.3 mixture of BPO/TEMPO, and therefore a comparison with theoretical molecular weight is not possible.

A similar relationship is observed when the polydispersities of the macromolecules prepared using **12** and the BPO/TEMPO system are compared. Both systems give very low polydispersity material (1.10−1.25) at molecular weights below 20 000, with the unimolecular initiator **12** typically giving lower polydispersity materials. As the molecular weight increases, the polydispersity also increases with the BPO/TEMPO systems, again giving polymers with higher polydispersities than **12** (Figure 8). It should be noted that in both cases the polydispersities are well below the theoretical limiting polydispersity of 1.5 for a conventional free radical process. These results are in accord with recent MALDI-TOF mass spectral analysis of polystyrenes produced by both unimolecular and bimolecular initiating systems.[27]

Comparison of the molecular weight control and polydispersities for the macromolecules prepared from AIBN/TEMPO and the corresponding unimolecular initiators, such as **18**, revealed similar trends to that observed above. Molecular weights could be controlled to a higher degree with the unimolecular initiators, and the polydispersities of the products obtained were lower than for the bimolecular, AIBN/TEMPO, system. In fact, the polymers obtained from the AIBN/TEMPO system had the highest polydispersities and poorest molecular weight control of any of the systems studied. From these results, it can be concluded that unimolecular initiators allow the preparation of macromolecules with greater control over molecular weight and polydispersity than the corresponding bimolecular systems. This general behavior can be rationalized by an examination of the initial steps in both processes. For the bimolecular systems, such as BPO/TEMPO, the initial step is decomposition of the benzoyl peroxide followed by reaction of the radical with a styrene monomer and subsequent trapping of this species with TEMPO. Moad[24] has elegantly shown that this series of reactions

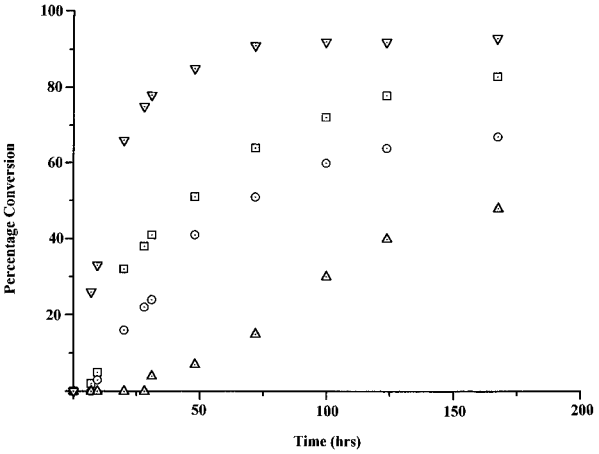


Figure 9. Percentage conversion as a function of time for the polymerization of styrene at 120 °C using the unimolecular initiator **3** with no additional solvent (▽), in a 1:1 mixture of styrene and chlorobenzene (□), in a 1:2 mixture of styrene and chlorobenzene (○), and in a 1:4 mixture of styrene and chlorobenzene (△).

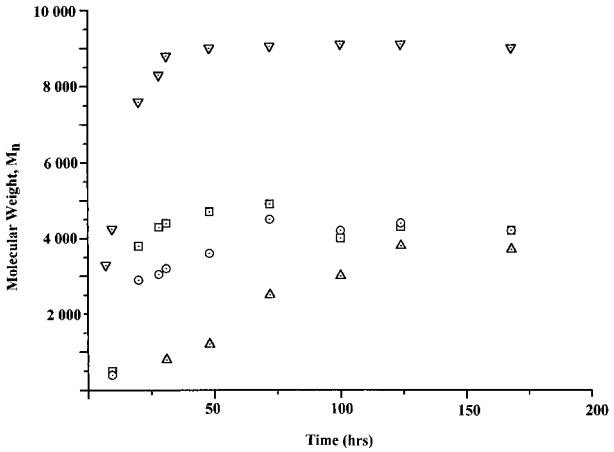


Figure 10. Evolution of molecular weight, M_n, as a function of time for the polymerization of styrene at 120 °C using the unimolecular initiator **3** with no additional solvent (▽), in a 1:1 mixture of styrene and chlorobenzene (□), in a 1:2 mixture of styrene and chlorobenzene (○), and in a 1:4 mixture of styrene and chlorobenzene (△).

is complicated by a variety of side reactions which lead to loss of initiator efficiency and the generation of unwanted side products. This results in slightly higher polydispersities and a lower degree of control over molecular weights. In contrast, this inefficient initiating step does not occur with the unimolecular initiators since the TEMPO adducts are preformed and actually resemble the unimers in some cases. Therefore the polymerizations occur with a higher initiator efficiency and a lower amount of undesirable side products, giving rise to accurate control over molecular weights and lower polydispersities.

Effect of Solvent. While it is customary to conduct living free radical polymerization under bulk conditions, it is not essential and in some cases, for example with high melting point or incompatible monomers, it may be beneficial to have solvent present. To investigate the effect of solvent on living free radical polymerizations, the polymerization of styrene at 120 °C was studied in the absence of solvent and in 1:1, 1:2, and 1:4 (weight ratio) solutions of styrene and chlorobenzene. Both the unimolecular initiator **3**, and the bimolecular system of BPO and TEMPO were investigated.

For **3** a dramatic effect on all aspects of the polymerization reaction was observed on increasing the amount of solvent. For example, the rate of polymerization was found to decrease with increasing solvent, with the percentage conversion after 48 h being 85% for the polymerization with no solvent, 51% for 1:1, 41% for 1:2, and only 7% for the 1:4 reaction (Figure 9). This decrease in reaction rate reflects the dilution of the polymerization mixture and has been observed by others.[22] Similarly, the molecular weight of the polymers obtained was found to decrease as the amount of solvent increased (Figure 10). While the solvent reactions were found to give low-polydispersity materials (1.15−1.25) under typical reaction times, the polydispersity increased significantly at longer reaction times (>72 h), with bimodal distributions being observed in some cases. A possible explanation for this is that at extreme reaction times autopolymerization of styrene becomes a significant process, which leads to uncontrollable molecular weights and an increase in the polydispersity. It was observed that changing the solvent from chlorobenzene to the more polar diglyme gave similar decreased polymerization rates though even more polar solvents may actually have a beneficial effect of the rate of polymerization.[28]

Repetition of the same solvent experiments with the bimolecular BPO/TEMPO system was also found to give decreased reaction rates, and if the reaction times were held to less than 72 h, the products were found to have low polydispersities (1.15−1.25). These results suggest that solvents can be used in living free radical polymerizations to prepare well-defined macromolecules, though the amount of solvent should be minimized and the polymerization should not be forced to completion.

Conclusions

Synthetic methodologies for the preparation of a variety of TEMPO-based unimolecular initiators have been investigated. Nitroxide derivatives were prepared by treatment of Grignard reagents with an excess of TEMPO, by the reaction of benzyl halides with the sodium salt of the reduced form of TEMPO, or by the capture of carbon-centered radicals by TEMPO. This last method was also employed for the synthesis of AIBN derivatives bearing a variety of ester groups. For the benzylic derivatives, it was found that the α-methyl group was essential for the free radical polymerization to proceed with living character. However, a variety of functional groups could be substituted at the β-carbon atom, or on the phenyl ring, without affecting the polymerization rate or the polydispersity of the polymers obtained.

When compared to the corresponding bimolecular systems, it was found that both series of unimolecular initiators gave similar polymerization rates and polydispersities for the preparation of polymers with molecular weights of the order of 10 000 amu. It was, however, found that the molecular weight control was greater for the unimolecular initiators than for the bimolecular systems at higher molecular weights (>10 000). In general, the polydispersities of both systems increased as the molecular weight increased. Finally, it was shown that the addition of solvent to the polymerization mixture led to a decrease in polymerization rate and significantly lower conversions.

Acknowledgment. The authors gratefully acknowledge support from the NSF Center for Polymeric

Interfaces and Macromolecular Assemblies, the IBM Corp., and Shipley Co.

References and Notes

(1) Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206
(2) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(3) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.
(4) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127. Otsu, T.; Matsunaga, T.; Kuriyama, A.; Yoshida, M. *Eur. Polym. J.* **1989**, *25*, 643. Turner, S. R.; Blevins, R. W. *Macromolecules* **1990**, *23*, 1856.
(5) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32. Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4,581,429, March 27, 1985. Johnson, C. H. L.; Moad, G.; Solomon, D. H.; Spurling, T.; Vearing, D. J. *Aust. J. Chem.* **1990**, *43*, 1215.
(6) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(7) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228. Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. *Macromolecules* **1995**, *28*, 1841. Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391. Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746. Li, I.; Howell, B. A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P. B.; Priddy, D. B. *Macromolecules* **1995**, *28*, 6692.
(8) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456.
(9) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.
(10) Hawker, C. J.; Elce, E.; Dao, J.; Russell, T.; Volksen, W.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.
(11) Yoshida, E.; Ishizone, T.; Hirao, A.; Nakahama, S.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3119. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Prepr.* **1994**, *35(2)*, 582. Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromol. Symp.* **1994**, *88*, 89.
(12) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11314.
(13) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993. Hedrick, J. L.; Hawker, C. J.; Dipietro, R.; Jerome, R.; Charlier, Y. *Polymer* **1995**, *36*, 4855.
(14) Saban, M. D.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 7032.
(15) Hawker, C. J.; Carter, K. R.; Hedrick, J. L.; Volksen, W. *Polym. Prepr.* **1995**, *36(2)*, 110. Elce, E.; Mecerreyes, D.; Hawker, C. J.; Hedrick, J. L.; Jerome, R. *Macromolecules*, submitted.
(16) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Polym. Prepr.* **1994**, *35(2)*, 582.
(17) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. Druliner, J. D. *Macromolecules* **1991**, *24*, 6079. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. Matyjaszewski, K.; Gaynor, S.; Wang, J. S. *Macromolecules* **1995**, *28*, 2093.
(18) Anderson, J. E.; Casarini, D.; Corrie, J. E. T.; Lunazzi, L. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1299. Catala, J. M.; Bubel, F.; Hammouch, S. O. *Macromolecules* **1995**, *28*, 8441.
(19) Li, I.; Howell, B. A.; Ellaboudy, A.; Kastl, P. E.; Priddy, D. B. *Polym. Prepr.* **1995**, *36(1)*, 469.
(20) Korolenko, E. C.; Cozens, F. L.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 14123.
(21) Connolly, T. J.; Baldovi, M. V.; Mohat, N.; Scaiano, J. C. *Tetrahedron Lett.*, in press.
(22) Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K. *Polym. Prepr.* **1996**, *37(1)*, 485.
(23) Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. *Proc. SPIE*, in press.
(24) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.
(25) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2(2)*, 66.
(26) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* **1996**, *29*, 3050.
(27) Jasieczek, C. B.; Haddleton, D. M.; Shooter, A. J.; Buzy, A.; Jennings, K. R.; Gallagher, R. T. *Polym. Prepr.* **1996**, *37(1)*, 845.
(28) Odell, P. G.; Hamer, G. K. *Polym. Mater. Sci. Eng.* **1996**, *74*, 404.

MA951905D