3078 *Macromolecules* **2003,** *36,* 3078−3084

New Seven- and Eight-Membered Cyclic Alkoxyamines for the Living Free Radical Polymerization

Tobias Schulte and Armido Studer*

Fachbereich Chemie der Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Received November 5, 2002; Revised Manuscript Received March 4, 2003

ABSTRACT: A straightforward synthesis of new seven- and eight-membered cyclic alkoxyamines from the corresponding lower homologous keto−alkoxyamines via ring-enlargement using TMS−diazomethane is described. The use of these ring-enlarged cyclic alkoxyamines as regulators/initiators for the radical polymerization of styrene and *n*-butyl acrylate is presented. Efficient controlled and living styrene polymerization (molecular weight of up to 40 000) can be obtained using the seven- and eight-membered alkoxyamine initiators. The influence of the ring-enlargement on the quality of the polymerization process (polymerization time, livingness, PDI) is discussed. The rate constant of the C−O bond cleavage of these new alkoxyamines has been measured. In addition, the thermal decomposition of the alkoxyamines has been studied. Furthermore, EPR data of the corresponding new nitroxides are presented.

Introduction

Well-defined polymers with polydispersities below the theoretical limit for a conventional radical polymerization (1.5) can nowadays be prepared by living free radical polymerization. Nitroxide-mediated polymerizations (NMP),[1] atom transfer radical polymerizations (ATRP),[2] and RAFT polymerizations[3] belong to this category. The NMP and ATRP processes are controlled by the persistent radical effect (PRE).[4] The control of the polymerization in the NMP is based on the reversible formation of a dormant alkoxyamine from the corresponding nitroxide and the chain growing polymer radical. The concentration of free radicals remains low during the entire polymerization, thus ensuring a very low fraction of irreversible termination via polymer radical dimerization/disproportionation. The equilibrium constant between the nitroxide-capped polymer and the free nitroxide and polymer radical, respectively, is therefore of great importance in these processes.[4] Various parameters influence the equilibrium.[5] On the basis of experimental results and on calculations, it has been predicted that in cyclic nitroxides the ring size influences the C−O bond dissociation energy (BDE) of the corresponding alkoxyamines and hence the equilibrium. The BDE increases from seven- to six- to five-membered cyclic nitroxides.[6]

Herein we present our results on the synthesis of new alkoxyamines formally deriving from seven- and eight-membered cyclic nitroxides.[7] Their efficiency as regulators for the polymerization of styrene and *n*-butyl acrylate will be discussed. Furthermore, rate constants for the C−O bond homolysis of these new alkoxyamines, decomposition studies and EPR data of the corresponding nitroxides will be presented.

Experimental Section

Materials. (1-Bromoethyl)benzene (Aldrich, 97%), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (Aldrich, 98%), (trimethylsilyl)diazomethane (Aldrich, 2 M in hexane) and pyridinium toluene-4-sulfonate (Fluka, 99+%) were used as received. Styrene (BASF) and *n*-butyl acrylate (Fluka, 99+%) were both distilled over CaH_2 to remove the stabilizer. Benzene was distilled over sodium and CH_2Cl_2 was distilled over CaH_2 before use. All other chemicals were used as received.

General Data. ^{1}H NMR and ^{13}C NMR spectra were recorded on a AMX 500 (500 MHz, Bruker), ARX 300 (300 MHz, Bruker) or ARX 200 (200 MHz, Bruker). Chemical shifts δ in ppm relative to $SiMe_4$ as internal standard. TLC: silica gel 60 F_{254} plates (Merck); detection with UV or dipping into a solution of $KMnO_4$ (1.5 g in 333 mL of 1 *m* NaOH) or a solution of $Ce(SO_4)_2 \cdot H_2O$ (10 g), phosphormolybdic acid hydrate (25 g), concentrated H_2SO_4 (60 mL), and H_2O (940 mL), followed by heating. Flash chromatography (FC): silica gel 60 (40−63 μm, Merck or Fluka); at ca. 0.4 bar. Melting points: 510 apparatus (Büchi); uncorrected. IR spectra were recorded on a IR 750 (Nicolet Magna) or a IFS-200 (Bruker). Mass spectra were recorded as electrospray mass spectrometry (ESI−MS) or field desorption mass spectrometry (FD-MS) on a CH7 (Varian) and as HRMS on a 95S (MAT). Size exclusion chromatography (SEC) was carried out with THF as eluent at a flow rate of 1.0 mL/min at room temperature on a system consisting of a L6200A intelligent pump (Merck Hitachi), a set of two Plgel 5 μm MIXED-C columns (300 × 7.5 mm, Polymer Laboratories), and a RI-101 detector (Shodex). Data were acquired through a PL Datastream unit (Polymer Laboratories) and analyzed with Cirrus GPC software (Polymer Laboratories) based upon calibration curves built upon polystyrene and poly(methyl methacrylate) standards (Polymer Laboratories polystyrene medium MW calibration kit S-M-10 to determine the molecular weight of polystyrene and Polymer Laboratories poly(methyl methacrylate) medium MW calibration kit M-M-10 to determine the molecular weight of *n*-butyl acrylate) with peak molecular weights ranging from 500 to 3 000 000. EPR spectra were recorded on a ESP 300 E (Bruker) equipped with a high-temperature cavity (Bruker) and a B-TC 80/15 (Bruker). The nitroxide concentrations were determined by double integration of the EPR spectra and calibration with a TEMPO solution in *tert*-butylbenzene.

2,2,6,6-Tetramethyl-1-(1-phenylethoxy)-4-piperidinone (1). (1-Bromoethyl)benzene (6.69 mL, 49.02 mmol), 2,2,6,6-tetramethyl-4-piperidinone-*N*-oxyl[8] (10.00 g, 58.82 mmol), Cu powder (3.26 g, 51.46 mmol), $Cu(OTf)_2$ (182 mg, 0.49 mmol), and 4,4′-di-*tert*-butyl-2,2′-bipyridyl (264 mg, 1.97 mmol) were suspended under Ar in benzene (200 mL). The reaction mixture was stirred under Ar at 65−70 °C for 20 h. The solids were removed by filtration over SiO_2. Purification by FC (pentane/ethyl acetate, 14:1) afforded **1** (10.73 g, 79%) as a colorless solid. Mp: 72 °C. IR (KBr): 3000 s, 2969 w, 2958 w, 2923 w, 1715 s, 1448 m, 1364 m, 1305 s, 1229 m, 1196 m, 1058

---

* Corresponding author. E-mail: studer@mailer.uni-marburg.de.

10.1021/ma025806t CCC: $25.00

s, 1025 m, 957 m, 764 s, 705 s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.35-7.26$ (m, 5 H, CH), 4.87 (q, $J = 6.6$ Hz, 1 H, CH), 2.65−2.46 (m, 2 H, CH$_2$), 2.27−2.05 (m, 2 H, CH$_2$), 1.54 (d, $J = 6.6$ Hz, 3 H, CH$_3$), 1.44 (s, 3 H, CH$_3$), 1.23 (s, 3 H, CH$_3$), 1.06 (s, 3 H, CH$_3$), 0.77 (s, 3 H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 208.9$, 145.0, 128.6, 127.7, 127.2, 83.8, 63.4, 54.1, 34.3, 34.0, 23.3, 23.1, 23.0. MS (ESI): 298 (100, [M + Na]$^+$), 276 (80, [M + H]$^+$), 274 (24), 225 (24), 193 (20), 178 (24), 172 (84, [M − C$_8$H$_7$]$^+$), 105 (32, (M − C$_9$H$_{17}$NO$_2$]$^+$), 74 (40). HRMS (ESI): calcd for C$_{17}$H$_{25}$NO$_2$ (M$^+$), 275.1885; found, 275.1894.

General Procedure (GP1) for the Ring Expansion Reactions. The alkoxyamine was dissolved in CH$_2$Cl$_2$, and molecular sieve (MS) 3 Å was added. The solution was cooled to ca. −78 °C. After addition of BF$_3$·OEt$_2$, (trimethylsilyl)-diazomethane (TMSCHN$_2$, 2 M in hexane) was slowly added. The resulting yellow solution was stirred for 20 min at ca. −78 °C. The mixture was allowed to warm to room temperature, saturated NaHCO$_3$ and pentane were added, and the phases were separated. The organic layer was washed with H$_2$O and brine and dried over MgSO$_4$. The solvent was removed under reduced pressure and the yellow crude product was dissolved in MeOH. Pyridinium toluene-4-sulfonate (PPTS) was added and the solution was stirred for 12 h at room temperature. NEt$_3$ was added, and the solvent was removed under reduced pressure. Purification by FC (SiO$_2$) afforded the ring-enlarged alkoxyamine.

2,2,7,7-Tetramethyl-1-(1-phenylethoxy)-4-azepanone (2). **2** was prepared according to GP1 with 2,2,6,6-tetramethyl-1-(1-phenylethoxy)-4-piperidinone (**1**) (3.00 g, 10.89 mmol), CH$_2$Cl$_2$ (100 mL), MS 3 Å (20.00 g), BF$_3$·OEt$_2$ (1.51 mL, 11.98 mmol), TMSCHN$_2$ (7.10 mL, 14.16 mmol), saturated NaHCO$_3$ (110 mL), MeOH (130 mL), PPTS (336 mg, 1.34 mmol), and NEt$_3$ (0.66 mL). Purification by FC (pentane/ethyl acetate, 9:1) afforded **2** (2.35 g, 75%) as a colorless solid. Mp: 54 °C. IR (KBr): 3003 w, 2876 w, 2924 w, 1710 s, 1361 m, 1301 s, 1061 m, 761 s, 704 s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.32-7.23$ (m, 5 H, CH), 4.85−4.73 (m, 1 H, CH), 2.89 (dd, $J_1 = 12.0$ Hz, $J_2 = 19.7$ Hz, 1 H, CH$_2$), 2.51−2.05 (m, 4 H, CH$_2$), 1.94−1.66 (m, 1 H, CH$_2$), 1.49−1.45 (m, 3 H, CH$_3$), 1.38−1.35 (m, 3 H, CH$_3$), 1.18 (d, $J = 6.0$ Hz, 3 H, CH$_3$), 0.91 (s, CH$_3$), 0.77 (s, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 212.2$, 145.1, 130.0, 128.6, 127.5, 127.4, 127.2, 83.5, 83.4, 63.8, 63.7, 63.5, 54.3, 54.2, 38.4, 36.8, 36.5, 34.5, 34.3, 33.3, 32.8, 25.9, 25.8, 24.9, 23.1, 22.9. MS (FD): 289 (36, [M]$^+$), 184 (96, [M − C$_8$H$_9$]$^+$), 105 (100, [M − C$_{10}$H$_{18}$NO$_2$]$^+$). HRMS (ESI): calcd for C$_{18}$H$_{27}$NO$_2$ (M$^+$), 289.2024; found, 289.2029.

2,2,8,8-Tetramethyl-1-(1-phenylethoxy)-5-azocanone (3) and 2,2,8,8-tetramethyl-1-(1-phenylethoxy)-4-azocanone (4). These compounds were prepared according to GP1 with 2,2,7,7-tetramethyl-1-(1-phenylethoxy)-4-azepanone **2** (3.00 g, 10.37 mmol), CH$_2$Cl$_2$ (40 mL), MS 3 Å (30 g), BF$_3$·OEt$_2$ (1.43 mL, 11.40 mmol), TMSCHN$_2$ (5.7 mL, 11.40 mmol), saturated NaHCO$_3$ (40 mL), MeOH (45 mL), PPTS (318 mg, 1.27 mmol), and NEt$_3$ (0.60 mL). Purification by FC (pentane/ethyl acetate, 9:1) afforded **3** (316 mg, 10%) as a colorless solid and **4** (714 mg, 23%) as a viscous colorless oil. Analytical data for **3** are as follows. Mp: 50 °C. IR (KBr): 3443 w, 2976 w, 1691 s, 1495 m, 1364 m, 1213 m, 1130 m, 766 m, 704 s cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.38-7.22$ (m, 5 H, CH), 4.76 (q, $J = 10.1$ Hz, 1 H, CH), 2.75−2.27 (m, 5 H, CH$_2$), 1.70−1.49 (m, 3 H, CH$_2$), 1.44 (d, $J = 10.1$ Hz, 3 H, CH$_3$), 1.39 (s, 3 H, CH$_3$), 1.28 (s, 3 H, CH$_3$), 1.18 (s, 3 H, CH$_3$), 0.77 (s, 3 H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 210.6$, 144.6, 128.4, 127.7, 127.6, 82.7, 64.2, 64.1, 40.4, 40.2, 39.0, 38.3, 31.8, 31.5, 26.1, 25.6, 22.4. MS (FD): 303 (100, [M]$^+$), 198 (36, [M − C$_8$H$_9$]$^+$), 105 (80, [M − C$_{11}$H$_{20}$NO$_2$]$^+$). HRMS (ESI): calcd for C$_{19}$H$_{29}$NO$_2$ (M$^+$), 303.2198; found, 303.2198. Analytical data for **4** are as follows. IR (film): 2976 w, 2932 w, 1713 s, 1452 s, 1379 s, 1363 s, 1174 s, 1061 s, 930 m, 762 s, 700 s cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.28-7.22$ (m, 5 H, CH), 4.82−4.72 (m, 1 H, CH), 2.71−2.53 (m, 1 H, CH$_2$), 2.31−2.11 (m, 3 H, CH$_2$), 1.82−1.51-(m, 2H, CH$_2$), 1.50−1.41 (m, 5 H, CH$_2$, CH$_3$), 1.36, 1.30 (2s, CH$_3$), 1.22, 1.18 (2s, CH$_3$), 1.07, 1.04 (2s, CH$_3$), 0.67 (s, 3 H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 210.9$, 145.7, 128.7, 128.5, 127.4, 127.2, 127.0, 83.9, 83.7, 62.3, 62.1, 60.4, 60.2, 60.1, 39.5, 34.9, 34.5, 32.7, 32.1, 31.8, 27.4, 23.6, 21.2, 20.9, 17.8. MS (ESI): 304 (12, [M + H]$^+$), 290 (10), 221 (28), 200 (56), 168 (48), 99 (28), 74 (12). HRMS (ESI): calcd for C$_{19}$H$_{29}$NO$_2$ (M$^+$), 303.2198; found, 303.2185.

General Procedure (GP2) for the Reduction Reactions. The alkoxyamine was dissolved in MeOH at 0 °C, and NaBH$_4$ was added in small portions. After 30 min, the suspension was allowed to warm to room temperature. Then MeOH was added until the residue was dissolved. After being stirred for 12 h at room temperature, the reaction mixture was treated with saturated NH$_4$Cl and a white precipitate was formed. H$_2$O was added and the mixture was extracted with diethyl ether (4×). The combined organic layers were dried over MgSO$_4$. The solvent was removed under reduced pressure and the crude product was dried in vacuo.

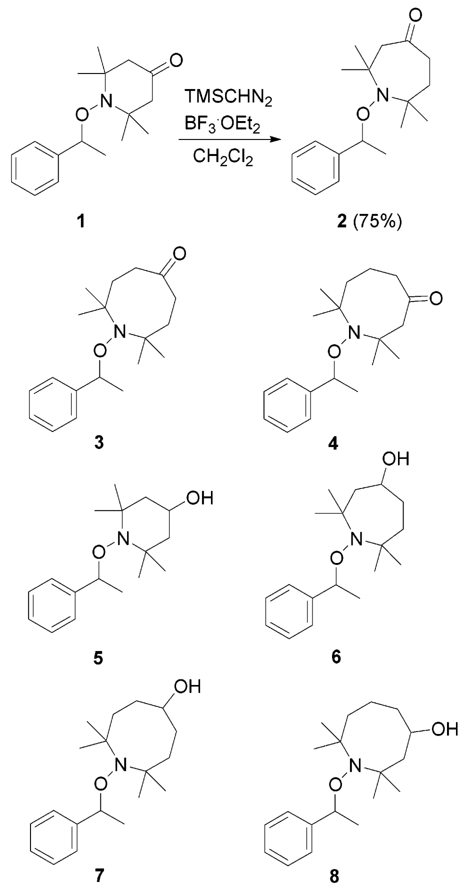
2,2,7,7-Tetramethyl-1-(1-phenylethoxy)-4-azepanol (6). **6** was obtained according to GP2 with **2** (930 mg, 3.20 mmol), MeOH (5 mL), NaBH$_4$ (448 mg, 11.84 mmol), and saturated NH$_4$Cl (5 mL) to afford the product (932 mg, 99%) as a 3:1 mixture of diastereoisomers. IR (film): 2974 w, 2934 w, 1478 m, 1452 m, 1362 s, 1160 s, 1058 m, 1034 m, 927 w, 762 s, 700 s cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.31-7.25$ (m, 5 H, CH), 4.84−4.73 (m, 1 H, CH), 4.06−4.01 (m, 1 H, CH), 2.17−2.10 (dd, $J_1 = 6.6$ Hz, $J_2 = 13.9$ Hz, 1 H, CH$_2$), 2.10−1.10 (m, 15 H, CH$_2$, CH$_3$), 0.84 (s, CH$_3$, both isomers), 0.76 (s, CH$_3$, minor isomer), 0.67 (s, CH$_3$, major isomer). ^{13}C NMR (75 MHz, CDCl$_3$, both isomers): $\delta = 144.0$, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 127.6, 84.2, 84.0, 83.6, 69.4, 67.9, 64.5, 64.3, 64.0, 49.1, 45.2, 45.0, 37.7, 37.0, 36.8, 34.0, 33.5, 33.2, 33.1, 32.8, 32.6, 31.6, 30.5, 27.7, 27.5, 26.4, 26.1, 25.5, 22.9, 22.8. MS (ESI): 292 (100, [M + H]$^+$), 274 (26, [M − CH$_3$]$^+$), 236 (16), 209 (35), 188 (80, [M − C$_8$H$_7$]$^+$), 170 (46), 156 (80), 137 (58), 132 (22), 121 (58), 105 (68, [M − C$_{10}$H$_{20}$NO$_2$]$^+$). HRMS (ESI): calcd for C$_{18}$H$_{29}$NO$_2$ (M$^+$), 291.2198; found, 291.2189.

2,2,8,8-Tetramethyl-1-(1-phenylethoxy)-5-azocanol (7). **7** was prepared according to GP2 with **3** (300 mg, 1.00 mmol), MeOH (2 mL), NaBH$_4$ (139 mg, 3.7 mmol) and saturated NH$_4$Cl (3 mL) to afford the product (287 mg, 95%) as a viscous colorless oil. IR (film): 3438 w, 2975 w, 2929 w, 1451 w, 1363 w, 1059 w, 1029*w* cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 7.26-7.16$ (m, 5 H, CH), 4.81 (q, $J = 6.8$ Hz, 1 H, CH), 3.87−3.66 (m, 1 H, CH), 2.54−1.56 (m, 6 H, CH$_2$), 1.49−1.09 (m, 14 H, CH$_2$, CH$_3$), 0.77 (s, 3 H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 144.4$, 128.4, 128.2, 128.0, 127.3, 127.3, 127.0, 125.3, 83.1, 67.7, 65.8, 64.9, 64.6, 63.7, 41.0, 31.9, 31.4, 25.8, 25.2, 23.5, 15.2. MS (ESI): 306 (100, [M + H]$^+$), 169 (20), 138 (18), 105 (6, [M − C$_{11}$H$_{22}$NO$_2$]$^+$). HRMS (ESI): calcd for C$_{19}$H$_{31}$NO$_2$ (M$^+$), 305.2355; found, 305.2358.

2,2,8,8-Tetramethyl-1-(1-phenylethoxy)-4-azocanol (8). **8** was obtained ccording to GP2 with **4** (310 mg, 1.02 mmol), MeOH (2 mL), NaBH$_4$ (143 mg, 3.8 mmol), and saturated NH$_4$Cl (3 mL). Purification by FC (pentane/ethyl acetate, 5:1) afforded **8** (98 mg, 31%) as a viscous colorless oil. IR (film): 3378 w, 2975 w, 2932 w, 1451 m, 1363 m, 1157 m, 1059 m, 928 m, 762 m, 699 s cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, both isomers): $\delta = 7.26-7.17$ (m, 5 H, CH), 4.83−4.66 (m, 1 H, CH), 4.06−3.75 (m, CH), 2.45−1.66 (m, CH$_2$), 1.63−0.70 (m, CH$_2$, CH$_3$), 0.60 (s, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, both isomers): $\delta = 144.3$, 128.1, 128.0, 127.4, 127.2, 127.1, 126.8, 126.6, 83.5, 83.1, 68.9, 67.7, 44.5, 41.0, 37.2, 36.5, 32.6, 31.9, 31.7, 31.3, 30.0, 25.8, 25.0, 23.5, 22.3, 20.2, 17.5, 17.3. MS (ESI): 306 (20, [M + H]$^+$), 262 (12), 202 (16), 169 (48), 151 (24), 138 (56), 121 (100), 105 (68, [M − C$_{11}$H$_{22}$NO$_2$]$^+$). HRMS (ESI): calcd for C$_{19}$H$_{31}$NO$_2$ (M$^+$), 305.2355; found, 305.2351.

Typical Procedure for the Polymerization of Styrene. A Schlenk tube was charged with the alkoxyamine initiator **2** (38 mg, 0.131 mmol) and styrene (1.5 mL, 13.106 mmol). The tube was subjected to three freeze−thaw cycles and sealed off under argon. The polymerization was carried out under argon at 125 °C for 6 h. The resulting mixture was cooled to room temperature, dissolved in CH$_2$Cl$_2$, and poured into an aluminum dish, and residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetrically; molecular weight and polydispersity index

Scheme 1. Various Alkoxyamines Studied



(PDI) were determined by size exclusion chromatography (SEC). Conversion = 84%. M_n = 9000 g mol^{-1}. PDI = 1.10.

Typical Procedure for the Polymerization of *n*-Butyl Acrylate. A Schlenk-tube was charged with the alkoxyamine initiator **2** (61 mg, 0.210 mmol) and *n*-butyl acrylate (3 mL, 21.019 mmol). The tube was subjected to three freeze−thaw cycles and sealed off under argon. The polymerization was carried out under argon at 125 °C for 14 h. The resulting mixture was cooled to room temperature, dissolved in CH_2Cl_2, and poured into an aluminum dish, and residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetrically; molecular weight and polydispersity index (PDI) were determined by size exclusion chromatography (SEC). Conversion = 59%. M_n = 11 200 g mol^{-1}. PDI = 1.44.

Results and Discussion

Synthesis of the Alkoxyamines. Alkoxyamine **1**[8] was prepared from phenethyl bromide and 4-Oxo-TEMPO using the Matyjaszewski protocol.[9] Alkoxyamine **2** was readily obtained starting from the six-membered alkoxyamine **1** in a one-step reaction via ring homologization using commercially available TMS−diazomethane (75%, Scheme 1).[10]

In analogy, ring-homologization of alkoxyamine **2** provided the two separable regioisomeric eight-membered alkoxyamines **3** (10%) and **4** (23%). Alcohol **5** is a known compound[11] and was included in the present study for comparison. Reduction of ketone **2** with $NaBH_4$ in MeOH afforded the seven-membered cyclic alcohol **6** as a 3:1 mixture of diastereoisomers in quantitative yield. The alcohols **7** (95%) and **8** (31%, diastereoisomeric ratio = 1:1) were obtained from the corresponding ketones **3** and **4** using the same method.

Table 1. Polymerization of Styrene Using Alkoxyamines 1−8 as Regulators/Initiators

entry	alkoxyamine (amount)	time (h)	temp (° C)	$M_{n,exp}$	$M_{n,th}$	PDI	conversion (%)
1	**1** (1%)	6	125	3000	2900	1.23	28
2	**1** (0.2%)	6	125	15 200	22 400	1.37	43
3	**2** (1%)	6	125	9000	8700	1.10	84
4	**2** (0.4%)	6	125	18 600	21 600	1.20	83
5	**2** (0.2%)	6	125	32 000	34 400	1.21	66
6	**2** (0.1%)	6	125	45 700	73 900	1.38	71
7	**2** (0.2%)	25	105	24 900	38 000	1.18	73
8	**2** (0.1%)	25	105	52 000	92 700	1.39	89
9	**2** (0.2%)	115	85	22 200	45 800	1.53	88
10	**3** (1%)	3	125	5000	5600	1.17	54
11	**3** (0.2%)	6	125	31 500	40 600	1.34	78
12	**4** (1%)	6	125	5600	6000	1.29	58
13	**4** (0.2%)	6	125	23 700	35 400	1.33	68
14	**5** (1%)	6	125	2200	2700	1.27	26
15	**5** (0.2%)	6	125	13 200	19 300	1.38	37
16	**6** (1%)	6	125	3300	3100	1.23	30
17	**6** (0.2%)	6	125	17 000	27 100	1.36	52
18	**7** (1%)	6	125	6400	5100	1.41	49
19	**7** (0.2%)	6	125	31 000	41 700	1.62	80
20	**8** (1%)	6	125	3600	3700	1.23	36
21	**8** (0.2%)	6	125	19 000	24 000	1.32	46

Polymerizations. The polymerization of styrene was studied first. The initial polymerizations were conducted in sealed tubes using 0.2 or 1% of the alkoxyamine initiator at 125 °C and were stopped after 6 h. The conversion was determined gravimetrically. The PDI and the molecular weight of the polymers were analyzed using SEC. The results are summarized in Table 1.

With the six-membered ketone **1** a low conversion was obtained (entry 1, 28%). Decreasing the initiator concentration afforded PS with a higher PDI (1.37) and a higher conversion (entry 2). We were pleased to find that the ring-enlarged seven-membered ketone **2** provided better results. Using 1% of initiator **2**, a high conversion was obtained and polystyrene (PS) with a narrow PDI was formed (84%, PDI = 1.10, entry 3). Decreasing the initiator amount afforded PS with slightly increased PDI (entry 5, PDI = 1.21). The eight-membered symmetrical ketoalkoxyamine **3** afforded even better results. Quantitative conversion was obtained in 6 h. After 3 h a conversion of 54% was already obtained and PS with a narrow PDI was formed (entry 10, PDI = 1.17). As for the seven-membered ring, a slightly increased PDI value was observed upon decreasing the initiator concentration (entry 11, PDI = 1.34). The isomeric unsymmetrical eight-membered alkoxyamine **4** provided similar results (entries 12 and 13).

We then turned to the question whether the keto group is important for the polymerization process. To this end, alcohols **5**−**8** were used as regulators/initiators for the polymerization of styrene. As in the keto series, the lowest conversion was obtained with the six-membered cyclic alkoxyamine **5** as initiator (entries 14 and 15). Surprisingly, the homologous hydroxyalkoxyamine **6** turned out to be a far less efficient initiator/regulator than the corresponding ketone **2** (compare entries 16 and 17 with entries 3 and 4). Similar results were obtained for the eight-membered cyclic alkoxyamines **7** and **8** (entries 18−21). From these initial polymerization studies we can conclude that indeed, as predicted by theory,[6] ring-enlargement positively influences the regulator/initiator efficiency of cyclic alkoxyamines. We found that a keto function within the ring is far superior than a hydroxymethylene unit. Transannular interactions of the keto group with the alkoxyamine oxygen atom can be excluded, since IRstretching frequencies of the C═O double bond in these ketones did not show any indication of transannular interactions: **1**, $\nu = 1715\ \mathrm{cm}^{-1}$; **2**, $\nu = 1710\ \mathrm{cm}^{-1}$; **3**, $\nu = 1691\ \mathrm{cm}^{-1}$; **4**, $\nu = 1715\ \mathrm{cm}^{-1}$. In addition, also for the free nitroxides no indications of transannular interactions were found (vide infra). The effect of the keto group will be further discussed below.

The seven-membered cyclic ketone **2** was used for further styrene polymerization studies (entries 4, 6−9). Decreasing the amount of initiator to 0.1% afforded PS with a higher molecular weight (M_n = 45 700); however, the PDI also slightly increased (PDI = 1.38, entry 6). The polymerization was also conducted at 105 °C (entries 7 and 8). Controlled polymerization was obtained using 0.2% of initiator **2** (M_n = 24 900; PDI = 1.18). Again, reducing the initiator concentration provided PS with increased PDI. Polymerization at 85 °C for 115 h was not controlled (entry 9, PDI = 1.53). Thus, alkoxyamine **2**, *which is readily prepared on a large scale*, is an efficient regulator/initiator for the preparation of PS with a molecular weight of up to 40 000.

In all the experiments we found that decreasing the initiator concentration leads to an increase of the PDI. This can be understood by the increase of the influence of the thermal polymerization of styrene by autoinitiation. Indeed, theory predicts higher PDI's in NMP if additional initiation is considered.[12d] In most of our experiments, the difference between M_n and the theoretical number-average molecular weight ($M_{n,th}$) increases upon decreasing the initiator concentration (see Table 1). This indicates an increased fraction of additional chains deriving from autoinitiation of styrene.[5m] According to theory,[12d] additional initiation should lead to higher conversion in NMP. This is in agreement with most of our experiments, since as mentioned above, decreasing the initiator concentration should lead to a higher fraction of additional initiation, and this in turn will lead to higher conversion. For initiator **2**, however, a decrease of conversion upon decreasing the initiator concentration was obtained. A similar decrease of conversion upon decreasing the initiator concentration has previously been reported for NMP of styrene.[5m] Currently, we do not understand why initiator/regulator **2** showed concentration effects on the polymerization conversions different from those of the other systems studied.

To check whether the styrene polymerization using initiator **2** is a living/controlled process, we determined the conversion as a function of time and we analyzed the molecular weight as a function of monomer conversion (Figure 1). The linear increase of $\ln([M_0]/[M])$ vs time and molecular weight vs monomer consumption proves the controlled character of the polymerization.

We further tested whether the polymerization is living. To this end, PS prepared using alkoxyamine **2** (PDI = 1.15, M_n = 7900) was used as macroinitiator for the bulk polymerization of styrene (250 equiv styrene were used). Reaction was conducted at 125 °C for 6 h providing PS with a slightly larger PDI (M_n = 25 100, 83% conversion, PDI = 1.33, Table 2, entry 1, Figure 2). This shows that the **2**-mediated styrene polymerization is living. However, the non symmetrical GPC trace b in Figure 2 indicates loss of control during the polymerization. Probably, decomposition of the dormant alkoxyamine is occurring which leads to an increased PDI (see below). We repeated the experiment using PS prepared with alkoxyamine **3** (entry 2). Reinitiation could be accomplished and controlled polymerization was obtained (PDI = 1.23). With the regioisomeric eight-membered alkoxyamine **4** macroinitiation was again successful and PS with a PDI of 1.42 was formed. The position of keto group in the eight-membered ring influences the polymerization process. In general, the symmetrical ketoalkoxyamine **3** provided slightly better results than alkoxyamine **4**.

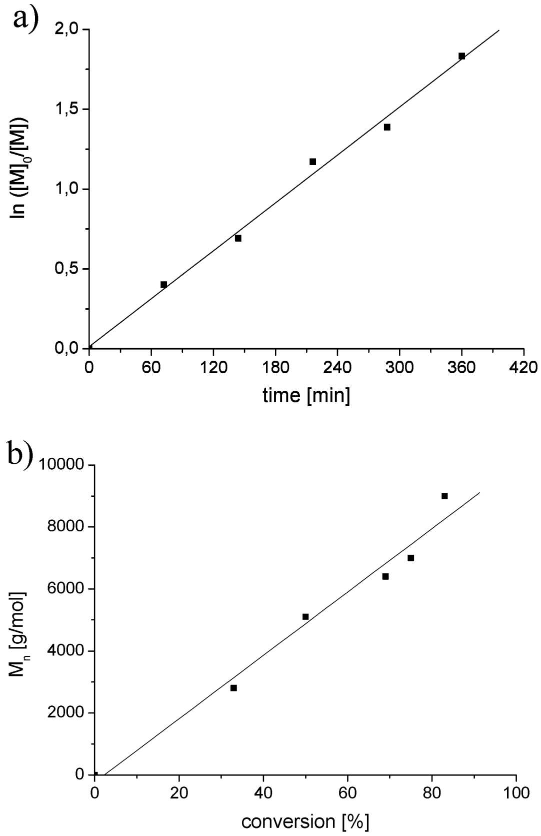


Figure 1. (a) Monomer conversion vs time for the polymerization of styrene using initiator **2 (**1 mol % **2**, 125 °C, 6 h). (b) Molecular weight vs monomer conversion for the polymerization of styrene using initiator **2** (1 mol % **2**, 125 °C, 6 h).

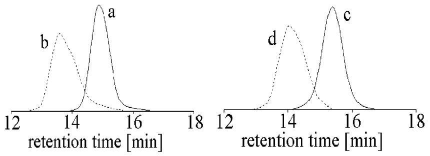


Figure 2. GPC traces for the bulk polymerization of styrene using alkoxyamines **2** and **3** before (traces a and c) and after reinitiation (traces b and d): (a) = PS-**2** (PDI = 1.15, M_n = 7900); (b) = PS-**2** (PDI = 1.33, M_n = 25 100); (c) = PS-**3** (PDI = 1.17, M_n = 5000); (d) = PS-**3** (PDI = 1.23, M_n = 18 500)).

Table 2. Polymerization of Styrene Using Various Macroinitiators at 125 °C

entry	PS−alkoxyamine (M_n/PDI/amount)	time (h)	M_n	PDI	conversion (%)
1	PS-**2** (7900/1.15/0.4%)	6	25 100	1.33	83
2	PS-**3** (5000/1.17/0.4%)	3	18 500	1.23	60
3	PS-**4** (5600/1.29/0.4%)	6	15 600	1.42	52
4	PS-**6** (3300/1.23/0.4%)	6	13 500	1.59	43
5	PS-**7** (6400/1.41/0.4%)	6	16 800	1.65	54
6	PS-**8** (3600/1.23/0.4%)	6	9900	1.64	23

Macroinitiation using PS prepared with the seven- and eight-membered alcohols **6**−**8** provided PS with broad polydispersities (PDI > 1.5, entries 4−6). In

Table 3. Polymerization of *n*-Butyl Acrylate Using Alkoxyamines 1−4 and 6−8 at 125 °C

entry	alkoxyamine (amount)	% nitroxide	time (h)	M_n	PDI	conversion (%)
1	**1** (1%)		14	2100	1.60	13
2	**2** (1%)		14	11 200	1.44	59
3	**2** (0.4%)		20	15 600	1.53	48
4	**2** (0.2%)		20	23 700	1.52	40
5	**2** (0.1%)		20	52 500	1.57	34
6	**2** (0.4%)	0.01	20	25 100	2.25	59
7	**2** (0.4%)	0.02	20	22 300	2.23	55
8	**2** (0.4%)	0.03	20	21 700	2.51	67
9	**3** (1%)		14	13 800	1.44	71
10	**4** (1%)		14	10 600	1.80	55
11	**6** (1%)		14	3400	1.38	16
12	**7** (1%)		14	5300	1.56	36
13	**8** (1%)		14	3500	1.42	17

contrast to the keto series, polymerizations of styrene using the alkoxyamines **6**−**8** are not living.

We next focused on the polymerization of *n*-butyl acrylate (Table 3). The reactions were conducted at 125 °C using the alkoxyamines **1**−**4** and **6**−**8** as regulators/initiators under different conditions. With the six-membered ketone **1** only 13% conversion was obtained after 14 h (entry 1). A better result was obtained using alkoxyamine **2** (59% conversion, PDI = 1.44, entry 2). With alkoxyamine **3** a similar result was observed (entry 9). A larger PDI was measured for poly butyl acrylate prepared with alkoxyamine **4** (entry 10). Polymerizations with the alcohol initiators **6**−**8** were not efficient, and low conversions were obtained (entries 11−13). A decrease of the initiator concentration did not provide better results, as shown for the polymerization using alkoxyamine **2** (entries 3−5). The addition of free nitroxide has been shown to improve the polymerization process.[5g,12] We therefore studied the polymerization of *n*-butyl acrylate with alkoxyamine **2** in the presence of various amounts of nitroxide **10** (entries 6−8). In contrary to our expectation, conversion and PDI increased. We can conclude that our new alkoxyamines are not perfect regulator/initiators for the acrylate polymerization. With the seven- and eight-membered keto−alkoxyamines **2** and **3,** acceptable conversions were obtained; however, only modest control of the polymerization was observed (PDI around 1.4).

Kinetics of the C−O Bond Homolysis. In nitroxide-mediated living radical polymerizations the rate constant k_d for the C−O bond homolysis is an important parameter affecting the conversion times and polydispersities.[4,5,13] We therefore determined the rate constant k_d for the C−O bond homolysis of the various alkoxyamines presented in Figure 1 (Table 4). The kinetic experiments were conducted in *tert*-butylbenzene at 407 K. Oxygen was used to scavenge the styryl radical and the concentration of the released nitroxide was measured by EPR spectroscopy, as previously described.[5e,5h,5i,14] The experimental cleavage rate constants k_d were calculated using eq 1. The activation energies E_a were estimated from the rate constants using $A = 2.6 \times 10^{14}$ s^{-1}.[5i]

$$\ln\left(\frac{[\text{nitroxide}]_\infty - [\text{nitroxide}]_t}{[\text{nitroxide}]_\infty}\right) = -k_d t \qquad (1)$$

The smallest rate constant was measured for the six-membered ketoalkoxyamine **1** (entry 1). As expected, ring-enlargement (→ **2**) reduces the activation energy for the C−O bond homolysis: A 4-fold increase of the rate constant was obtained (entry 2). The seven-membered ketoalkoxyamine **2** and both regioisomeric eight-membered alkoxyamines **3** and **4** showed very similar rate constants (entries 2−4). Thus, going from the seven- to the eight-membered ring does not alter the rate constant. These kinetics are in agreement with the polymerization results presented above, where slow polymerization was obtained using six-membered alkoxyamine initiator/regulator **1** (28% conversion, 6 h) and efficient polymerizations were observed using alkoxyamines **2** and **3** (84%, 6 h; 54%, 3 h).

In the "alcohol series" the enlargement from the six- to the seven-membered ring influences the C−O bond homolysis to an even greater extent. Alkoxyamine **6** reacts about 14-times faster than alkoxyamine **5**[5l] (entries 5 and 6). Interestingly, for the eight-membered alkoxyamines **7** and **8** slightly smaller rate constants were measured as compared to the lower homologue **6** (entries 7 and 8**).** In general, homolysis of the reduced alkoxyamines occurs faster than homolysis of the corresponding ketones. This is in contrary to the polymerization results where the keto series always provided better results. Probably, ketoalkoxyamines are more stable than the corresponding alcohols and are therefore better initiators/regulators (see below).

In Table 4, the EPR data of the new nitroxides depicted in Figure 3 are summarized. The seven-membered ketonitroxide **10** and the corresponding hydroxy derivative **14** have a very similar nitrogen hyperfine coupling constant a_N (entries 2 and 6). Similar a_N values were also measured for the unsymmetrical eight-membered cyclic ketonitroxide **12** and the corresponding reduced congener **16** (entries 4 and 8). The symmetrical ketonitroxide **11** has a smaller a_N value than the corresponding alcohol **15** (entries 3 and 7). Stabilization of the seven- and eight-membered ketonitroxides by transannular interactions as depicted for **10** → **10′** and **11** → **11′** can be excluded, since these

Table 4. Rate Constants for the C−O Bond Homolysis and Decomposition Rates of Alkoxyamines 1−4 and 6−8 and EPR Parameters of the Nitroxides 9−12 and 14−16

entry	alkoxyamine	k_d (s^{-1})[a]	E_a (kJ/mol)[b]	k_{dec} (s^{-1})[c]	nitroxide	a_N (G)[d]	*g*
1	**1**	5.7×10^{-4}	137.6	5.9×10^{-6}	**9**	15.09	2.006
2	**2**	2.0×10^{-3}	133.3	5.2×10^{-5}	**10**	15.52	2.006
3	**3**	1.7×10^{-3}	133.8	1.6×10^{-5}	**11**	14.94	2.006
4	**4**	1.1×10^{-3}	135.3	3.1×10^{-5}	**12**	15.87	2.006
5	**5**	3.3×10^{-3}[e]	133.6[f]	1.3×10^{-5}[g]	**13**		
6	**6**	2.7×10^{-2}	124.6	1.3×10^{-4}	**14**	15.23	2.006
7	**7**	1.3×10^{-2}	127.0	5.7×10^{-5}	**15**	15.51	2.006
8	**8**	7.4×10^{-3}	128.9	4.8×10^{-5}	**16**	15.73	2.006

[a] Measured at 407 K. [b] E_A was calculated using $A = 2.6 \times 10^{14}$ s^{-1}, see ref 5i. Statistical errors between 2 and 3 kJ/mol. [c] Measured at 398 K. [d] EPR data were recorded in *t*-BuPh saturated with O_2 and are given with an error of ± 0.14 G. [e] Determined at 413 K (ref 5l). [f] E_A was calculated using $A = 2.6 \times 10^{14}$ s^{-1} and Fukuda's k_d value which was determined at 413 K. [g] Measured by Fukuda at 413 K in deuterated toluene (ref 5l).

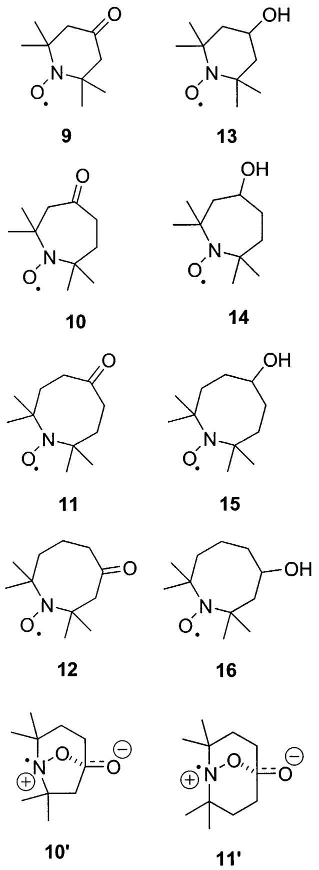


Figure 3. Various nitroxides studied.

interactions would lead to a higher spin density at the nitrogen atom (see **10′** and **11′**) and therefore to an increase of a_N.[15]

Thermal Stability of the Alkoxyamines. An important side reaction in NMP is the decomposition of the alkoxyamine leading to a terminally unsaturated polymer and the corresponding hydroxylamine. This process can occur via a β-hydrogen atom transfer from the transient polymer radical to the nitroxide or via a nonradical direct ionic elimination.[5l,16] We decided to study the thermal decomposition of the various alkoxyamines to provide styrene and the corresponding hydroxylamine. To this end, the alkoxyamine was dissolved in a NMR tube in perdeutero-*p*-xylene (0.03−0.06 M). The degassed sample was heated to 125 °C within the cavity of a 500 MHz ^{1}H NMR spectrometer, and the decomposition was followed by monitoring the decrease of the alkoxyamine signals as well as the increase of the styrene resonances. The signal of the benzylic H atom at around 4.7 was used to estimate the alkoxyamine concentration. Similar experiments have previously been described.[5l,16] Spectra were recorded every 5 min. In Figure 4, a series of ^{1}H NMR spectra (in the range of 4.5−6.7 ppm) recorded during the decomposition study of alkoxyamine **2** are presented as a representative example. The decomposition rate constants (k_{dec}) for the various alkoxyamines were determined using eq 2, according to Fukuda's work[5l] ([S] = styrene concentration; [A] = alkoxyamine concentration).

$$\ln([S]/[A] + 1) = k_{dec}t \qquad (2)$$

In Figure 5, a plot of ln([S]/[A] + 1) vs time is depicted for the decomposition of the alkoxyamines **2** and **6**. The decomposition rate constants obtained from the slopes are summarized in Table 4.

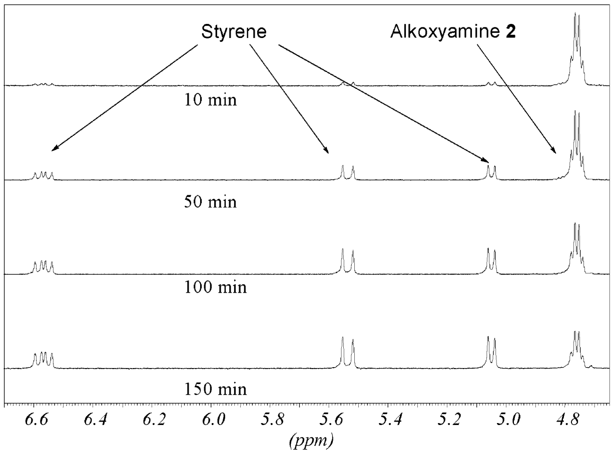


Figure 4. ^{1}H NMR spectra (in the range of 4.5−6.7 ppm) recorded during the decomposition study of alkoxyamine **2**.

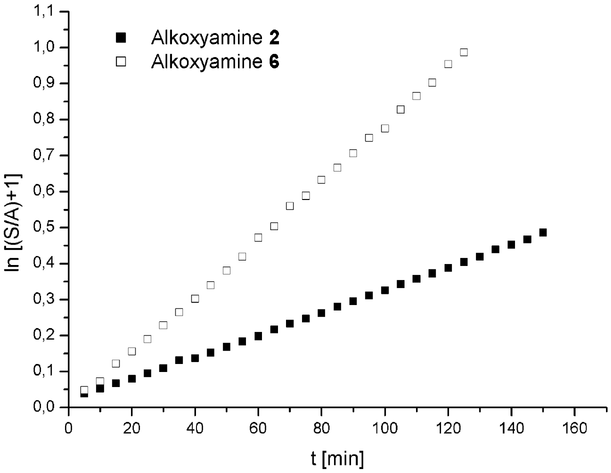


Figure 5. Plot of ln([S]/[A] + 1) vs time for the decomposition of the alkoxyamines **2** and **6**.

As shown in Figure 5, hydroxyalkoxyamine **6** decomposes faster than the corresponding keto derivative **2** (**6**, $k_{dec} = 1.3 \times 10^{-4}$ s^{-1}; **2**, $k_{dec} = 5.2 \times 10^{-5}$ s^{-1}).[17] The same trend was observed also for the six- and eight-membered alkoxyamines, where the hydroxyalkoxyamine always provided a larger k_{dec} than the corresponding ketoalkoxyamine (compare entries 1 and 5; 4 and 8; and 3 and 7 in Table 4). This is in agreement with the experimental polymerization results, where the keto series always provided better results. Thus, although homolysis of the hydroxyalkoxyamines occurs faster than homolysis of the corresponding ketones, polymerization is more efficient for the ketones due to increased thermal stability of the ketoalkoxyamines.

Conclusions

In this work we presented a straightforward synthesis for the preparation of seven- and eight-membered cyclic alkoxyamines. The new alkoxyamines, six-, seven- and eight-membered cyclic systems, were tested as regulators/initiators for the polymerization of styrene and *n*-butyl acrylate. We showed that ring-enlargement positively influences the quality of the polymerization process (polymerization time, livingness, PDI). The seven-membered cyclic alkoxyamines are far superior than the corresponding six-membered alkoxyamines.

The seven- and the corresponding eight-membered rings provided similar results. Efficient controlled and living styrene polymerization (molecular weight of up to 40 000) was achieved using ketoalkoxyamines **2** and **3**. In addition, the kinetics of the C−O bond homolysis of the alkoxyamines were presented. We found that the seven- and eight-membered cyclic alkoxyamines have similar rate constants, whereas the six-membered systems are homolysing slower. This is in agreement with the polymerization results. Furthermore, we found that a keto function within the ring in these cyclic alkoxyamines is important ("keto effect"). Although C−O bond homolysis of the hydroxyalkoxyamines occurs faster than homolysis of the corresponding ketones, the ketoalkoxyamines are better initiator/regulators. The reason for the improved efficiency of the keto−alkoxyamines as compared to the corresponding hydroxy derivatives lies in the increased thermal stability of the ketoalkoxyamines.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (STU 280/1-1) and the Swiss Federal Office for Education and Science (COST D12 action, D12/0005/98) for funding. Dr. Olaf Burghaus is acknowledged for assistance during the EPR experiments and Meike Cordes and Christoph Knoop for conducting some experiments. Furthermore, we thank two reviewers for helpful suggestions.

References and Notes

(1) (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US Patent 4,581,429; P. Eur. Pat. Appl. 135280 (*Chem. Abstr.* **1985**, *102*, 221335q). (b) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (c) Review: Hawker, C. J.; Bosman, A. W.; Hart, E. *Chem. Rev.* **2001**, *101*, 3661.

(2) (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.

(3) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. In *Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; p 278.

(4) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581.

(5) (a) Goto, A.; Terauchi, T.; Fukuda, T.; Miyamoto, T. *Macromol. Rapid Commun.* **1997**, *18*, 673. (b) Goto, A.; Fukuda, T. *Macromol. Rapid Commun.* **1997**, *18*, 683. (c) Skene, W. G.; Belt, S. T.; Conolly, T. J.; Hahn, P.; Scaiano, J. C. *Macromolecules* **1998**, *31*, 9103. (d) Ohno, K.; Tsujii, Y.; Miyamoto, T.; Fukuda, T.; Goto, M.; Kobayashi, K.; Akaike, T. *Macromolecules* **1998**, *31*, 1064. (e) Bon, S. A. F.; Chambard, G.; German, A. L. *Macromolecules* **1999**, *32*, 8269. (f) Goto, A.; Fukuda, T. *Macromol. Chem. Phys.* **2000**, *201*, 2138. (g) Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5929. (h) Marque, S.; Fischer, H.; LeMercier, C.; Tordo, P. *Macromolecules* **2000**, *33*, 4403. (i) Marque, S.; Fischer, H.; Baier, E.; Studer, A. *J. Org. Chem.* **2001**, *66*, 1146. (j) Drockenmuller, E.; Catala, J.-M. *Macromolecules* **2002**, *35*, 2461. (k) Bertin, D.; Chauvin, F.; Marque, S.; Tordo, P. *Macromolecules* **2002**, *35*, 3790. (l) Goto, A.; Kwak, Y.; Yoshikawa, C.; Tsujii, Y.; Sugiura, Y.; Fukuda, T. *Macromolecules* **2002**, *35*, 3520. (m) LeMercier, C.; Acerbis, S.; Bertin, D.; Chauvin, F.; Gigmes, D.; Guerret, O.; Lansalot, M.; Marque, S.; Le Moigne, F.; Fischer, H.; Tordo, P. *Macromol. Symp.* **2002**, *182*, 225.

(6) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722.

(7) Hintermann, T.; Kramer, A.; Nesvadba, P.; Fink, J. *Polym. Prepr.* **2002**, *43*, 86.

(8) Oxo−TEMPO has previously been used as regulator for the controlled polymerization of styrene: Han, C. H.; Drache, M.; Baethge, H.; Schmidt-Naake, G. *Macromol. Chem. Phys.* **1999**, *200*, 1779.

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

(10) Mori, Y.; Yaegashi, K.; Furukawa, H. *Tetrahedron* **1997**, *53*, 12917.

(11) Hawker, C. J.; Barclay, G. G.; Dao, J. *J. Am. Chem. Soc.* **1996**, *118*, 11467.

(12) (a) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904. (b) Benoit, D.; Hawker, C. J.; Huang, E. E.; Lin, Z.; Russell, T. P. *Macromolecules* **2000**, *33*, 1505. (c) Lacroix-Desmazes, P.; Lutz, J.-F.; Chauvin, F.; Severac, R.; Boutevin, B. *Macromolecules* **2001**, *34*, 8866. (d) Souaille, M.; Fischer, H. *Macromolecules* **2002**, *35*, 248.

(13) Sobek, J.; Martschke, R.; Fischer, H. *J. Am. Chem. Soc.* **2001**, *123*, 2849.

(14) (a) Kovtun, G. A.; Aleksandrov, A. L.; Golubev, V. A. *Bull. Acad. Chim. U.S.S.R., Div. Chem.* **1974**, *10*, 2115. (b) Howard, J. A.; Tait, J. C. *J. Org. Chem.* **1978**, *43*, 4279. (c) Grattan, D. W.; Carlsson, D. J.; Howard, J. A.; Wiles, D. M. *Can. J. Chem.* **1979**, *57*, 2834.

(15) For an increase of a_N due to H-bonding, see: (a) Haire, D. L.; Kotake, Y.; Janzen, E. G. *Can. J. Chem.* **1988**, *66*, 1901. (b) Kotake, Y.; Kuwata, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3686. (c) Janzen, E. G.; I-Ping Liu, J. *J. Magn. Reson.* **1973**, *9*, 510. (d) Janzen, E. G.; Lopp, I. G. *J. Magn. Reson.* **1973**, *7*, 1107.

(16) Ananchenko, G. S.; Fischer, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3604.

(17) We also studied the thermal stability of the free nitroxides **10** and **14** in *t*-BuPh (0.06 mM) at 407 K using EPR spectroscopy. Experiments were stopped after 3 h. No decomposition was observed (within the error limits of the integration of the EPR signals) during that time. The *t*-BuPh solution of nitroxide **10** (0.06 mM) was further heated at 393 K for 9 days. EPR analysis revealed that still 5% of the nitroxide is present in the solution after 9 days, proving the high thermal stability of **10**.

MA025806T