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Nitroxide-Mediated Radical Polymerization/Increase of Steric Demand in Nitroxides. How Much Is Too Much?

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ABSTRACT: The influence of increasing steric demand in the nitroxide moiety of cyclic alkoxyamines derived from side chain modified TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) derivatives on nitroxide-mediated polymerization (NMP) of *n*-butyl acrylate and styrene is described. Polymerizations at low temperatures (as low as 70 °C) with good control over the molecular weight distribution (polydispersity index, PDI < 1.2) can be achieved using sterically highly demanding nitroxides. Polymerization efficiency increases with the size of the nitroxide substituents. It is shown that in these sterically highly hindered alkoxyamines it is not the rate of homolysis (k_d) but the rate of recombination (k_c) of the persistent nitroxide with the transient macroradical that is mainly responsible for the enhanced polymerization efficiency (lowering of the reaction time). However, for too bulky nitroxides, the trapping reaction of the nitroxide with the macroradical becomes too slow and uncontrolled NMP is obtained.

Introduction

Nowadays, free radical polymerization is one of the most important methods to produce mass polymers like polystyrene, polyacrylates, and poly(vinyl chloride). However, one of the major drawbacks of these processes is the low control over the reaction which leads to a broad molecular weight distribution.

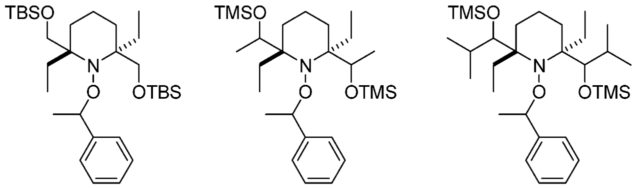
During the past decade, several methods for controlled living free radical polymerization such as ATRP (atom transfer radical polymerization),[1] RAFT (reversible addition−fragmentation chain transfer polymerization),[2] and NMP (nitroxide mediated polymerization)[3] have been developed. These new methods allow the synthesis of polymers with defined molecular weights and polydispersities far below the theoretical limit (PDI < 1.5).

ATRP and NMP are controlled by the persistent radical effect (PRE).[4] In NMP alkoxyamines are used as initiators and dormant alkoxyamine species are reversibly formed from the corresponding nitroxides and the growing macroradical. The structural properties of the nitroxide moiety—that are H-bonding[5−10] and polar[11] and steric effects[12]—are of major importance for the polymerization process. These factors alter the equilibrium constant between nitroxide-capped polymer and free nitroxide and polymer radical.[4,5,8,11−13]

In the present paper we will introduce two new sterically highly hindered alkoxyamines **2** and **3** (Figure 1). These alkoxyamines are used as initiators/regulators for the controlled living radical polymerization of styrene and *n*-butyl acrylate. The results will be compared with those previously obtained for the smaller parent compound **1**.[8]

Experimental Section

Materials. Oxalyl chloride (Fluka, ≥96%), dimethyl sulfoxide (Aldrich, anhydrous, 99.9%), lithium (Aldrich, granule, 99.9%), 2-chloropropane (Aldrich, 99%), methyllithium (Fluka, ∼5% in diethyl ether), chlorotrimethylsilane (Acros, 98%), *N*,*N*-dimethylformamide (Acros, 99%), and imidazole (Aldrich, 99%) were used as received. Styrene (BASF) and *n*-butyl acrylate (Fluka, 99+%) were both distilled from CaH_2 under reduced pressure to remove the stabilizer and were stored at 4 °C under an argon atmosphere. Dichloromethane (DCM) and pentane were distilled from phosphorus pentoxide, while tetrahydrofuran (THF) was distilled from potassium before use.



1 **2** **3**

Figure 1. New sterically highly hindered alkoxyamines.

General Data. ^1H NMR (500 MHz, 400 MHz, 300 MHz) and ^{13}C NMR (125 MHz, 100 MHz, 75 MHz) spectra were recorded on a AMX 500 (Bruker), ARX 300 (Bruker) or ARX 200 (Bruker). Chemical shifts δ were measured in ppm relative to $SiMe_4$ as internal standard. TLC: silica gel *60* F_{254} plates (Merck); detection with UV or dipping into a soln. 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 0.1−0.4 bar. Melting points: SMP 10 (Bibby-Stuart Scientific); uncorrected. IR spectra were recorded on a Digilab FTS 4000 equipped with a MKII Golden Gate Single Reflection ATR System, a IR 750 (Nicolet Magna), or a *IFS-200* (Bruker). ESI-MS and HRMS were performed using a Bruker MicroTof. Elemental analysis was performed using a Vario EL III (Elementar). 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 L-6200A Intelligent Pump (Merck Hitachi), a set of two PLgel 5 μm MIXED-C columns (300 × 7.5 mm, Polymer Laboratories, linear range of molecular weight: 200−2000 000 g/mol), and a Knauer Differential refractometer (λ = 950 ± 30 nm) detector. Data were analyzed with PSS WinGPC compact V 7.20 software based upon calibration curves built upon polystyrene standards (Polymer Laboratories, Polystyrene Medium MW Calibration Kit S-M-10) or poly(methyl methacrylate) standards (Polymer Laboratories Poly(methyl methacrylate) Medium MW Calibration Kit M-M-10) with peak molecular weights ranging from 500 to 3000000 g/mol or from 1000 to 1500000 g/mol, respectively.

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***trans*-2,6-Diethyl-2,6-bis(formyl)-1-(1-phenylethoxy)piperidine (5).** At −78 °C dimethyl sulfoxide (0.58 mL, 8.2 mmol, 4.4 equiv) was added dropwise to a solution of oxalyl chloride (0.36 mL, 4.1 mmol, 2.2 equiv) in DCM (37 mL). After 10 min, a solution of diol **4** (602 mg, 1.87 mmol, 1.0 equiv) in DCM (12 mL) was added dropwise and the reaction mixture was allowed to warm to −60 °C during 1 h. After the reaction was cooled to −78 °C, NEt$_3$ (2.51 mL, 18.0 mmol, 9.6 equiv) was added and the solution was allowed to warm to −40 °C. After 2 h of stirring at this temperature the mixture was allowed to warm to room temperature, and stirring was continued for another hour. The reaction was stopped upon the addition of brine (10 mL). The phases were separated and the organic layer was extracted with DCM (3 × 10 mL). The combined organic layers were dried over MgSO$_4$. Purification of the crude product by FC (MTBE/pentane, 1:9) yielded a mixture of diastereoisomers due to a stereogenic center at the nitrogen atom (dr = 2.5:1 (^{1}H NMR of mixture)) of the desired aldehyde **5** (540 mg, 1.70 mmol, 91%) as a yellowish oil. For analytical purposes, the diastereoisomers (sample) were separated by renewed chromatography.

Major Isomer. Mp = 71−72 °C. IR (neat): 2974 s, 2943 s, 2880 m (C−H), 1734 s (C═O), 1716 s (C═O), 1603 w (C═C), 1494 w (C═C), 1452 s (C═C), 1379 m, 1060 m, 763 m, 701 s cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 9.61 (s, 2 H, CHO); 7.40−7.21 (m, 5 H, Ar−H); 4.70 (q, 1 H, ^3J = 6.6 Hz, C*H*CH$_3$); 2.43−1.07 (m, 10 H, 5 × CH$_2$); 1.39 (d, 3 H, ^3J = 6.6 Hz, CHC*H*$_3$); 1.06−0.77 (m, 3 H, CH$_2$C*H*$_3$); 0.71−0.37 (m, 3 H, CH$_2$C*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 204.7 (C═O), 201.5 (C═O), 143.1 (C), 128.3 (2 × CH), 127.8 (CH), 126.8 (2 × CH), 84.3 (CH), 73.6 (br, C), 72.1 (br, C), 26.4 (CH$_3$), 22.6 (CH$_3$), 22.1 (CH$_2$), 15.5 (CH$_3$), 9.3 (CH$_2$), 7.0 (CH$_2$). MS (ESI$^+$): 340 ([M + Na]$^+$), 318 ([M + H]$^+$). HRMS (ESI$^+$): calcd for [M + Na]$^+$, 340.1883; found, 340.1909. Anal. Calcd for C$_{19}$H$_{27}$NO$_3$: C, 71.89; H, 8.57; N, 4.41. Found: C, 71.65; H, 8.57; N, 4.17. **Minor Isomer.** IR (neat): 2973 m, 2943 m, 2880 w (C−H), 1732 s (C═O), 1715 s (C═O), 1452 m (C═C), 1379 m, 1339 w, 1316 w, 1241 s, 1058 m, 1029 w, 987 w, 922 m, 787 m, 760 s, 699 s cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 10.16 (br s, 1 H, CHO); 8.70 (br s, 1 H, CHO); 7.38−7.23 (m, 5 H, Ar−H); 4.75 (*q*, 1 H, ^3J = 6.7 Hz, C*H*CH$_3$); 2.34−0.98 (m, 10 H, 5 × CH$_2$); 1.49 (d, 3 H, ^3J = 6.7 Hz, CHC*H*$_3$); 0.97−0.64 (m, 6 H, 2 × CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 204.8 (C═O), 201.2 (C═O), 142.7 (C), 128.4 (CH), 128.2 (CH), 127.1 (CH), 126.7 (CH), 83.4 (CH), 72.8 (C), 65.8 (C), 27.1 (CH$_2$), 22.1 (CH$_3$), 15.2 (CH$_2$). MS (ESI$^+$): 340 ([M + Na]$^+$), 318 ([M + H]$^+$). HRMS (ESI$^+$): calcd for [M + Na]$^+$, 340.1883; found, 340.1903.

Isopropyllithium (11). A lithium granule (11.0 g, 1.59 mol, 2.00 equiv) was suspended in pentane. 2-Chloropropane (72.5 mL, 793 mmol, 1.00 equiv) was added dropwise at 0 °C. The reaction mixture was heated to reflux for 8 h. Isopropyllithium was obtained after filtration as a yellowish solution in pentane. The concentration was determined by titration (c = 1.24 mol/L).

***trans*-2,6-Diethyl-2,6-bis(1-hydroxyethyl)-1-(1-phenylethoxy)piperidine (6).** Methyllithium (1.64 M in Et$_2$O; 2.82 mL, 4.63 mmol, 2.10 equiv) was added slowly to a solution of dialdehyde **5** (700 mg, 2.10 mmol, 1.00 equiv) in THF (42 mL). The reation mixture was allowed to warm to −10 °C during 3 h. The reaction was stopped upon the addition of water (10 mL). The aqueous phase was extracted with Et$_2$O (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL) and dried over MgSO$_4$. Purification by FC(MTBE/pentane, 1:4) yielded the desired diol **6** as a mixture of diastereoisomers as a yellowish oil (662 mg, 2.12 mmol, 86%). The diastereoisomers were not separated.

IR (neat): 3459 m, br (O−H), 2970 s, 2879 m (C−H), 1454 m (C═C), 1401 m, 1371 m, 1280 m, 1204 w, 1115 m, 1054 s (C−O), 914 s, 762 s, 701 s cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): mixture of diastereoisomers: δ = 7.40−7.20 (m, 5 H, Ar−H); 4.92−4.60 (m, 2 H, PhC*H*CH$_3$, C*H*(OH)CH$_3$); 4.38−2.35 (m, 3 H, C*H*(OH)-CH$_3$, 2 × OH); 2.35−0.46 (m, 25 H, CH$_2$CH$_2$CH$_2$, C*H*$_2$CH$_3$, CH$_2$C*H*$_3$, CH(OH)C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): mixture of diastereoisomers: δ = 143.2 (C), 143.1 (C), 128.6 (CH), 128.5 (CH), 128.3 (2 × CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 126.3 (CH), 126.1 (2 × CH), 125.9 (CH), 84.8 (CH), 84.7 (CH), 83.9 (CH), 83.6 (CH), 72.7 (CH), 72.2 (CH), 71.5 (CH), 71.2 (CH), 70.1 (CH), 69.7 (CH), 68.8 (C), 68.6 (C), 67.7 (C), 67.5 (C), 31.9 (CH$_2$), 31.7 (CH$_2$), 30.2 (CH$_2$), 27.9 (CH$_2$), 27.7 (CH$_2$), 27.0 (CH), 26.7 (CH$_2$), 26.4 (CH$_2$), 26.3 (CH$_2$), 25.7 (CH$_2$), 24.1 (CH$_3$), 23.9 (CH$_3$), 23.8 (CH3), 23.1 (CH$_3$), 22.6 (CH$_2$), 22.5 (CH$_2$), 22.0 (CH$_2$), 19.2 (CH$_3$), 18.8 (2 × CH$_3$), 18.4 (CH$_3$), 15.7 (CH$_2$), 15.6 (CH$_2$), 15.3 (CH$_3$), 14.9 (CH$_2$), 14.7 (CH$_3$), 11.4 (CH$_3$), 11.3 (CH$_3$), 11.0 (CH$_3$), 7.8 (CH$_3$), 7.7 (CH$_3$), 7.6 (CH$_3$). MS (ESI$^+$): 372 [M + Na]$^+$, 350 [M + H]$^+$. HRMS (ESI$^+$): calcd for [M + H]$^+$, 350.2690; found, 350.2689.

***trans*-2,6-Diethyl-2,6-bis(1-hydroxy-2-methylpropyl)-1-(1-phenylethoxy)piperidine (7).** Isopropyllithium (1.24 M in pentane; 2.49 mL, 3.09 mmol, 2.10 equiv) was added slowly to a solution of dialdehyde **5** (467 mg, 1.47 mmol, 1.00 equiv) in THF (28 mL). The reation mixture was allowed to warm to −10 °C during 3 h. The reaction was stopped upon addition of water (8 mL). The aqueous phase was extracted with Et$_2$O (3 × 8 mL). The combined organic layers were washed with brine (3 × 8 mL) and dried over MgSO$_4$. Purification by FC(MTBE/pentane, 1:4) yielded the desired diol **7** as a mixture of diastereoisomers as a yellowish oil (482 mg, 1.19 mmol, 81%). The diastereoisomers were not separated.

IR (neat): 3471 w (O−H), 3350 w (O−H), 2956 s, 2876 m (C−H), 1462 m (C═C), 1407 w, 1372 m, 1262 w, 1205 w, 1166 w, 1107 w, 1053 m, 1018s (C−O), 907 s, 799 m, 760 s, 701 s cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): mixture of diastereomers: δ = 7.39−7.23 (m, 5 H, Ar−H); 4.94−4.71 (m, 1 H, PhC*H*CH$_3$); 4.44−2.59 (m, 4 H, 2 × C*H*(OH)CH(CH$_3$)$_2$, 2 × CH(O*H*)CH(CH$_3$)$_2$); 2.56−0.24 (m, 33 H, 2 × CH(OH)C*H*(CH$_3$)$_2$, 2 × CH(OH)CH(C*H*$_3$)$_2$, 5 × CH$_2$, 2 × CH$_2$C*H*$_3$, PhCHC*H*$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 144.0 (C), 143.5 (C), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.9 (CH), 127.5 (CH), 127.0 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 85.0 (CH), 84.8 (CH), 84.7 (CH), 83.4 (CH), 80.1 (CH), 79.5 (CH), 78.8 (CH), 78.6 (C), 77.6 (C), 77.4 (C), 77.2 (C), 76.8 (CH), 76.6 (CH), 70.3 (C), 68.5 (C), 31.3 (CH$_2$), 31.0 (CH$_2$), 30.1 (CH), 29.7 (CH$_3$), 29.6 (CH$_3$), 29.5 (CH$_2$), 28.7 (CH), 28.5 (CH$_2$), 27.5 (CH$_3$), 26.6 (CH), 26.3 (CH$_2$), 26.0 (CH$_2$), 25.0 (CH$_2$), 24.7 (CH$_3$), 24.2 (CH$_2$), 24.0 (CH$_3$), 23.9 (CH$_3$), 23.8 (CH$_3$), 23.4 (CH), 22.1 (CH), 18.8 (CH$_3$), 18.2 (CH$_3$), 17.6 (CH$_3$), 16.8 (CH$_3$), 16.5 (CH$_2$), 16.4 (CH$_3$), 15.2 (CH$_2$), 14.9 (CH$_2$), 11.4 (CH$_3$), 11.2 (CH$_3$), 7.9 (CH$_3$), 7.6 (CH$_3$). MS (ESI$^+$): 428 ([M + Na]$^+$), 406 ([M + H]$^+$); HRMS (ESI$^+$): calcd for [M + H]$^+$, 406.3316; found, 406.3311; calcd for [M + Na]$^+$, 428.3135; found, 428.3133.

***trans*-2,6-Diethyl-2,6-bis(1-trimethylsilanoxyethyl)-1-(1-phenylethoxy)piperidine (2).** Trimethylchlorosilane (1.24 mL, 9.77 mmol, 5.00 equiv) was added to a solution of diol **6** (683 mg, 1.95 mmol, 1.00 equiv) and imidazole (797 mg, 11.7 mmol, 6.00 equiv) in DMF (30 mL). The mixture was stirred at room temperature for 7 h. The reaction was stopped upon addition of water (30 mL) and pentane (30 mL). The aqueous layer was extracted with pentane (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL) and dried over MgSO$_4$. Purification by FC (pentane) yielded the desired bis(silyl ether) **2** as a colorless oil (603 mg, 1.22 mmol, 63%).

IR (neat): 2958 m, 2879 w (C−H), 1453 w (C═C), 1371 w, 1249 m, 1085 s, 1054 m (C−O), 989 m, 913 m, 835 s, 757 m, 700 m cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): mixture of diastereoisomers: δ = 7.37−7.15 (m, 5 H, Ar−H); 4.67−3.27 (m, 3 H, C*H*Ph, 2 × C(OTMS)*H*); 2.34−0.49 (m, 25 H, 5 × CH$_2$, 5 × CH$_3$); +0.42 to −0.14 (m, 15 H, 3 × Si(CH$_3$)); −0.14 to −0.37 (s, 3 H, Si-(CH$_3$)). ^{13}C NMR (100 MHz, CDCl$_3$): mixture of diastereoisomers: δ = 146.6 (C), 146.5 (C), 128.3 (2 × CH), 127.9 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.6 (CH), 126.3 (CH), 125.9 (CH), 125.8 (CH), 83.4 (CH), 83.1 (2 × CH), 75.1 (CH), 74.9 (CH), 74.4 (CH), 69.9 (CH), 68.4 (C), 68.2 (C), 66.8 (C), 66.4 (C), 31.6 (CH$_2$), 30.9 (CH$_2$), 30.8 (CH$_2$), 29.3 (CH$_2$), 29.7 (CH$_2$), 29.0 (CH$_2$), 28.5 (CH$_2$), 28.0 (CH$_2$), 27.0 (CH$_2$), 25.1 (CH$_3$), 25.0 (CH$_3$), 24.3 (CH$_3$), 24.1 (CH$_3$), 24.0 (2 × CH$_3$), 23.2 (2 × CH$_2$), 23.2 (CH$_2$), 22.2 (CH$_3$), 22.0 (2 × CH$_3$), 21.9 (2 × CH$_3$), 19.4 (CH$_3$), 18.9 (CH$_3$), 16.1 (CH$_2$), 15.9 (CH$_2$), 15.6

(CH$_2$), 11.7 (CH$_3$), 11.5 (CH$_3$), 11.4 (CH$_3$), 8.8 (CH$_3$), 8.2 (CH$_3$), 8.0 (CH$_3$), 0.6 (2 × CH$_3$), 0.1 (CH$_3$). MS (ESI$^+$): 516 ([M + Na]$^+$), 494 ([M + H]$^+$). HRMS: calcd for [M + H]$^+$, 494.3480; found, 494.3476.

***trans*-2,6-Diethyl-2,6-bis(1-trimethylsilanoxy[2-methylpropyl])-1-(1-phenylethoxy)piperidine (3).** Trimethylchlorosilane (0.640 mL, 5.04 mmol, 5.00 equiv) was added to a solution of diol **7** (498 mg, 1.01 mmol, 1.00 equiv) and imidazole (412 mg, 6.05 mmol, 6.00 equiv) in DMF (20 mL). The mixture was stirred at room temperature for 8 h. The reaction was stopped upon addition of water (20 mL) and pentane (20 mL). The aqueous layer was extracted with pentane (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL) and dried over MgSO$_4$. Purification by FC(pentane) yielded the desired bis(silyl ether) **3** as a colorless oil (441 mg, 0.802 mmol, 79%).

IR (neat): 2956 m, 2878 w (C−H), 1454 w (C=C), 1370 w, 1250 m, 1108 m, 1052 s (C−O), 878 s, 833 s, 753 m, 700 m cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): mixture of isomers: δ = 7.37−7.17 (m, 5 H, Ar−H); 4.92−2.28 (m, 3 H, C*H*Ph, 2 × C*H*(OTMS); 2.26−0.31 (m, 33 H, 2 × C*H*(CH$_3$)$_2$, 5 × CH$_2$, 7 × CH$_3$) +0.31 to −0.39 (m, 18 H, 2 × Si(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 146.1, 145.3 (2 ×), 145.1 (2 ×), 128.2 (2 ×), 127.9, 127.8, 127.3, 127.1, 127.0, 126.8 (2 ×), 126.6, 126.3 (2 ×), 126.1, 125.7, 125.5, 84.1, 84.0, 83.7 (2 ×), 83.4, 83.0, 82.9, 82.3, 82.0, 81.4, 79.4, 70.2, 70.1, 69.4, 69.3, 31.8, 31.6, 30.6, 29.9, 29.7, 29.3, 29.1, 28.9, 28.0, 27.9, 27.6, 26.2, 25.8, 25.6, 25.1, 24.6), 24.3, 24.2, 24.1, 23.9, 23.8, 23.5, 19.2, 19.1, 17.4, 17.3, 17.2, 16.8, 16.5, 15.4, 14.9, 14.0, 11.9, 8.5, 8.1, 1.3, 1.1, 1.0, 0.7. MS (ESI$^+$): 572 ([M + Na]$^+$), 550 ([M + H]$^+$). HRMS (ESI): calcd for ([M + H]$^+$), 550.4106; found, 550.4102.

***trans*-2,6-Diethyl-2,6-bis(1-trimethylsilanoxyethyl)-1-(1-phenylethoxy)piperidine-*N*-oxyl (8).** A solution of **2** (65 mg, 0.13 mmol, 1.0 equiv) in toluene (4 mL) was heated to 100 °C and oxygen gas was bubbled through the mixture for 2 h. After cooling to room temperature the solvent was removed in vacuo and the orange residue was purified by FC (pentane/MTBE, 1:50) to yield the desired nitroxide **8** (41 mg, 0.11 mmol, 80%) as an orange oil.

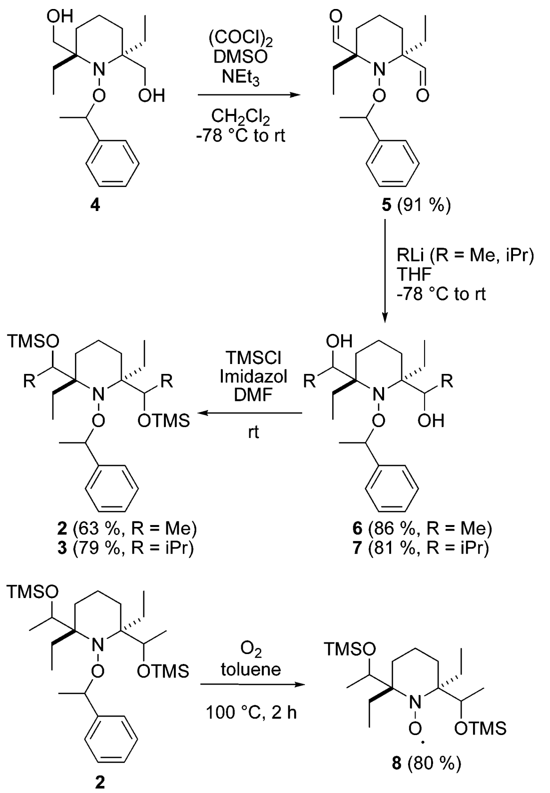
IR (neat): 2958 m, 2881 w (C−H), 1459 w, 1378 w, 1251 m, 1117 m, 1099 m (C−O), 991 m, 859 s, 839 s cm^{-1}. MS (ESI$^+$): 799 ([2M + Na]$^+$), 411 ([M + Na]$^+$). HRMS (ESI): calcd for [M + Na]$^+$, 411.2595; found, 411.2570.

Typical Procedure for the Nitroxide-Mediated Polymerization of Styrene. Alkoxyamine **2** (43.1 mg, 87.3 μmol, 1.00 equiv) was dissolved in styrene (1.00 mL, 8.73 mmol, 100 equiv). The solution was degassed in three freeze−thaw cycles. The reaction mixture was sealed under argon and heated to 90 °C during 6 h. The polymerization was stopped upon cooling to room temperature and the polymer was dissolved in dichloromethane (DCM). The solution was poured into a Petri dish and residual monomer was removed in a vacuum-drying cabinet at elevated temperature (60 °C) for 12 h. Conversion was determined gravimetrically (502 mg, 50%), molecular weight and polydispersity index were determined by size exclusion chromatography (SEC) (M_n = 8600, PDI = 1.15).

Typical Procedure for the Nitroxide-Mediated Polymerization of *n*-Butyl Acrylate. Alkoxyamine **2** (30.9 mg, 62.6 μmol, 1.00 equiv) was dissolved in *n*-butyl acrylate (900 μL, 6.26 mmol, 100 equiv). The solution was degassed in three freeze−thaw cycles. The reaction mixture was sealed under argon and heated to 90 °C during 4.3 h. The polymerization was stopped upon cooling to room temperature and the polymer was dissolved in dichloromethane (DCM). The solution was poured into a Petri dish and residual monomer was removed in a vacuum-drying cabinet at elevated temperature (60 °C) for 12 h. Conversion was determined gravimetrically (607 mg, 72%), molecular weight and polydispersity index were determined by size exclusion chromatography (SEC) (M_n = 11 800, PDI = 1.18).

Typical Procedure for the Polymerization of *n*-Butyl Acrylate for the Determination of the Equilibrium Constant *K* Using the Method of Lacroix-Demazes. Alkoxyamine **2** (20.5 mg, 42.2 μmol, 1.00 equiv) and the free nitroxide **8** (8.2 mg, 21 μmol, 0.5 equiv) were dissolved in *n*-butyl acrylate (0.60 mL, 4.2 mmol, 100 equiv). The solution was degassed in three freeze−thaw cycles. The reaction mixture was sealed under argon and heated to 105 °C for 2 h. The polymerization was stopped upon cooling to room temperature. The polymer was dissolved in DCM and hydroquinone (3.3 mg) was added. The mixture was poured into a Petri dish and residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. Conversion was determined gravimetrically (237 mg, 39%).

Scheme 1. Synthesis of the Sterically Highly Hindered Alkoxyamines 2 and 3 and Nitroxide 8[a]



[a] DMF = dimethylformamide, DMSO = dimethyl sulfoxide, THF = tetrahydrofuran, TMSCl = trimethylchlorosilane.

Results and Discussion.

Synthesis of Alkoxyamines 2 and 3. Alkoxyamines **2** and **3** were synthesized starting from known[8] diol **4**. Swern oxidation of **4** yielded dialdehyde **5** in a very good yield (91%).

Alkylation of **5** was performed in THF at low temperatures using methyllithium or isopropyllithium solutions, respectively. The methylated diol **6** and the isopropylated diol **7** were isolated in good yields (86% and 81%, respectively) as mixtures of diastereoisomers. Because of the complexity of the NMR spectra, the diastereomeric ratio could not unambiguously be determined. Silylation of **6** and **7** was readily achieved using trimethylchlorosilane (TMSCl) in DMF with imidazol as a base. The silyl ethers **2** and **3** were obtained in good yields (**2**: 63%; **3**: 79%). Free nitroxide **8** was liberated upon heating alkoxyamine **2** in toluene in the presence of oxygen and was isolated in 80% yield.

We have previously shown that diastereomeric cyclic nitroxides as regulators in NMP provide similar results.[8] Therefore, the tedious separation of the diastereoisomers was not attempted.

Polymerization Studies. Polymerizations using alkoxyamines **1**, **2**, and **3** were performed in sealed tubes in neat styrene or *n*-butyl acrylate. Temperature and alkoxyamine concentration were systematically varied.

Styrene polymerization using **2** at 105 °C occurred highly efficiently (Table 1, entry 8). Thus, in just 1.5 h a 54% conversion was obtained. For comparison NMP of styrene with

Table 1. Polymerizations of Styrene and *n*-Butyl Acrylate Using Alkoxyamines 1, 2 and 3

entry	alkoxyamine (mol %)	monomer	temp (°C)	time (h)	$M_{n,theor}$[c] (g/mol)	M_n[d] (g/mol)	PDI[e]	convn (%)	ref
1	**1** (1)	styrene	105	15	8900	9500	1.12	85	8
2	**1** (1)[a]	styrene	90	29	5800	4800	1.16	50	t.w.
3	**1** (1)[a]	styrene	70	72	3570	3200	1.29	29	t.w.
4	**1** (1)	*n*-butyl acrylate	105	24	9200	13300	1.20	72	8
5	**1** (1)[a]	*n*-butyl acrylate	90	54	7000	7700	1.51	50	t.w.
6	**1** (1)[a]	*n*-butyl acrylate	70	96	4900	6300	2.12	34	t.w.
7	**1** (0.4)[a]	*n*-butyl acrylate	90	64	18300	25000	1.29	57	8
8	**2** (1)[a]	styrene	105	1.5	6100	8100	1.20	54	t.w.
9	**2** (1)[a]	styrene	90	6	5700	8600	1.15	50	t.w.
10	**2** (1)[a]	styrene	70	26	6300	6800	1.16	56	t.w.
11	**2** (0.5)[a]	styrene	90	6	11300	15600	1.20	52	t.w.
12	**2** (1)	*n*-butyl acrylate	105	0.33	10700	12900	1.46	80	t.w.
13	**2** (1)[a]	*n*-butyl acrylate	90	4.3	9700	11800	1.18	72	t.w.
14	**2** (1)[a]	*n*-butyl acrylate	70	87	11800	11300	1.16	88	t.w.
15	**2** (0.5)[a]	*n*-butyl acrylate	105	1.15	23300	26700	1.23	89	t.w.
16	**2** (0.5)[a]	*n*-butyl acrylate	90	3	19500	22000	1.22	74	t.w.
17	**3** (1)[a]	styrene	105	0.55	7700	10700	1.93	69	t.w.
18	**3** (1)[a]	styrene	90	1.55	7500	12500	1.76	67	t.w.
19	**3** (1)[a]	styrene	70	6	6700	9900	1.39	59	t.w.
20	**3** (1)[b]	styrene	70	6	6800	9500	1.39	60	t.w.
21	**3** (1)[a]	*n*-butyl acrylate	125	4	12300	11900	1.89	92	t.w.
22	**3** (1)[a]	*n*-butyl acrylate	90	2	10500	10800	1.87	78	t.w.
23	**3** (1)[a]	*n*-butyl acrylate	70	3	11100	12800	1.38	82	t.w.
24	**3** (1)[a]	*n*-butyl acrylate	50	4	6100	9000	1.86	43	t.w.

[a] Remaining monomer was removed under high vacuum at elevated temperature. [b] The polymer was precipitated from methanol and dried under high vacuum. [c] $M_{n,theor}$ = theoretical number-average molecular weight calculated from the conversion and the alkoxyamine concentration. [d] M_n = number-average molecular weight. [e] PDI = polydispersity index. t.w. denotes this work.

the smaller parent alkoxyamine **1**, which is known to be a highly efficient initiator/regulator, was far slower under the same conditions (entry 1). Styrene polymerization with alkoxyamine **2** worked well at 90 °C (entries 9 and 11). To document the efficiency of alkoxyamine **2** for NMP of styrene we conducted the **1**-mediated styrene polymerization at 90 °C (entry 2). As expected, polymerization was far slower as compared to the **2**-mediated styrene polymerization. Whereas using **2** a 50% conversion was reached after 6 h, 29 h was necessary in order to get the same conversion with the smaller alkoxyamine **1** (compare entries 2 and 9). Importantly, PDI did not increase upon switching from **1** to **2**. Even at 70 °C a rather efficient polymerization was obtained using bulky alkoxyamine **2** (entry 10). Hence, in 26 h at 70 °C, a 56% conversion was achieved. To the best of our knowledge, this is the first report on an efficient nitroxide-mediated polymerization of styrene at that low temperature! At these low temperatures autoinitiation is slow and narrow polydispersities are obtained as shown in the experiments. With the smaller alkoxyamine **1** at 70 °C under the same conditions only 29% conversion was reached for the polymerization of styrene in 72 h (entry 3).

Even more pronounced is the effect in the polymerization of *n*-butyl acrylate upon going from the parent alkoxyamine **1** to the sterically more demanding congener **2**. As previously shown, polymerization of *n*-butyl acrylate using **1** at 105 °C for 24 h afforded poly-*n*-butyl acrylate with a PDI of 1.20 in 72% conversion (entry 4).[8] Switching to the bulky alkoxyamine **2** delivered in just 20 min poly-*n*-butyl acrylate in 80% conversion with slightly higher PDI (entry 12). Lowering the reaction temperature revealed even larger differences between the **1** and **2**-mediated acrylate polymerization. Hence, using 1 mol % of initiator **2** at 90 °C a 72% conversion was obtained in 4.3 h (entry 13). To our delight, at this temperature a narrow PDI was obtained (PDI = 1.18). Importantly, no additional nitroxide is necessary to get a low polydispersity![12,14] With the parent alkoxyamine **1** under the same conditions, only 50% conversion was reached in 54 h, documenting the importance of the size of the substituents at the nitroxide moiety (entry 5). In addition, PDI increased to 1.51. Thus, acrylate polymerization with the smaller alkoxyamine at lower temperature has to be conducted in the presence of free nitroxide.[8] We were very pleased to observe that controlled polymerization of *n*-butyl acrylate with **2** can be achieved even at 70 °C (entry 14, 88% in 87 h, PDI = 1.16). Under these conditions, polymerization with the smaller alkoxyamine **1** was not controlled (entry 6, 34% in 70 h, PDI = 2.12).

We could also show that higher molecular weight poly-*n*-butyl acrylate can prepared with **2**. To get reasonable polymerization times, the reactions were performed at higher temperatures (105 °C, entry 15; 90 °C, entry 16). Again, polymerization with **2** was far faster and better controlled than using parent **1** (compare entries 7 and 16).

We continued our studies with the even more bulky alkoxyamine **3**. As expected, polymerization time could be further decreased. Polymerizations at 105 and 90 °C were faster as compared to the analogous experiments using alkoxyamine **2** (compare entries 8 with 17 and 9 with 18). However, polymerizations with **3** were not controlled under these conditions (PDI > 1.5). We therefore decided to lower the reaction temperature. Styrene polymerization at 70 °C showed reasonable conversion (59%) in just 6 h, however, a PDI of 1.39 was obtained showing that control of the process is still not satisfactory (entries 19 and 20). A similar picture was observed for the **3**-mediated polymerization of *n*-butyl acrylate: fast and uncontrolled polymerization (entries 21−23). Even at 50 °C, polymerization could be initiated (entry 24). However, PDI remained broad (PDI = 1.86).

We believe that the nitroxide deriving from alkoxyamine **3** is too bulky. The trapping reaction of the nitroxide with the C-radical becomes too slow. Therefore, alkoxyamine **3** behaves like a low-temperature radical initiator without any regulator capacity (see below).

Kinetics of the C−O Bond Homolysis: EPR Studies. The activation energy of the C−O-bond homolysis E_a was determined by EPR spectroscopy. The kinetic experiments were performed in *tert*-butylbenzene as previously described.[5,8,11,15] The solutions were saturated with oxygen to scavenge the

Table 2. Kinetic Data on the C−O Bond Homolysis

alkoxyamine	monomer	E_A[a,b] [kJ/mol]	k_d[c,d] [s^{-1}]	k_c[e] [$M^{-1} s^{-1}$]	K[f] [M]	ref.
1	styrene	122.2	3.1×10^{-3}	1.6×10^{7}	1.4×10^{-9}	8, 16
2	styrene	122.0	3.3×10^{-3}	4.6×10^{5}	7.2×10^{-9}	t.w.
3	styrene	116.2	2.1×10^{-2}	n.d.	n.d	t.w.

[a] E_A = activation energy of C−O-bond homolysis, determined at 130 °C (for alkoxyamines **1** and **2**) or 105 °C (for alkoxymine **3**) by kinetic EPR experiments using Arrhenius factor $A = 2.4 \times 10^{14}$ s^{-1}. [b] Statistical errors between 2 and 3 kJ/mol. [c] Rate constant of homolysis at 105 °C. [d] Statistical errors maximal 60%. [e] Recombination rate constant determined at 130 °C for **1** and at 105 °C for **2**. [f] Equilibrium constant at 130 °C for **1** and at 105 °C for **2**. n.d. denotes not determined. t.w. denotes this work.

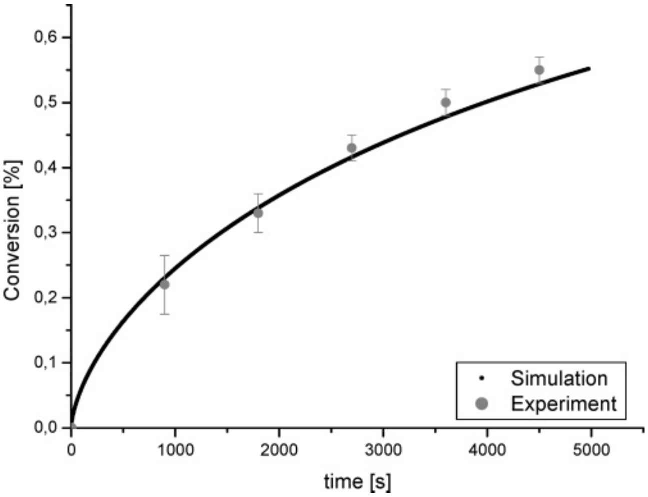


Figure 2. Conversion as a function of time for the experimental (bulk polymerization, styrene/alkoxyamine = 100:1) and simulated values for styrene polymerization using alkoxyamine **2** at 105 °C ($K = 7.2 \times 10^{-9}$ M).

liberated styryl radicals and the concentration of the released nitroxide was measured by EPR spectroscopy upon heating.

The activation energies E_a were then estimated from the rate constants using Arrhenius factor $A = 2.4 \times 10^{14}$ s^{-1}.[5,15] The results are summarized in Table 2.

Surprisingly, although alkoxyamine **2** turned out to be the far more efficient initiator/regulator than **1**, similar activation energies for the C−O-bond homolysis were obtained for **1** and **2** (Table 2). The increasing steric hindrance does obviously not lead to a decreased C−O bond energy. The reason for the enhanced polymerization efficiency of **2** as compared to **1** lies therefore in the recombination reaction of the macroradical with the nitroxide (see below).

However, exchanging methyl by bulkier isopropyl groups leads to a decrease of the activation energy of the C−O bond homolysis. Hence, E_A was reduced by about 6 kJ/mol upon going from the methyl to the isopropyl derivative. In fact we showed that polymerizations using **3** could be initiated even at 50 °C.

Determination of the Equilibrium Constants *K*. For alkoxyamine initiator **2** the equilibrium constant *K* between the dormant alkoxyamine and the macroradical and nitroxide, respectively, was determined for the polymerization of styrene and *n*-butyl acrylate. In the case of the styrene polymerization the conversions of bulk polymerizations at 105 °C were determined after defined polymerization times. The recombination rate constant k_c and the equilibrium constant *K* was then estimated by fitting theoretical calculations to the experimental data as previously described (Figure 2).[16] The best fit was achieved for $k_c = 4.6 \times 10^{5}$ M^{-1} s^{-1}. This leads to an equilibrium constant *K* of 7.2×10^{-9} M (Table 2).

In the case of the *n*-butyl acrylate polymerization *K* was determined using the method of Lacroix-Demazes.[17] As suggested by Fukuda[18] and Fischer[19] at large quantities of additional nitroxide the conversion of the polymerization can be described by eq 1 (k_p = propagation rate constant; K = equilibrium constant between active and dormant chains ($K = k_d/k_c$); k_d = dissociation rate constant for the C−O bond homolysis; k_c = rate constant for the cross coupling of the C-centered radical with the nitroxide; $[I]_0$ = initial alkoxyamine concentration; $[Y]_0$ = concentration of added free nitroxide):

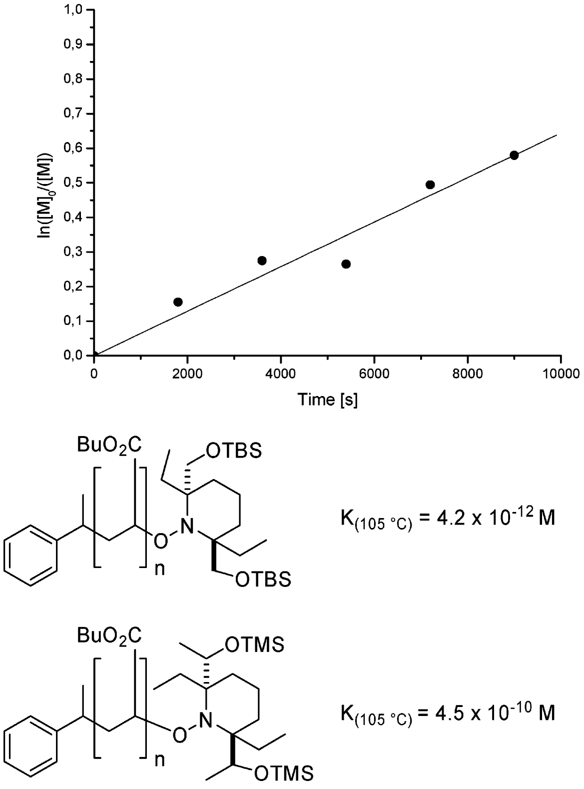


Figure 3. ln($[M]_0$/[M]) as a function of time for the determination of *K* according to eq 1 ($k_p = 7.1 \times 10^{4}$ M^{-1} s^{-1})[20] and *K* values for the **1** and **2**-mediated *n*-butyl acrylate polymerization at 105 °C.

$$\ln([M]_0/[M]) = k_p K([I]_0/[Y]_0)t \qquad (1)$$

To determine the equilibrium constant *K*, several bulk polymerizations of *n*-butyl acrylate were performed using 1 mol % of alkoxyamine **2** in the presence of 0.5 mol % of the corresponding free nitroxide **8**. The polymerizations were stopped after 1800, 3600, 5400, 7200, 9000, or 10800 s. The conversions were determined gravimetrically and set into relation with the reaction time as previously shown (Figure 3).[8] Using eq 1, *K* for the **2**-mediated *n*-butyl acrylate polymerization was then readily extracted from the slope of the curve and was calculated to $K = 4.5 \times 10^{-10}$ M at 105 °C. For comparison, a *K* value of 4.2×10^{-12} M was obtained for the **1**-mediated acrylate polymerization at 105 °C.[8]

In the polymerization of styrene the equilibrium is shifted to the homolysed species as can be seen from the value of the equilibrium constant *K*. This is due to a slower radical recombination between the growing macroradical and the free nitroxide since similar rate constants for the C−O-bond homolysis were obtained for **1** and **2** in the kinetic EPR experiments. The recombination reaction of the growing polystyrene macroradical with the nitroxide deriving from alkoxyamine **1** is about 40 times faster than the recombination of the growing polystyrene macroradical with nitroxide **8**.[21] Hence K is about 40 times larger in the **2**-mediated styrene polymerization as compared with the analogous process mediated with **1**. This is in good agreement with the higher polymerization efficiency of **2**. The even better results in the polymerization of poly(*n*-butyl acrylate) are also in agreement with the results obtained in the kinetic experiments. The equilibrium is further shifted to the homolysed species as the K value is around 110 times larger for the **2**-mediated *n*-butyl acrylate polymerization as compared to the **1**-mediated polymerization. Obviously, steric effects are slightly more important in the acrylate polymerization than in the styrene polymerization.

For alkoxyamine **3** the equilibrium constants were not determined, as the described methods for determining K are suitable for controlled polymerization processes only. However, it is clear that for **3** the equilibrium is shifted even further toward the free radicals. This is due to a faster homolysis as experimentally proved and to a large extent to a slower recombination reaction.

Conclusions

We showed that the size of the 2,2,6,6-substituents in piperidine *N*-oxyl radicals heavily influences the outcome of the nitroxide mediated radical polymerization of styrene and *n*-butyl acrylate. The increase of the steric demand of the substituents leads to an increase of the polymerization efficiency. Controlled polymerizations can be performed at temperatures as low as 70 °C using alkoxyamine **2**. The polymerization results were further supported by kinetic EPR experiments. However, if the substituents become too large, fast and uncontrolled polymerizations are obtained. The trapping reaction of the nitroxide with the macroradical and the nitroxide has been shown to be slow. Hence, at least for piperidine *N*-oxyl radicals the size of the substituents in nitroxide **8** defines the upper limit for improving the polymerization efficiency in terms of steric factors. Further improvement of the polymerization process can probably be obtained upon changing the polarity.[11] Work along this line is in progress.

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