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Synthesis and Evaluation of Sterically Hindered 1,1-Diadamantyl Nitroxide as a Low-Temperature Mediator for the Stable Free Radical Polymerization Process

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ABSTRACT: An efficient procedure for the oxidation of 1,1-diadamantylamine with *m*-chloroperbenzoic acid (*m*-CPBA) to the corresponding sterically hindered nitroxide in high yield (72%) is reported. The corresponding styrene-based alkoxyamine was synthesized by an atom transfer radical addition (ATRA) reaction. Because of the bulkiness of the adamantyl substituents, the cleavage of the C−ON bond of the alkoxyamine occurred readily at temperatures below 100 °C. However, in spite of the low bond dissociation temperature of the alkoxyamine, the (co)polymerizations of styrene and *n*-butyl acrylate proceeded poorly. The results in this paper support the argument that the most important determinant in a nitroxide-mediated polymerization of styrene and acrylate is the ability to control the excess concentration of nitroxide in solution either by an inherent instability of the nitroxide or by the use of additives that destroy the excess nitroxide. Thus, for the 1,1-diadamantyl nitroxide case, and maybe more generally, while a lower C−O bond dissociation energy of an alkoxyamine moiety at the end of the chain may allow lower polymerization temperatures and faster reactions rates, it does not enable polymerizations to proceed to high conversions if the excess nitroxide is not controlled in some manner.

Introduction

The chemistry of nitroxides has been extensively studied over the past decades, and the ability of these compounds to trap radicals has found important applications. Of particular recent interest to polymer chemists is the use of nitroxides as mediating agents for the living-radical polymerization of vinylic monomers as a mean of controlling the molecular parameters of the polymer.[1] This stable free radical polymerization (SFRP) technique is based on the reversible capping of growing radical polymeric chains by nitroxide radicals, resulting in an equilibrium between dormant nitroxide end-capped polymer chains and active propagating radical chains. The rate of cleavage of the C−ON bond, linking the end of the polymer chain with the nitroxide moiety, relative to its regeneration, regulates the position of the equilibrium between the dormant and active species.[2] Kazmaier et al.,[3] using semiempirical molecular orbital calculations, showed that the C−O bond dissociation energy of an alkoxyamine varies according to the nitroxide used. At about the same time, Moad and Rizzardo studied the actual factors that influence the strength of the C−O bond and found that polar, steric, and electronic factors all play a role, to different extents, depending on the nitroxide.[2a] Thus, for secondary and tertiary alkoxyamines, the steric bulk of the nitroxide is the most important determinant, where a bulky substitute causes an increase in the rate of C−O bond dissociation. The role of sterically congested nitroxides on the speed of alkoxyamine cleavage was further elaborated on in a paper by Fischer et al.[4] Miura et al.[5] took advantage of the lower C−O bond dissociation energies of bulky nitroxides to show that lower temperature styrene polymerizations could be achieved by using bulky spiro nitroxides. The synthesis and application of a nitroxide containing one adamantyl substituent to living radical polymerization have been reported.[6] Braslau et al.[6b] recently concluded that both steric bulk and an inherent instability of the nitroxide were both factors in the success of nitroxides having the ability to polymerize acrylate monomers. This prompted them to synthesize 1-adamantyl-3-methyl-2-phenylazabutane-1-nitroxide, an acyclic nitroxide containing both an α-hydrogen and an adamantyl group. The corresponding alkoxyamine was investigated as an initiator for the polymerization of styrene, *N,N*-dimethylacrylamide, *tert*-butyl acrylate, and *n*-butyl acrylate. In all cases, the polymerizations proceeded well, providing polymers with molecular weights up to 12 200 g mol^{-1}. The molecular weight distributions were typically less than 1.5.

However, we have argued that the inherent instability of a nitroxide at the high temperatures under which polymerizations are conducted is the most important factor in determining whether an acrylate polymerization would proceed with a particular nitroxide.[7] It is common knowledge that acyclic nitroxides containing α-hydrogens are more unstable than the TEMPO-type nitroxides. The instability of acyclic nitroxides at high temperatures has been advanced to explain a deviation in a $\ln([M]_0/[M])$ vs time plot for the polymerization of *n*-butyl acrylate.[8]

Studer and Siegenthaler[9] recently concluded that enhanced rates of polymerization mediated by TEMPO-based sterically hindered nitroxides is primarily based on a low rate of recombination (k_c) of the nitroxide with the propagating polymer chain and not the increased rates of C−O bond homolysis (k_d) of the alkoxyamine moiety at the end of the polymer chains. No mention was made about the contribution of nitroxide stability to the outcome of the polymerizations although it is important to note that acrylate polymerizations proceeded quite well at low temperatures with two of the reported sterically hindered nitroxides. Even with the most sterically hindered nitroxide reported in the paper, acrylate conversions were very high although the polydispersities were high (1.9) as well.

We recently were successful in synthesizing 1,1-diadamantyl nitroxide (**2**) and found it to be an unusually stable nitroxide at high temperatures. In light of the results reported by Studer,

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we were particularly interested in seeing how **2** would perform in controlling radical polymerizations. We anticipated that the steric bulk of the nitroxide would provide a high k_d and a low k_c for the C−O bond of the alkoxyamine moiety, but we were also mindful of the high thermal stability of **2** and anticipated that this high stability would pose problems due to an increase in free nitroxide caused by unavoidable termination reactions. In other words, we anticipated that if there were no means of controlling the excess nitroxide levels in the reaction solution, the polymerizations would be inhibited.

The synthesis of **2** was first reported by Morat et al.[10] and involved the reaction of 1 equiv of 1-nitroadamantane with 3 equiv of sodium in the presence of 2 equiv of 1-adamantyl bromide in refluxing diethyl ether for 88 h. However, only an 18% yield of product was realized. In the same paper it was reported that **2** could not be obtained by simply oxidizing amine **1**, an obvious approach to the desired nitroxide.

In this paper, we demonstrate that the synthesis of the desired 1,1-diadamantyl nitroxide (**2**) can actually be achieved in good yield following the previously disparaged oxidation pathway. Alkoxyamines were then synthesized using **2**, and the cleavage temperature of the C−O bond was evaluated by ^{1}H NMR measurements. Finally, the ability of **2** to mediate the (co)-polymerization of styrene and *n*-butyl acrylate at different temperatures was examined.

Experimental Section

Materials. 1-Adamantyl bromide, 1-adamantylamine, *m*-chloroperbenzoic acid (*m*-CPBA), oxone, hydrogen peroxide (H_2O_2), sodium tungstate dihydrate (Na_2WO_4), tetrabutylammonium hydrogen sulfate, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), copper powder (Cu^0), copper(II) bromide, pyridine, glyceraldehyde dimer, camphorsulfonic acid (CSA), benzoic acid, phenylethyl bromide, *N*-bromosuccinimide (NBS), tetrahydrofuran (THF), chloroform, chlorobenzene, toluene, 2-propanol, tetrachloromethane (or carbon tetrachloride) (CCl_4), and dichloromethane were purchased from Sigma-Aldrich and used as received. 2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO) (Chemipan, Russia) was purified by sublimation. Benzoyl peroxide (BPO), 75% in water (Sigma-Aldrich), was purified by crystallization in methanol. 1,1-Diadamantyl nitroxide (**2**) stabilized *n*-butyl acrylate was prepared by passing *n*-butyl acrylate (Sigma-Aldrich) through a 4-methoxyphenol inhibitor removal column (Aldrich) and adding **2** at a concentration of 35 mg/L of *n*-butyl acrylate. Styrene monomer was prepared in the same way using a 4-*tert*-butylcatechol inhibitor removal column.

Characterization. Molecular weights and polydispersities were estimated by size exclusion chromatography (SEC) using a Waters/Millipore liquid chromatograph equipped with a Waters model 510 pump, Ultrastyragel columns HR1, HR2, and HR4, and a Waters model 410 differential refractometer (RI). Polystyrene standards in the range of 400−188 000 g/mol were used for calibration. THF was used as the eluent at a flow rate of 0.35 mL/min. SEC was performed on samples taken directly from the reaction mixture. In the case of bulk polymerizations, unreacted monomer was removed by evaporation with a stream of air before SEC analysis.

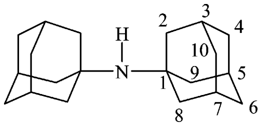
500 MHz ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-500 spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal reference, except for the samples used in the kinetic measurements (see Crossover Reactions section).

Mass spectra were recorded on a Micromass 70S-250 sector mass spectrometer with an EI/CI source and accurate mass capability.

Elemental analyses were carried out with a Perkin-Elmer model 2400II CHN coupled with an analyzer Perkin-Elmer AD-6 autobalance. Samples were calibrated against an internal standard, acetanilide (C: 71.09; H: 6.71; N: 10.36), before and after running samples.

X-ray data were collected on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation, and measurements were made using a combination of ϕ scans and ω scans with κ offsets to fill the Ewald sphere. The data were processed using the Denzo-SMN package.[11] Absorption corrections were carried out using SORTAV.[12] The structure was solved and refined using SHELXTL V6.1[13] for full-matrix least-squares refinement that was based on F^2. All H atoms were included in the calculated positions and allowed to refine in the riding-motion approximation with U∼iso∼ tied to the carrier atom.

1,1-Diadamantylamine (1). 1,1-Diadamantylamine was prepared according to a published procedure,[14] except that the reaction between the 1-adamantyl bromide and the 1-adamantylamine was carried out inside a Parr bomb reactor (acid digestion) placed in an oven at 220 °C for 40 h instead of a thick-walled sealed glass tube buried in sand. The desired amine was obtained in a 60% yield, and the NMR characteristics of the product were in agreement with the reported values. ^{1}H NMR ($CDCl_3$): δ 2.87 (1H, N−*H*, broad peak), 2.03−1.48 (30H, adamantyl substituent, m). ^{13}C NMR ($CDCl_3$): δ 53.47(C_1), 43.84 ($C_{2,8,9}$), 36.77 ($C_{4,6,10}$), 29.69 ($C_{3,5,7}$). EI MS: M^+, *m/z* 285; major fragment ions: 270, 242, 228, 107, 191, 135, 120, 93, 79, 67, 55. HR MS: M^+, *m/z* 285.246 151; Calcd for $C_{20}H_{31}N$ = 285.245 650.



1,1-Diadamantyl Nitroxide (2). 1,1-Diadamantylamine (**1**) (10 g, 35 mmol) was dissolved in 125 mL of chloroform in a round-bottom flask fitted with an addition funnel containing *m*-CPBA (77 wt %) (15.5 g, 70 mmol) in 250 mL of chloroform. Both solutions were degassed by bubbling argon through them for 10 min. The amine solution was cooled to −78 °C in an acetone/dry ice bath. At that temperature the amine was not completely soluble, and a white precipitate appeared. The *m*-CPBA solution was added dropwise over a period of 20 min. After complete addition of the oxidant, the reaction mixture was allowed to warm to 0 °C over 3 h. At 0 °C all the reaction components were soluble in the chloroform, and the solution had an orange coloration, typical of nitroxides. The reaction solution was poured into chloroform (200 mL) and washed with an aqueous 20% sodium hydroxide solution (200 mL). The organic layer was separated, dried over sodium sulfate, filtered, and evaporated to dryness under vacuum before purification by flash chromatography through a neutral alumina column with dichloromethane as eluent. The product was an orange solid (7.6 g, 25 mmol, 72% yield) that was further crystallized in hexanes. Measured mp 185−187 °C (mp mentioned in ref 8: 200 °C). EA: Calcd for $C_{20}H_{30}NO$: C, 79.95%; H, 10.06%; N, 4.66%. Found: C, 80.41%; H, 10.39%; N, 4.63%). EI MS: M^+, *m/z* 300; major fragment ions: 286, 135, 119, 107, 93, 79, 67, 55. HR MS: M^+, *m/z* 300.232 930; Calcd for $C_{20}H_{30}NO$ = 300.232 740. X-ray analysis further confirmed the structure of the product (see Figure 1).

1-(Benzoyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (BST) (4) was prepared as described[15] and crystallized from 2-propanol.

1-(Benzoyloxy)-2-phenyl-2-(1,1-diadamantylaminoxy)-ethane (BSA) (6). The following reaction was carried out according to a procedure by Matyjaszewski[16] and modified as follows: 1,1-diadamantyl nitroxide (**2**) (5.00 g, 16.6 mmol) and benzoic acid 2-bromo-2-phenylethyl ester (**11**) (4.25 g, 13.9 mmol) were dissolved in 45 mL of toluene in a three-necked round-bottom flask equipped with a reflux condenser, a septum, and a thermometer. Argon gas was introduced via a syringe needle through the septum for 30 min to deoxygenate the reaction mixture. Pentamethyldiethylenetriamine (PMDETA) (98 mg, 0.57 mmol), copper powder (Cu^0) (903 mg, 143 mmol), and $CuBr_2$ (31 mg, 0.14 mmol) were added to the reaction medium under an argon atmosphere. The

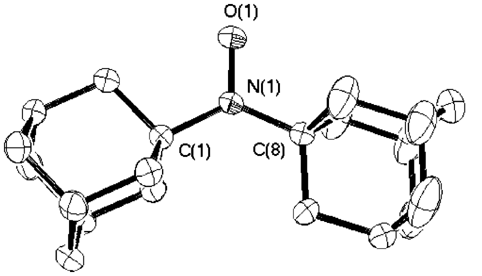


Figure 1. ORTEP view of 1,1-diadamantyl nitroxide (**2**) with hydrogen atoms removed for clarity. Relevant structural parameters: O(1)−N(1) 1.288(3) Å, N(1)−C(1) 1.504(4) Å, N(1)−C(8) 1.504(4) Å, O(1)−N(1)−C(1) 117.1(2)°, O(1)−N(1)−C(8) 112.9(2)°, C(1)−N(1)−C(8) 130.0(2)°.

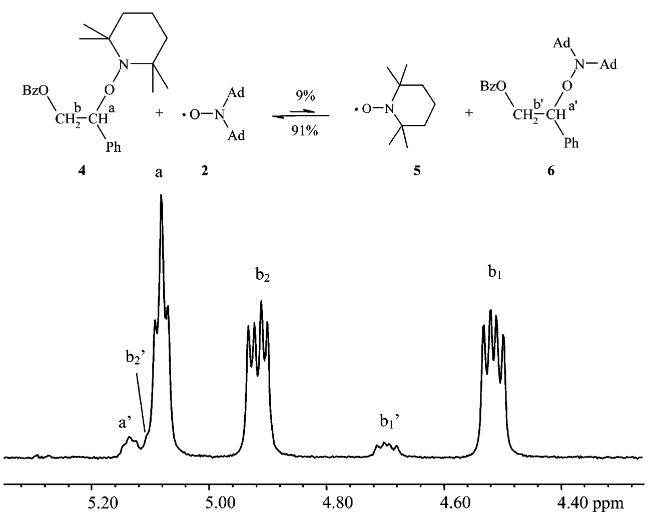


Figure 2. ^{1}H NMR in toluene-d_8 at 120 °C for the exchange reaction between BST **4** and 1,1-diadamantyl nitroxide (**2**) after 20 min.

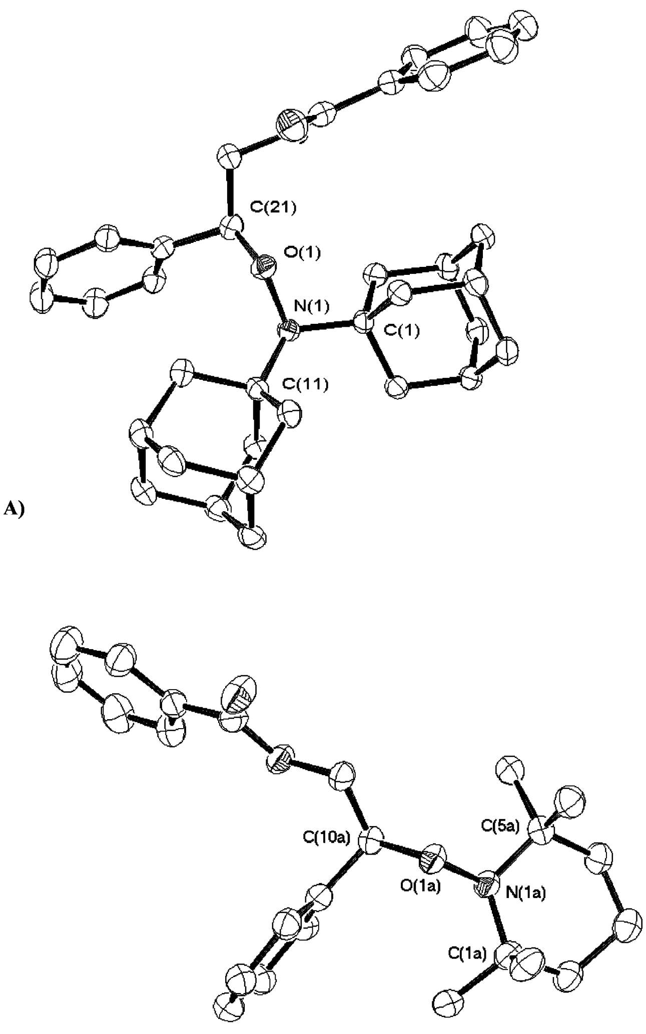
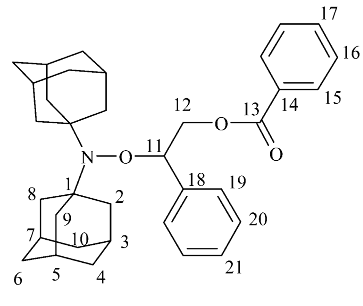


Figure 3. ORTEP views of BSA **6** (A) and BST **4** (B) with hydrogen atoms removed for clarity. Relevant structural parameters of BSA: O(1)−N(1) 1.473(2) Å, O(1)−C(21) 1.448(3) Å, N(1)−O(1)−C(21) 112.72°, C(1)−N(1)−C(11) 120.7°. Relevant structural parameters of BST: O(1a)−N(1a) 1.464(3) Å, O(1a)−C(10a) 1.448(4) Å, N(1a)−O(1a)−C(10A) 112.2°, C(1a)−N(1a)−C(5a) 117.1°.

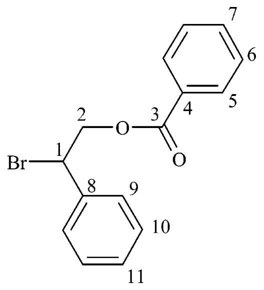


reaction mixture was heated for 20 h in an oil bath to maintain a reaction temperature of 75 °C. The mixture was then cooled to room temperature before being filtered through an alumina column with hexanes in order to remove the beige precipitate formed during the reaction and the residual copper catalyst. The hexanes solution was evaporated to yield an oil that was redissolved in 2-propanol. Storage of the resulting solution in a fridge at 4 °C allowed the formation of white crystals. Filtration provided 3.6 g of BSA (6.8 mmol, yield 49%).

Measured mp 112−113 °C. EA: Calcd for $C_{35}H_{43}NO_3$: C, 79.96%; H, 8.24%; N, 2.66%. Found: C, 79.60%; H, 8.30%; N, 2.64%. EI MS: M^+, *m/z*; major fragment ions: 300, 225, 135, 105, 77. ^{1}H NMR ($CDCl_3$) : δ 7.90 (2 H_{15}, m), 7.51 (1 H_{17}, m), 7.41 (2 H_{16}, m), 7.38 (2 H_{19}, m), 7.33 (2 H_{20}, m), 7.27 (1 H_{21}, m), 5.04 (1 H_{11}, dd, J = 7.02 Hz et 4.24 Hz), 4.96 (1 H_{12}, dd, J = 10.99 Hz et 4.23 Hz), 4.60 (1 H_{12}, dd, J = 10.99 Hz et 7.07 Hz), 2.04−1.50 (30H, adamantyl groupments, m). ^{13}C NMR ($CDCl_3$) : δ 166.29 (C_{13}), 140.69 (C_{18}), 132.81 (C_{17}), 130.21 (C_{14}), 128.51 (C_{arom}), 128.25 (C_{arom}), 128.01 (C_{arom}), 127.74 (C_{arom}), 127.55 (C_{21}), 84.53 (C_{11}), 66.31 (C_{12}), 64.33 (C_1), 65.18 ($C_{1'}$), 42.08 ($C_{2,8,9}$), 36.68 ($C_{4,6,10}$), 30.24 ($C_{3,5,7}$). X-ray analysis further confirmed the structure of the product (see Figure 3A).

Benzoic acid 2-bromo-2-phenylethyl ester (9) was prepared following standard benzylic bromination conditions.[17] Benzoic acid phenethyl ester (**8**) (6.8 g, 30 mmol), preformed by classical benzoylation of 2-phenylethanol (**7**), benzoyl peroxide (BPO) (150 mg, 0.62 mmol), and *N*-bromosuccinimide (NBS) (6 g, 34 mmol) were dissolved in 40 mL of CCl_4, and the reaction mixture was purged with argon for 20 min. The reaction mixture was refluxed for 2 h followed by evaporation of the solvent under reduced pressure. Purification by silica gel chromatography using dichloromethane as eluent afforded **9** (8.7 g, 28 mmol) in 93% yield. ^{1}H NMR ($CDCl_3$): δ 7.98 (2 H_5, m), 7.56 (1 H_7, m), 7.47 (2 H_6, m), 7.43 (2 H_9, m), 7.38 (1 H_{11}, m), 7.35 (2 H_{10}, m), 5.27 (1 H_1, dd, J = 7.71 Hz et 6.68 Hz), 4.84 (1 H_2, dd, J = 11.80 Hz et 7.71 Hz), 4.75 (1 H_2, dd, J = 11.79 Hz et 6.68 Hz). ^{13}C NMR ($CDCl_3$): δ 165.83 (C_3), 138.03 (C_8), 133.23 (C_7), 129.67(C_{arom}), 129.48 (C_{11}), 128.98 (C_4), 128.84 (C_{arom}), 128.39 (C_{arom}), 127.78 (C_{arom}), 67.88 (C_2), 49.99 (C_1). The characteristics of the product were in agreement with characteristics reported elsewhere.[18]

Crossover Reactions. BST **4** (32 mg, 80 mmol) and a 2-fold excess of orange crystals of 1,1-diadamantyl nitroxide (**2**) (50 mg, 166 mmol) were dissolved in 10 mL of chlorobenzene in a round-bottom flask equipped with a condenser and a thermometer. The solution was purged with argon gas for 10 min and then heated at 110 °C for 4 h. Thin-layer chromatography in CH_2Cl_2 and ^{1}H NMR



revealed the formation of only a small amount of the desired BSA **6** (yield = 9%) that could not be isolated. The same reaction carried out in toluene-d_8 in a sealed NMR tube at 120 °C confirmed the above-mentioned observations (see Figure 2).

The reverse experiment involving BSA (14×10^{-3} mmol) in 0.7 mL of toluene-d_8 and a 2-fold excess of TEMPO was also carried out in a J-Young valved NMR tube. The solution was degassed with four freeze−pump−thaw cycles and sealed off under vacuum. The NMR tube was introduced into a preheated VWR heated circulator 1130-1S with a temperature stability of ±0.05 °C for prescribed time intervals and quenched at 0 °C. The [BSA]/[BST] ratio, monitored by ^{1}H NMR at different temperatures, reached 1/99 after 1 h at 80 °C (see Figure 4).

General Procedure for Polymerizations Initiated by BPO in the Presence of 1,1-Diadamantyl Nitroxide (2). BPO (65 mg, 0.27 mmol) and **2** (100 mg, 0.33 mmol) were dissolved in styrene (15 mL, 130 mmol) in a three-necked round-bottom flask equipped with a reflux condenser, a septum, and a thermometer. The solution was purged for 10 min with argon gas introduced via a syringe needle through the septum. The reaction mixture was heated under argon at 130 °C, and samples were removed at the times indicated in the tables to monitor the course of the polymerization. The same procedure was repeated at various temperatures, with different [monomer]/[nitroxide]/[BPO] ratios, in the presence of additives, such as glyceraldehyde dimer and pyridine, CSA and benzoic acid.

Similar reactions were repeated with *n*-butyl acrylate instead of styrene.

General Procedure for Polymerizations Initiated by the Alkoxyamine BSA 6. A solution of BSA (150 mg, 0.29 mmol) in styrene (10 mL, 87 mmol) was placed in a three-necked round-bottom flask equipped with a reflux condenser, a septum, and a thermometer. The solution was purged for 10 min with argon gas introduced via a syringe needle through the septum before heating the solution at 104 °C. Samples were removed regularly to follow the course of the polymerization (Table 3, entry 2). The same procedure was repeated at various temperatures, with different [monomer]/[BSA] ratios, in the presence of various additives (glyceraldehyde dimer and pyridine, CSA and benzoic acid). Polymerizations of *n*-butyl acrylate were also conducted under these conditions.

***n*-Butyl Acrylate Styrene Random Copolymerization.** A solution of BSA **6** (150 mg, 0.29 mmol) in *n*-butyl acrylate (5.6 mL, 40 mmol) and styrene (4.5 mL, 40 mmol) was heated at 104 °C for 8.5 h under argon to give a polymer with $M_n = 8200$ g/mol and $M_w/M_n = 1.35$.

Results and Discussion

A. Synthesis of 1,1-Diadamantyl Nitroxide.

1,1-Diadamantylamine (**1**) was prepared from 1-adamantylamine and 1-adamantyl bromide as described previously in 60% yield.[14] Oxidization of **1**, following a procedure based on hydrogen peroxide and a tungsten catalyst (Na_2WO_4),[19] gave nitroxide **2** in 4% yield (Table 1). Oxidation by dimethyloxirane, a strong oxidizing agent generated in-situ by reaction of oxone with acetone under phase-transfer conditions, was also investigated.[20] Although this approach is reported to efficiently oxidize many secondary amines, yields of **2** were typically less than 10%.

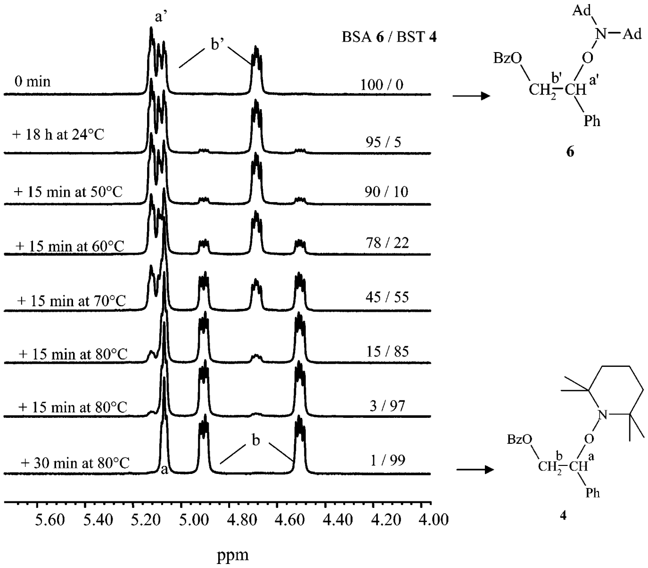


Figure 4. Exchange reaction between BSA **6** and 2 equiv of TEMPO at different temperatures in toluene-d_8.

Table 1. Synthesis of 1,1-Diadamantyl Nitroxide (2) by Oxidation of 1,1-Diadamantylamine (1)

oxidant	conditions	yield [%][a]
H_2O_2/Na_2WO_4	biphasic system[b]	4
oxone	biphasic system[c]	9
m-CPBA (2 equiv)	RT, 20 min	40
m-CPBA (1 equiv)	0 °C, 20 min	36
m-CPBA (2 equiv)	0 °C, 20 min	60
m-CPBA (2 equiv)	−78 → 0 °C, 3 h	72

[a] Isolated overall yields after flash chromatography through alumina with CH_2Cl_2 as eluent. [b] Toluene (40 mL)/H_2O_2 (25 mL, 35% aq), $Na_2WO_4 \cdot 2H_2O$ (0.46 mmol), tetrabutylammonium hydrogen sulfate (0.09 mmol), sodium acetate (0.6 mmol), 1-adamantylamine **1** (1.75 mmol), 90 °C, 4 h. [c] 1-Adamantylamine, **1** (2.5 mmol), oxone (31 mmol), acetone (80 mL), CH_2Cl_2 (60 mL), Na_2HPO_4(aq) buffer (100 mL), tetrabutylammonium hydrogen sulfate (0.25 mmol), 0 °C, KOH (2 N), pH 7.5−8.0.

Table 2. Bulk Radical Polymerization of Styrene Initiated by BPO in the Presence of 1,1-Diadamantyl Nitroxide[a]

entry	[styrene]/[·ON(Ad)$_2$]	T (°**C**)	time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	M_w/M_n
1	218	130	1	7	1500	1.18
			2	13	2700	1.29
			2.5	23	4600	1.39
			3	41	6600	1.47
			3.5	52	10100	1.59
			4	83	14300	1.61
2	410	130	0.5	4	1800	1.19
			1	7	3500	1.28
			1.5	17	5600	1.40
			2	36	8400	1.56
			2.5	61	12300	1.67
			3	77	17000	1.67
3	410	115	1	1.5	1200	1.17
			2	6	1900	1.21
			3	8	2700	1.27
			5	15	4900	1.38
			6	28	7100	1.47
			7	40	9000	1.60

[a] Entry 1: [styrene]/[·ON(Ad)$_2$]/[BPO] = 70/0.33/0.29 (mmol). Entry 2: [styrene]/[·ON(Ad)$_2$]/[BPO] = 130/0.33/0.24 (mmol). Entry 3: [styrene]/[·ON(Ad)$_2$]/[BPO] = 130/0.33/0.26 (mmol).

We next turned our attention to *m*-CPBA, a known efficient oxidant for secondary amines.[21] In the initial oxidation reaction, 2 equiv of *m*-CPBA were added to 1 equiv of **1** in chloroform at room temperature, giving the desired nitroxide **2** in 40% yield (see Table 1). However, when the same reaction was conducted

Table 3. Bulk Radical Polymerization of Styrene Initiated by BSA 6 and BST 4[a]

entry	T (°C)	time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,th}$ (g/mol)	M_w/M_n
1	80	1	5	640	1560	1.30
		2	6	983	1870	1.19
2	104	1	10	2730	3120	1.07
		3	20	4530	6250	1.09
		5	26	5370	8120	1.13
		7	30	5700	9370	1.18
		24	38	5950	11870	1.31
3	110	1	2	1200	620	1.17
		3	8	2700	2500	1.27
		5	15	4900	4690	1.38
		6	28	7100	8750	1.47
		7	40	9000	12500	1.60
4	123	1	32	7900	10000	1.26
		3	39	7700	12180	1.51
		5	50	7300	15620	1.56
5	104	1	15	6800	9370	1.06
		3	24	11000	15000	1.07
		5	30	13000	18750	1.08
		7	34	14100	21250	1.10
6	104	2	4	2300	1250	1.45
		3	8	2600	2500	1.46
		5	14	2900	4370	1.42
		7	18	3800	5620	1.38

[a] Entries 1−4: [styrene]/[BSA] = 87/0.29 (mmol). Entry 5: [styrene]/[BSA] = 87/0.145 (mmol). Entry 6: [styrene]/[BST] = 87/0.29 (mmol).

in an ice bath at 0 °C, the yield of **2** increased to 60%. A further improvement in yield to 72% was achieved by adding *m*-CPBA dropwise to a solution of **1** at −78 °C and then allowing the reaction mixture to warm to 0 °C over 2 h. The lower reaction temperature probably prevents further oxidation of the desired nitroxide **2** with the excess *m*-CPBA that otherwise could occur at ambient temperature.[22] However, without the excess oxidizing agent significant amounts of unreacted amine typically remained in the reaction mixture. Using 1 equiv of *m*-CPBA compared to the amine **1** at low temperature produced only a modest yield (36%) of product, in agreement with previous observations in the literature using other amines.[21]

Bright orange crystals of 1,1-diadamantyl nitroxide (**2**) were obtained by recrystallization in hexane. The single-crystal structure determination of **2** revealed a C(1)−N(1)−C(8) angle of 130.0(2)° (Figure 1), which is significantly larger than the corresponding angle reported for TEMPO (123.6°).[23]

B. Polymerization of Styrene and *n*-Butyl Acrylate in the Presence of 1,1-Diadamantyl Nitroxide. Styrene polymerizations, initiated with BPO, were conducted with 1,1-diadamantyl nitroxide (**2**) as the controlling agent, and by analogy to the reported polymerization of styrene initiated with the peroxide initiator in the presence of TEMPO,[24] the [$\cdot$ON(Ad)$_2$]/[BPO] ratio was adjusted to 1.1−1.2 (Table 2). When carried out at 130 °C, the polymerization clearly proceeded in a living manner (Table 2, entries 1 and 2). The molar masses increased with conversion, and as expected, increasing the [styrene]/[nitroxide] ratio resulted in higher molar masses. However, although the polydispersity was relatively narrow at the beginning of the polymerization (∼1.2), it tended to broaden as the polymerization continued. Decreasing the reaction temperature to 115 °C slowed down the polymerization without providing any improvement in the control of the molecular parameters (Table 2, entry 3).

Similar experiments were conducted with *n*-butyl acrylate at 130 °C using 1.2 equiv of BPO relative to 1,1-diadamantyl nitroxide. Invariably, no polymerization occurred for 2 h, at which point additional BPO was introduced causing a very rapid increase in conversion. The resulting poly(*n*-butyl acrylate) had a high polydispersity index, typical of what would be expected from an uncontrolled polymerization.

During these experiments, changes in the color of the reaction medium from orange, the color of the nitroxide, to green, the possible formation of an unstable nitroso intermediate, before all the color disappeared, suggested that decomposition of the nitroxide was occurring in the presence of BPO. To avoid this problem, we turned our attention to the synthesis of an alkoxyamine containing the 1,1-diadamantyl nitroxide.

C. Synthesis of BSA 6. The first attempt to synthesize the alkoxyamine **6** (BSA), followed an established procedure for the synthesis of BST.[15] Typically, an excess of BPO (2 equiv) was mixed at room temperature with a solution of 1,1-diadamantyl nitroxide (**2**) (1 equiv) in styrene. However, under these conditions, although a slight exothermic reaction was observed and the orange coloration typical of the nitroxide clearly changed to yellow, no trace of the desired alkoxyamine was detected by ^{1}H NMR.

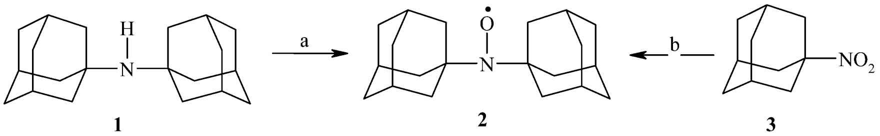
In a second approach, a solution of BST **4**, with a 2-fold excess of 1,1-diadamantyl nitroxide (**2**), was heated to 110 °C to promote a crossover reaction to produce BSA **6** (Figure 2).[25] The experiment was first conducted on a small scale in a sealed NMR tube in toluene-d_8. After 20 min of heating, new peaks assigned to BSA **6** (a′, b$_1$′, b$_2$′), in addition to the original signals for BST **4** (a, b$_1$, b$_2$), were evident in the ^{1}H NMR spectrum (Figure 2). The BSA/BST ratio at that point was 9/91. Continued heating of the reaction mixture caused no change in the ratio, indicating that under these reaction conditions the 9/91 ratio was the equilibrium ratio between the two alkoxyamines. A few attempts at performing the reaction on a larger scale in a round-bottom flask using chlorobenzene as the solvent failed to provide a pure sample of **6**.

On the surface, the equilibrium ratio largely favoring BST in this crossover experiment would suggest that the C−ON of the alkoxyamine derived from 1,1-diadamantyl nitroxide (**2**) is more labile that the one with TEMPO, but it could also suggest that the reaction of **2** with the ST radical is very slow.

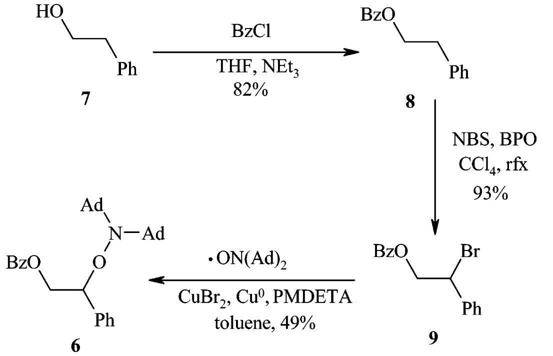
BSA **6** was eventually synthesized in good yield by an atom transfer radical addition (ATRA) reaction involving a halogen transfer between an organic halide and copper complex in the presence of **2**.[16] Bromo compound **9**, used as the precursor for BSA, was obtained by benzoylation of 2-phenylethanol (**7**) followed by bromination with *N*-bromosuccinimide initiated with BPO[17] (Scheme 2). For the ATRA reaction, **9** was reacted at 75 °C with CuBr$_2$, Cu^0, and PMDETA, in the presence of a large amount of **2** to give BSA **6** in 49% yield after purification.

In addition to elemental analysis, ^{1}H and ^{13}C NMR, and accurate mass spectrometry, the structure of **6** was characterized by X-ray analysis and compared to the structures of **4** and **2** (Figure 3). While the 1.47(3) Å O−N bond length in **6** is considerably longer than the corresponding bond in the free nitroxide **2** (1.288 Å), a comparison of BSA (**6**) and BST (**4**) did not reveal any dramatic differences regarding the C−O and N−O bond lengths and C−O−N angles between the two alkoxyamines. Thus, any difference in the rate of C−O bond dissociate between BSA and BST cannot be attributed to these parameters. On the other hand, the C(1)−N−C(11) bond angle of **2** is 130.0(2)° (Figure 1) while the C(1)−N(1)−C(11) bond angle in **6** is only 120.70(17)° (Figure 3A). Thus, the adamantyl groups move away from each other as the alkoxyamine dissociates, at a rate constant k_d, removing some steric strain, and move closer together, at a rate constant k_c, reestablishing the steric strain, as the diadamantyl nitroxide reacts with the ST radical to re-form the alkoxyamine. On the other hand, for

Scheme 1. (a) *m*-CPBA (2 equiv), $CHCl_3$, −78 → 0 °C, 3 h, 72%; (b) 1-Adamantyl Bromide (2 equiv), Sodium (3 equiv), Diethyl Ether, Reflux, 88 h, 18%



Scheme 2. Reaction Scheme for the Synthesis of BSA 6



the alkoxyamine containing the TEMPO moiety, a smaller change in the C5−N1−C1 angle (∼5°) occurs after the alkoxyamine dissociates or re-forms because of the rigid ring structure of TEMPO. Thus, in the equilibrium reaction between the alkoxyamine and the dissociated radicals, it is not unreasonable to assume that the values of k_d and k_c will increase and decrease, respectively, when **2** is used in place of TEMPO.

D. Evaluation of the C−ON Bond Strength of BSA. The poor yield of BSA **6** from the crossover experiments of BST **4** with **2** described earlier prompted us to examine the reverse crossover experiment of **6** with TEMPO to give **4**. It was expected that the results of this experiment would provide a C−O cleavage temperature for **6** and define an appropriate temperature for polymerization experiments with **6** as the initiator.

The exchange reaction was carried out in a J-Young valve-equipped NMR tube in toluene-d_8, using a 2-fold excess of TEMPO vs BSA **6**. Under the reaction conditions, all the radicals generated by the thermal homolysis of BSA **6** were effectively irreversibly trapped by TEMPO. ^{1}H NMR spectra (Figure 4) were recorded at different temperatures, and the BSA/BST ratio was systematically measured using the peaks at 4.68 ppm (b′) and 4.51 ppm (b).

After 18 h at room temperature, 5% of BST was detected, demonstrating that the cleavage of the C−ON bond of BSA occurs even at ambient temperature, albeit slowly. According to this result, the half-life of BSA at ambient temperature (24 °C) is ∼1 week. Increasing the reaction temperature of the sample from 50 °C stepwise to 80 °C resulted in a decrease of the signals corresponding to the BSA (a′, b′) and an increase of signals typical of BST (a, b). After 30 min at 80 °C, the reaction proceeded to essentially complete conversion (BSA/BST: 1/99) (Figure 4), prompting us to choose this temperature as a starting point to test the polymerization of both styrene and *n*-butyl acrylate in the presence of 1,1-diadamantyl nitroxide.[26]

E. Polymerization of Styrene Initiated by BSA 6. The polymerization of styrene conducted at 80 °C typically proceeded to 5−6% monomer conversion in the first 2 h and then slowed down and stopped (Table 3, entry 1). Although the polymerization took place above the cleavage temperature of the alkoxyamine **6**, it is reasonable to assume that at 80 °C there is not enough autopolymerization of styrene to regulate the excess nitroxide that results from unavoidable termination reactions.[27] A similar behavior was found and discussed for the polymerization of *n*-butyl acrylate, devoid of an autoinitiation reaction, under SFRP conditions with TEMPO.[28]

Above 100 °C, the autopolymerization of styrene is significant, and the polymerization proceeded in a controlled fashion (Table 3, entries 2 and 3). A noticeable increase in the molecular weight of the sample over the course of the polymerization was observed while a low polydispersity (M_w/M_n ∼ 1.10) was maintained at the beginning of the reaction. Moreover, the molar mass of polystyrene was effectively determined by the [styrene]/[BSA] molar ratio. Comparison of entries 2 and 5 in Table 3, at 30% conversion, shows that the $M_{n,SEC}$ was increased by 2.28 when the [styrene]/[BSA] molar ratio was increased by 2. However, after this point the molecular weight distributions started to broaden, probably due to irreversible termination, and the polymerization rate decreased. As expected, a further increase of the temperature to 123 °C, which is close to the optimal temperature for the SFRP system involving TEMPO, significantly increased the rate of the polymerization but to the detriment of the livingness of the system (Table 3, entry 4). For comparison, the polymerization of styrene initiated with BST at 104 °C (Table 3, entry 6) was slower than the corresponding polymerization with BSA (Table 3, entry 2).

In order to allow the reaction initiated with BSA to proceed to higher monomer conversion and to avoid the slowing down of the reaction, rate accelerating additives, such as camphorsulfonic acid,[29] glyceraldehyde associated with pyridine,[28] and benzoic acid, which proved efficient at speeding up the SFRP process in the presence of TEMPO, were investigated (Table 4). Addition of a small amount of CSA had almost no effect on the course of the polymerization (Table 4, entry 1), whereas the molar mass distribution became very broad in the presence of a larger amount of CSA (Table 4, entry 2). Addition of glyceraldehyde and pyridine to the reaction medium allowed the polymerization to proceed to higher conversion with a better control. Under these conditions, the conversion went well beyond 30% before the reaction began to deviate from ideal behavior (compare Table 4, entry 3 and Table 3, entry 2).

To a smaller extent, addition of benzoic acid to the medium also had a beneficial effect on the course of the polymerization. After 7 h of reaction, the monomer conversion for the polymerization conducted in the presence of benzoic acid reached 40% (Table 4, entry 4), 10% higher than a similar reaction without benzoic acid (Table 3, entry 2).

The addition of a combination of benzoic acid and glyceraldehyde (Table 4, entry 5) enabled an 85% monomer conversion in only 5 h at 104 °C, the best result for this series of experiments. Clearly, in this particular case the additives were efficient in destroying the excess nitroxide at a rate that enabled the polymerization to proceed well at a relatively low temperature. The active reagent in this case is the ene−diol tautomer of glyceraldehyde, the formation of which is catalyzed by the benzoic acid.[28]

The SEC chromatograms for the polystyrene samples in Table 4, entry 5, are instructive and shown in Figure 5. In spite of the low PDI of the polystyrene samples, there is a distinct tailing of the chromatographs at the low molecular end of the

Table 4. Bulk Radical Polymerization of Styrene Initiated by BSA 6 at 104 °C with Additives[a]

entry	additives	time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,th}$ (g/mol)	M_w/M_n
1	CSA	1	15	3000	4680	1.07
		2	19	3900	5940	1.07
		3	24	4500	7500	1.07
		5	28	5050	8750	1.09
		6	29	5250	9060	1.10
2	CSA	1	12	3600	3700	1.34
		2	20	6400	6200	1.62
		3	27	8100	8400	2.09
		4	32	9500	10000	2.48
		6	39	10600	12200	2.95
3	glyceraldehyde/pyridine	1	22	5100	6880	1.07
		2	29	6600	9060	1.07
		4	40	8700	12580	1.11
		6	44	9600	13750	1.18
		8	50	9800	15620	1.29
		10	58	9900	18120	1.34
4	benzoic acid	1	18	3750	5620	1.06
		2	25	6100	7810	1.05
		3	30	7150	9370	1.06
		5	35	8400	10940	1.08
		7	40	8800	12500	1.10
5	benzoic acid/glyceraldehyde	2	33	10700	10310	1.09
		3	58	14600	18120	1.13
		4	74	18400	23120	1.16
		5	85	21000	26550	1.17

[a] Entry 1: [styrene]/[BSA]/[CSA] = 87/0.29/0.013 (mmol). Entry 2: [styrene]/[BSA]/[CSA] = 87/0.29/0.43 (mmol). Entry 3: [styrene]/[BSA]/[glyceraldehyde dimer]/[pyridine] = 87/0.29/0.10/0.60 (mmol). Entry 4: [styrene]/[BSA]/[benzoic acid] = 87/0.29/3.2 (mmol). Entry 5: [styrene]/[BSA]/[benzoic acid]/[glyceraldehyde dimer] = 87/0.29/0.20/0.06 (mmol).

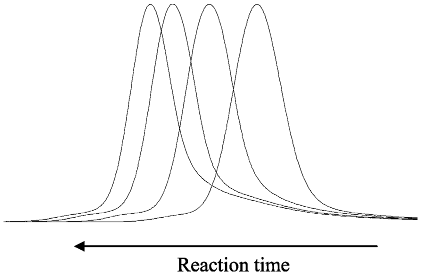


Figure 5. Evolution of SEC traces for the bulk polymerization of styrene initiated from BSA at 104 °C with glyceraldehyde and benzoic acid (reaction time = 2, 3, 4, and 5 h). [Styrene]/[BSA]/[benzoic acid]/[glyceraldehyde dimer] = 87/0.29/0.20/0.06 (mmol) (Table 4, entry 5).

distributions as the polymerization proceeds. The tailing is typically for nearly all the styrene polymerizations moderated with **2** and is probably a reflection of the low k_c value for the nitroxide and the propagating chain causing an increase in the concentration of the active chains leading to increased bimolecular termination as the polymerization proceeds in the early stages. As the free nitroxide accumulates above a critical level, it causes the polymerization to slow down by shifting the equilibrium between the dormant chains and the active propagating chains to the dormant chains.

In many of these polymerizations the actual M_n is smaller than the theoretical M_n. We suspect that this is a reflection of the tailing that is evident in the SEC plots at the low molecular weight end, reducing the measured M_n values.

F. Polymerization of *n*-Butyl Acrylate Initiated by BSA. The difficulty of polymerizing acrylates under SFRP conditions is well documented.[6,29] Two arguments have been advanced for these poor results. One argument is that equilibrium constant K of the TEMPO/acrylate bond is unfavorably small because of a low dissociation rate constant k_d and a high recombination rate constant k_c. As a result, bond cleavage is not much faster than monomer conversion, and the rate of recombination of TEMPO with the active polymer chain end is too fast.[30] The second argument is that there is a buildup of TEMPO concentration in the reaction mixture due to a small amount of unavoidable chain termination, and this excess nitroxide inhibits the polymerization.[8]

On the basis of the lower C−O styrene/1,1-diadamantyl nitroxide bond dissociation energy described earlier, it was anticipated that the 1,1-diadamantyl nitroxide/acrylate bond might be sufficiently labile for the polymerization of acrylates to proceed efficiently. However, this turned out not to be the case. Table 5 summarizes the results for the polymerization of *n*-butyl acrylate initiated by BSA at different temperatures with and without additives known to accelerate the rate of polymerization in the presence of TEMPO. With no additives present only a 6% monomer conversion was achieved after 6 h at 104 °C with approximately one monomer unit being added per hour (Table 5, entry 1). A 50% conversion was observed with BSA after 5 h at 124 °C (Table 5, entry 2). However, after 2 h, the molar mass actually decreased over time as the molecular weight distribution broadened. Addition of camphorsulfonic acid or glyceraldehyde associated with pyridine or benzoic acid invariably led to moderate monomer conversions with a relative dependence of the molar mass on the monomer conversion; however, molecular weight distributions were somewhat broad (Table 5, entries 3−5). These are typical results observed with TEMPO as the moderating nitroxide. Thus, under a variety of conditions no successful polymerizations of *n*-butyl acrylate were achieved, even in spite of the steric bulk of the nitroxide and the lower energy of activation for the C−O bond dissociation of BSA. What is interesting about these acrylate polymerizations is that after about 0.5 h the reaction mixture takes on an orange color. The color is initially faint but intensifies as the polymerization proceeds. Thin-layer chromatography of a concentrated solution of the reaction mixture in dichloromethane shows that an orange spot that runs the same as an authentic sample of 1,1-diadamantyl nitroxide (**2**), indicating the formation and accumulation of **2**. The color change observed with *n*-butyl acrylate occurs as well in the polymerization of styrene but at

Table 5. Homopolymerization of *n*-Butyl Acrylate Initiated by BSA[a]

entry	additives	T (°C)	time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,th}$ (g/mol)	M_w/M_n
1		104	1	5	1300	1500	1.42
			2	6	1600	1800	1.34
			3	6	1700	1800	1.31
			4	6	1800	1800	1.31
			6	7	1900	2100	1.30
2		124	1	32	7900	9610	1.26
			2	37	8000	11120	1.43
			3	39	7700	11720	1.51
			4	44	7400	13220	1.56
			5	50	7300	15025	1.56
3	glyceraldehyde dimer/pyridine	104	1	7	1800	2100	1.31
			2	8	2200	2400	1.27
			4.5	11	3000	3300	1.38
			6	12	3400	3610	1.49
			8	15	3900	4510	1.63
			23	21	4400	6310	2.44
4	glyceraldehyde dimer, benzoic acid	104	1.25	8	2200	2400	1.35
			2	9	2400	2700	1.32
			4	10	2900	3010	1.27
			6	11	3300	3300	1.31
			8	11	3400	3300	1.34
			11	12	3500	3610	1.37
			24	14	3600	4210	1.52
5	CSA	104	1	8	2800	2400	1.57
			2	10	3600	3010	1.78
			4	12	4300	3610	2.15
			6	13	4500	3910	2.27
			24	15	3900	4510	2.62

[a] [*n*-BuA]/[BSA] = 68/0.29 (mmol). Entry 3: [glyceraldehyde dimer] = 0.11 mmol, [pyridine] = 1.2 mmol. Entry 4: [glyceraldehyde dimer] = 0.06 mmol, [benzoic acid] = 0.20 mmol. Entry 5: [CSA] = 0.30 mmol.

Table 6. Copolymerization of *n*-Butyl Acrylate with Styrene Initiated by BSA[a]

time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	M_w/M_n
1	15	3900	1.25
2	19	5200	1.22
4	24	6700	1.21
6	28	7800	1.24
8.5	35	8200	1.32

[a] [*n*-BuA]/[styrene]/[BSA] = 39.5/39.5/0.29 (mmol) , 104 °C.

a much slower rate, and after about 5 h the color remains quite faint although observable.

Finally, the ability to achieve random copolymerization of *n*-butyl acrylate and styrene (50/50 molar ratio) in a controlled fashion was demonstrated in the presence of BSA (Table 6). The polymerization proceeded under controlled conditions until 30% conversion and then slowed down in a similar manner to the styrene homopolymerizations. Incorporation of both styrene (60%) and *n*-butyl acrylate (40%) in the final copolymer (8200 g/mol, $M_w/M_n = 1.35$) was demonstrated by ^{1}H NMR.

Conclusions

We initiated a study on the synthesis and use of 1,1-diadamantyl nitroxide (**2**) to mediate styrene and acrylate polymerizations under SFRP conditions based on previous publications showing an advantage to the use of sterically bulky nitroxides in reducing the C−O bond dissociation energies of alkoxyamines. What is striking about the results in this paper is how poorly **2** functioned under SFRP conditions for the polymerization of styrene, as well as acrylate, in light of the good results reported with other sterically hindered nitroxides. Problems in this study surfaced almost immediately with an inability to control the polymerization of styrene initiated with BPO. To circumvent these problems, the synthesis of the alkoxyamine BSA **6** was attempted by an exchange reaction of the TEMPO in BST with an excess of **2**, without much success. However, this result, in conjunction with the complete conversion in the reverse crossover reaction involving BSA, prepared eventually in good yield by an ATRA reaction with copper, demonstrated the higher thermal sensitivity of the C−ON of BSA compare to BST, a result which, at the time, was very encouraging. While the polymerization of styrene with BSA proceeded in a controlled manner at lower temperature than a corresponding polymerization with BST, the use of additives, such as benzoic acid and glyceraldehyde, in the polymerization medium was still required to enable the polymerization to go to high conversion while maintaining a good control of the molecular parameters of the polystyrene. Polymerizations of *n*-butyl acrylate polymerization initiated with BSA were no better than those initiated with BST. Moreover, addition of nitroxide destroying additives that proved efficiency for TEMPO did not improve the process in the case of BSA, which underlines the specific reactivity of **2** or, described another way, shows its insensitivity to reagents previously used to control excess TEMPO. We believe that the main reason for the poor results reported in this paper is the very high thermal stability of **2** and its accumulation in the reaction mixture due to unavoidable termination reactions between the propagating chains. As the styrene and *n*-butyl acrylate polymerizations proceeded, the reaction mixture turned orange, the color of the free nitroxide in solution. While the color change occurred in the styrene polymerization it occurred faster and to a larger degree in the *n*-butyl acrylate polymerizations. Thin-layer chromatography of a concentrated solution of the reaction mixture in dichloromethane showed an orange spot that ran the same as an authentic sample of **2**. Especially in the case of the *n*-butyl acrylate polymerizations the orange color of the reaction mixture did not change appreciably with the addition of any of the aforementioned rate accelerators. Regardless of the C−O bond dissociation energy, uncontrolled termination causes an increase in the concentration of free nitroxide, which causes an inhibition in the polymerization. If there is no means to get rid of that excess nitroxide, either by an inherent instability of the nitroxide at the reaction temperature or with the addition of additives that destroy the nitroxide in a controlled fashion, the polymerization remains inhibited. That some other nitroxides, such as *tert*-butylisopropylphenyl (TIPNO), are excellent SFRP mediators due to their inherent instability has been commented on before.[31] The results in this paper provide additional proof to the argument that the more important factor in the ability of a nitroxide to efficiently mediate acrylate polymerizations is the inherent instability of that nitroxide. While the lower C−O bond dissociation rates may allow lower polymerization temperatures, they do not enable polymerizations to proceed if the nitroxide does not possess some inherent degree of instability.

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Supporting Information Available: Tables of X-ray diffraction data (cif files) for 1,1-diadamantyl nitroxide (**2**), BST **4**, and BSA **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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