A Proximal Bisnitroxide Initiator Effective in Low Temperature Nitroxide Mediated Polymerizations

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Contents

1. Low Temperature Polymerization Studies

SI Table 1. Polymerizations of Styrene and *t*-Butyl Acrylate with Bisalkoxyamine **1** at 110 ºC

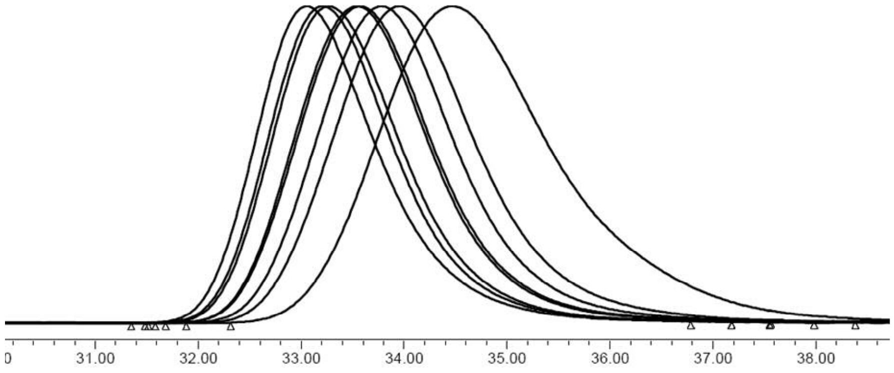
entry	monomer[a]	time (min)	% conv[b]	$M_{n,NMR}$[c] (g/mol)	$M_{n,GPC}$[d] (g/mol)	PDI[e]
1	St	180	54	11,900	12,900	1.17
2	*t*BA[f]	210	39	10,600	9,800	1.32
3	*t*BA[f]	45	10	1,900	400	3.21
4	*t*BA[f]	60	9	1,900	500	3.13
5	*t*BA[f]	75	11	2,000	700	3.20
6	*t*BA[f]	90	15	2,500	900	2.57
7	*t*BA[f]	105	24	3,700	3,700	1.45
8	*t*BA[f]	120	26	3,900	3,700	1.45

[a] 200 equiv used for entries 1 and 2, all other entries 100 equiv used. [b] Calculated from ^{1}H NMR integration. [c] Theoretical molecular weight calculated from percent conversion determined by ^{1}H NMR. [d] Number-average molecular weight measured by GPC. [e] Polydispersity index (M_w/M_n) from GPC. [f] 5% of bisnitroxide **3** was added (St = styrene, *t*BA = *t*-butyl acrylate).

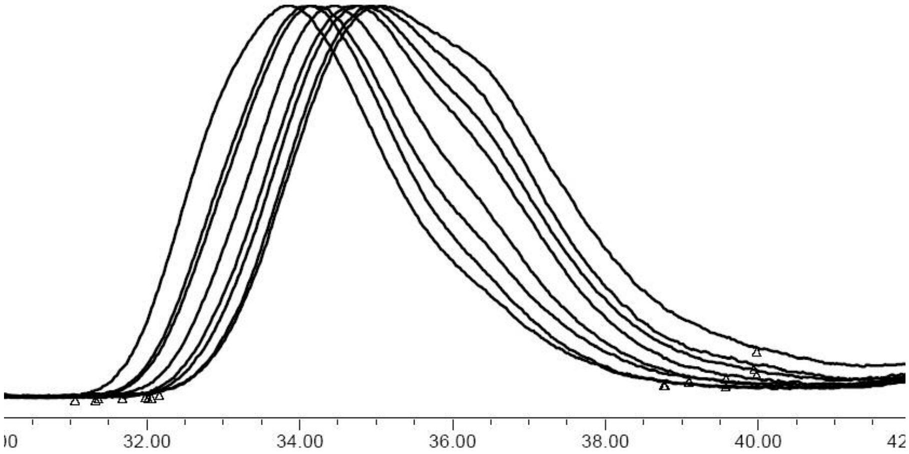
SI Table 2. Polymerizations of Styrene, *t*-Butyl Acrylate, and *n*-Butyl Acrylate with Bisalkoxyamine **1** at 90 ºC and 70 ºC

		temp	time		$M_{\mathrm{n,NMR}}$[c]	$M_{\mathrm{n,GPC}}$[d]	
entry	monomer[a]	(ºC)	(hours)	% conv[b]	(g/mol)	(g/mol)	PDI[e]
9	St	90	92	88	19,100	20,300	1.16
10	*t*BA[f]	90	92	71	18,800	20,900	1.38
11	St	70	119	33	7,500	8,000	1.24
12	*t*BA[f]	70	119	17	5,100	7,800	1.43
13	*n*BA[f]	70	119	13	4,000	3,200	1.48

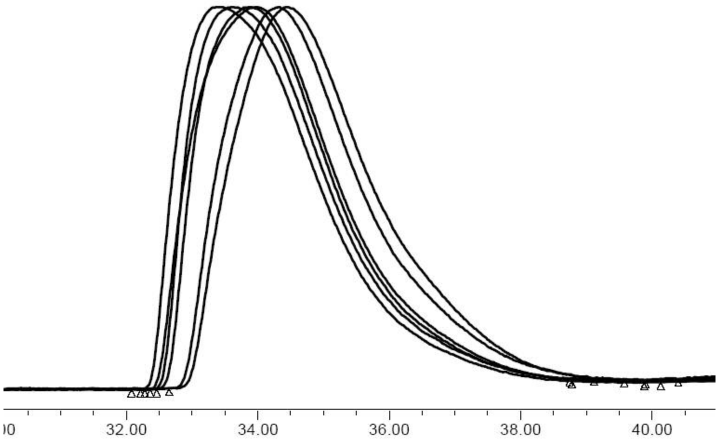
[a] 200 equiv used. [b] Calculated from ^{1}H NMR integration. [c] Theoretical molecular weight calculated from percent conversion determined by ^{1}H NMR. [d] Number-average molecular weight measured by GPC. [e] Polydispersity index (M_w/M_n) from GPC. [f] 5% of bisnitroxide **3** was added (St = styrene, *t*BA = *t*-butyl acrylate, *n*BA = *n*-butyl acrylate).



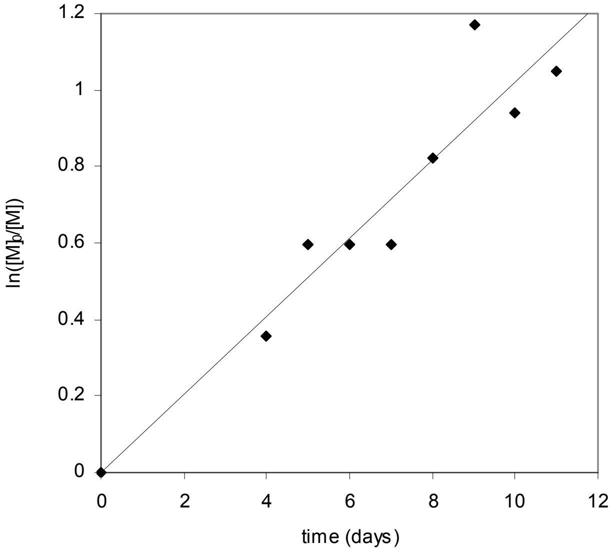
SI Figure 1: Time study GPC traces for polystyrene using initiator **1**. Percent conversions based on ^{1}H NMR data are (beginning from the right to left) 30, 45, 45, 45, 56, 69, 61, and 65. Each polymerization was run with 600 equivalents of styrene at 70 ºC.



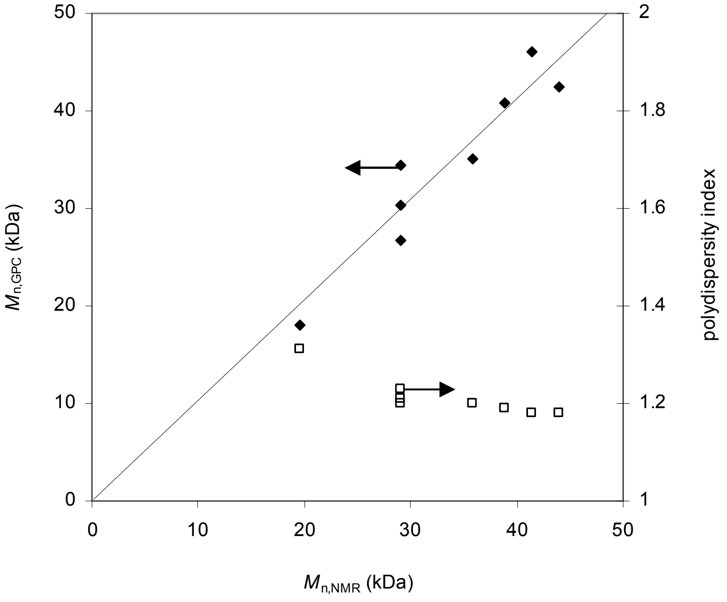
SI Figure 2: Time study GPC traces for poly(*t*-butylacrylate) using initiator **1**. Percent conversions based on ^{1}H NMR data are (beginning from the right to left) 10, 10, 11, 16, 17, 20, 17, and 24. Each polymerization was run with 600 equivalents of *t*-butylacrylate at 70 ºC.



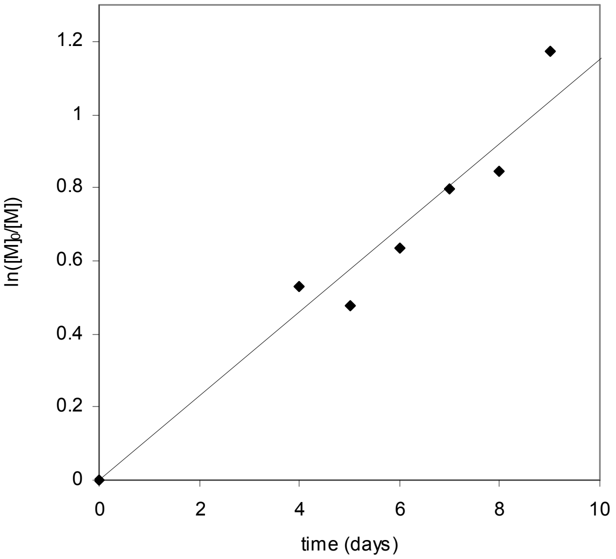
SI Figure 3: Time study GPC traces for poly(dimethylacrylamide) using initiator **1**. Percent conversions based on ^{1}H NMR data are (beginning from the right to left) 41, 38, 47, 55, 57, and 69. Each polymerization was run with 600 equivalents of dimethylacrylamide at 70 ºC.



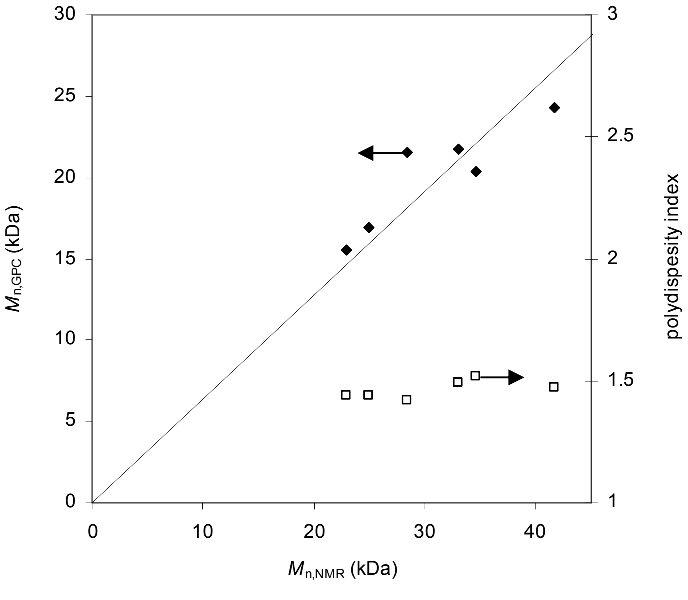
SI Figure 4. Styrene polymerization with initiator **1** at 70 ºC.



SI Figure 5. Evolution of $M_{\mathrm{n,GPC}}$ (molecular weight determined by GPC) and polydispersity index (M_w/M_n) as a function of $M_{\mathrm{n,NMR}}$ (molecular weight calculated from ^{1}H-NMR) for the polymerization of styrene at 70 ºC with bidirectional initiator **1**.



SI Figure 6. Dimethylacrylamide polymerization with bisalkoxyamine initiator **1** at 70 ºC.



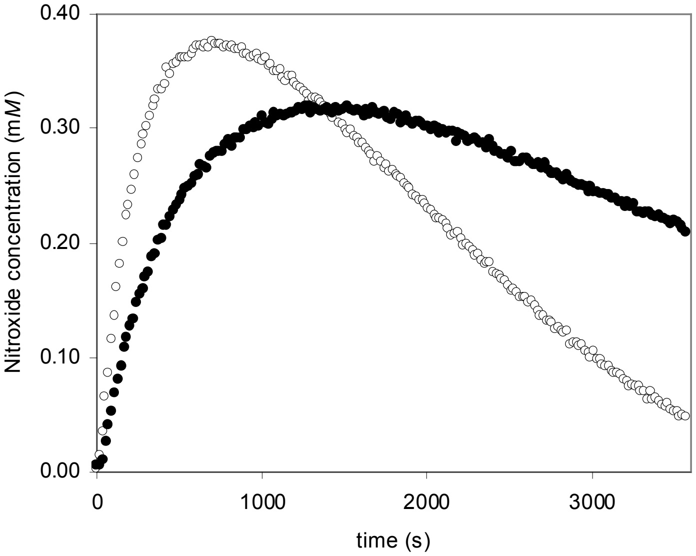
SI Figure 7. Evolution of $M_{n,GPC}$ (molecular weight determined by GPC) and polydispersity index (M_w/M_n) as a function of $M_{n,NMR}$ (molecular weight calculated from ^{1}H-NMR) for the polymerization of dimethylacrylamide at 70 ºC with bidirectional initiator **1**.

SI Table 3. Preparation of A and ABA Triblock Copolymers at 70 ºC

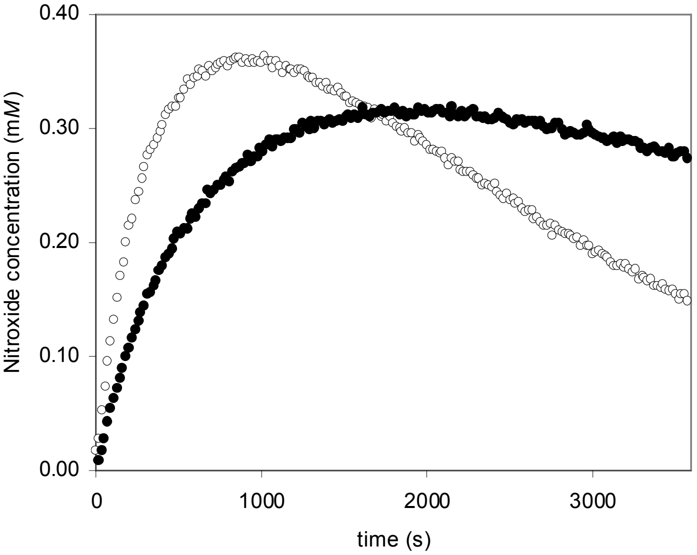
		time (days)	$M_{n,NMR}$[a] (g/mol)	$M_{n,GPC}$[b] (g/mol)	PDI[c]
A block	P*t*BA	5	4,300	4,100	1.57
ABA triblock	P*t*BA-PS[d]-P*t*BA	6	11,300	22,300	1.29
A block	P*n*BA	5	6,700	5,000	1.59
ABA triblock	P*n*BA-P*t*BA[d]-P*n*BA	6	10,000	7,600	1.49

[a] Theoretical molecular weight calculated from percent conversion determined by ^{1}H NMR integration. [b] Number-average molecular weight measured by GPC. [c] Polydispersity index (M_w/M_n) from GPC. [d] 400 equivalents used (St = styrene, *t*BA = *t*-butyl acrylate, *n*BA = *n*-butyl acrylate).

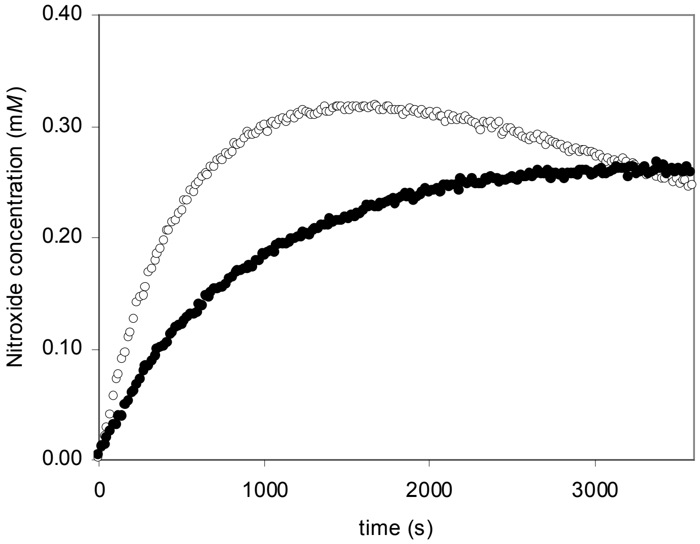
2. EPR Thermal Homolysis Studies



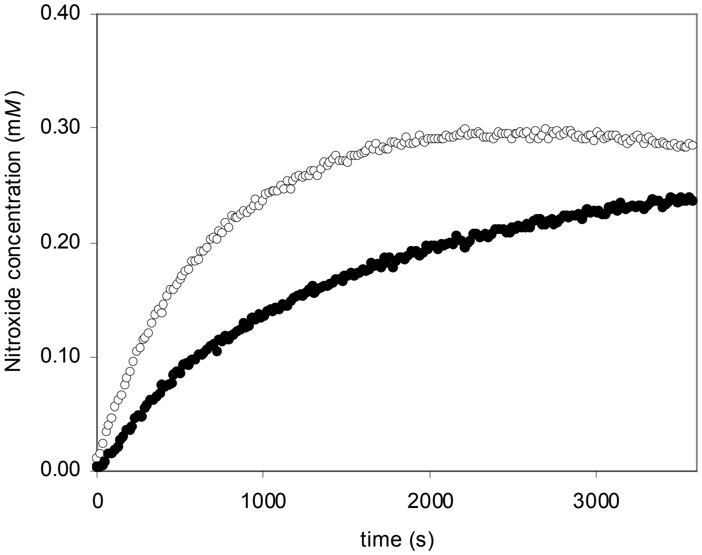
SI Figure 8. Nitroxide concentration measured by EPR as a function of time for the homolysis of bisalkoxyamine initiator **1** (○) and parent alkoxyamine initiator **2** (●) when heated at 378 K in the presence of oxygen.



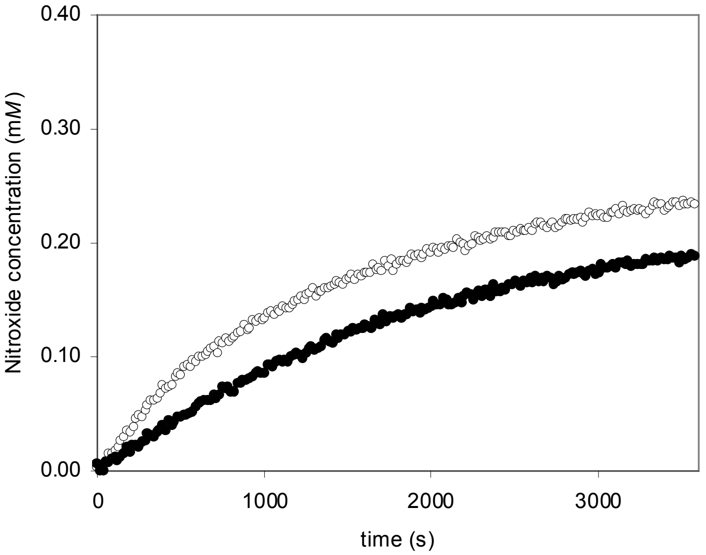
SI Figure 9. Nitroxide concentration measured by EPR as a function of time for the homolysis of bisalkoxyamine initiator **1** (○) and parent alkoxyamine initiator **2** (●) when heated at 373 K in the presence of oxygen.



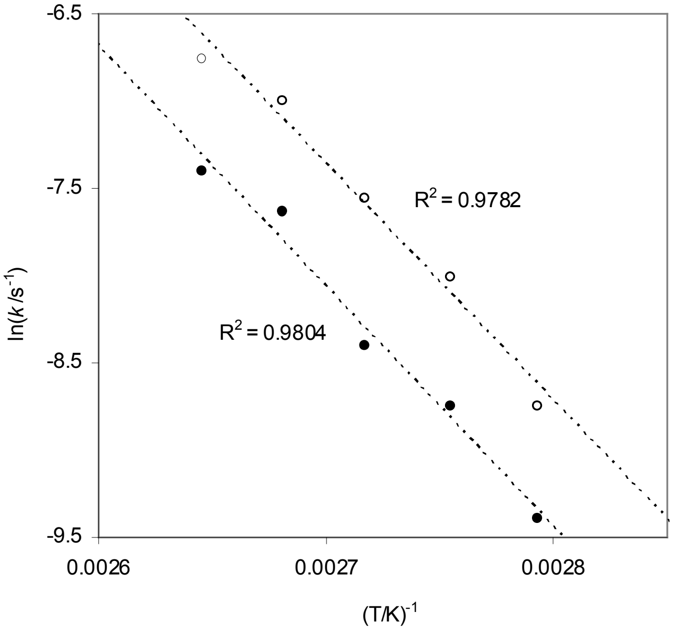
SI Figure 10. Nitroxide concentration measured by EPR as a function of time for the homolysis of bisalkoxyamine initiator **1** (○) and parent alkoxyamine initiator **2** (●) when heated at 368 K in the presence of oxygen.



SI Figure 11. Nitroxide concentration measured by EPR as a function of time for the homolysis of bisalkoxyamine initiator **1** (○) and parent alkoxyamine initiator **2** (●) when heated at 363 K in the presence of oxygen.

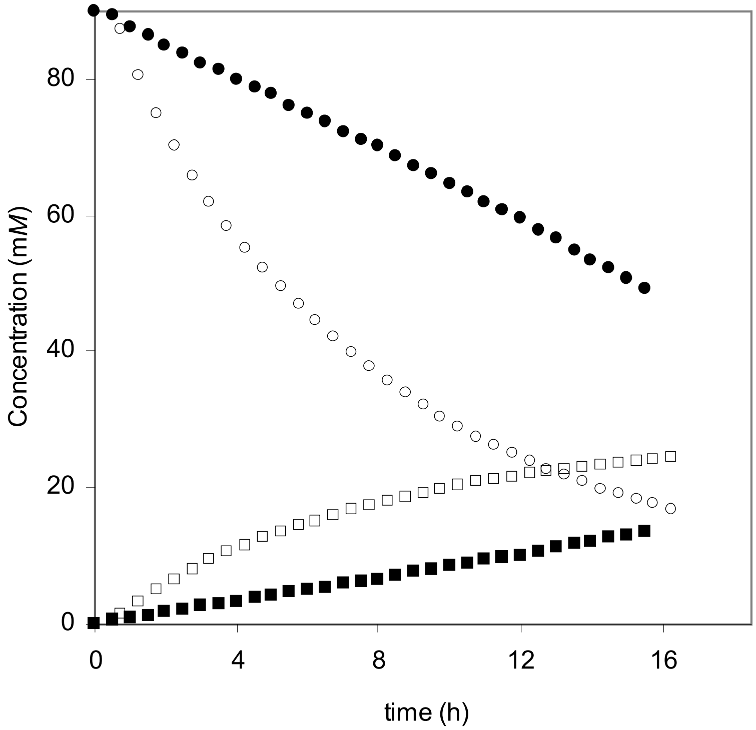


SI Figure 12. Nitroxide concentration measured by EPR as a function of time for the homolysis of bisalkoxyamine initiator **1** (○) and parent alkoxyamine initiator **2** (●) when heated at 358 K in the presence of oxygen.



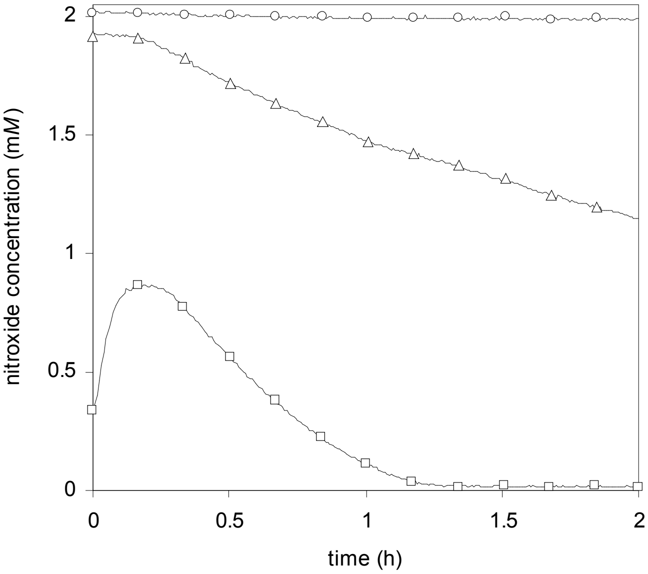
SI Figure 13. Arrhenius plot for the homolytic cleavage of bisalkoxyamine **1**(○) and mono alkoxyamine **2** (●).

3. ^{1}H-NMR Alkoxyamine Decomposition Studies

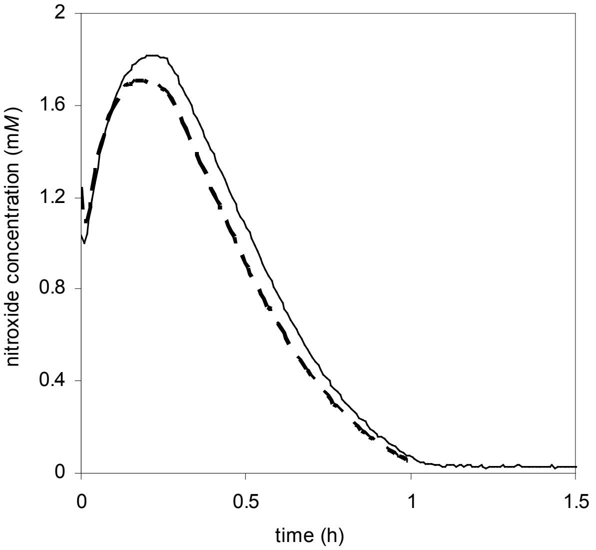


SI Figure 14. Alkoxyamine (A) and styrene (S) concentrations as a function of time when 90m*M* solutions of alkoxyamine **2** (● = [A]; ■ = [S]) and TEMPO-based alkoxyamine **5** (○ = [A]; □ = [S]) were heated at 125 ºC in *p*-xylene-d_{10}. Concentrations were calculated from ^{1}H-NMR integration values.

4. EPR Nitroxide Decomposition Studies



SI Figure 15. Variation of nitroxide concentration with time upon heating of bisnitroxide **3** (□), mononitroxide **4** (△), and TEMPO (○) at 120 °C. Scans were taken every 30 to 60 seconds; only selected data points are shown for clarity. Nitroxide samples **3** and **4** were synthesized, flashed, and stored in *t*-butyl benzene (2 m*M* nitroxide concentration) at 0 °C for 1 day prior to use.



SI Figure 16. Variation of nitroxide concentration with time upon heating a 4.0 m*M* solution of bisnitroxide **3** in *t*-butylbenzene at 120 °C. Bisnitroxide samples for trial 1 (▬ ▬ ▬) and trial 2 (———) were synthesized separately.

5. Kinetic Equations for the Homolytic Cleavage of Mono- and Bisalkoxyamine

The dissociation of a monoalkoxyamine, A, into a nitroxide $N^\bullet$ and a transient radical $P^\bullet$ is shown in equation SI.1.

$$\mathrm{A} \xrightarrow{k_\mathrm{d}} \mathrm{N}^\bullet + \mathrm{P}^\bullet \tag{SI.1}$$

The first order integrated rate law for this reaction is

$$\ln\left(\frac{[\mathrm{A}]_0 - [\mathrm{N}]}{[\mathrm{A}]_0}\right) = -k_\mathrm{d}t \tag{SI.2}$$

Eventually, all of the alkoxyamine turns into nitroxide, so $[\mathrm{A}]_0$ is equal to $[\mathrm{N}]_\infty$ and equation SI.2 can be written as the plateau method (equation SI.3).

$$\ln\left(\frac{[\mathrm{N}]_\infty - [\mathrm{N}]}{[\mathrm{N}]_\infty}\right) = -k_\mathrm{d}t \tag{SI.3}$$

When the nitroxide undergoes thermal decomposition, equation SI.3 cannot be used. Instead, the initial slope method (equation SI.4) is used.

$$k_\mathrm{d} = \frac{\left(\frac{d[\mathrm{N}]}{dt}\right)_{t=0}}{[\mathrm{A}]_0} \tag{SI.4}$$

The dissociation of a bisalkoxyamine occurs in two steps. There are two possible transient radicals that can dissociate from the bisalkoxyamine AA, hence the rate constant $2k_\mathrm{d}$. Once the monoalkoxyamine $\mathrm{AN}^\bullet$ forms, there is only one possible transient radical that can dissociate, so the rate constant in equation SI.6 is only k_d. This assumes that the dissociation of the second radical is independent of the dissociation of the first radical.

$$\mathrm{AA} \xrightarrow{2k_\mathrm{d}} \mathrm{AN}^\bullet + \mathrm{P}^\bullet \qquad \text{(SI.5)}$$

$$\mathrm{AN}^\bullet \xrightarrow{k_\mathrm{d}} {}^\bullet\mathrm{NN}^\bullet + \mathrm{P}^\bullet \qquad \text{(SI.6)}$$

The rate laws for $\mathrm{AN}^\bullet$ and ${}^\bullet\mathrm{NN}^\bullet$ are

$$\frac{d[\mathrm{AN}^\bullet]}{dt} = 2k_\mathrm{d}[\mathrm{AA}] - k_\mathrm{d}[\mathrm{AN}^\bullet] \qquad \text{(SI.7)}$$

$$\frac{d[{}^\bullet\mathrm{NN}^\bullet]}{dt} = k_\mathrm{d}[\mathrm{AN}^\bullet] \qquad \text{(SI.8)}$$

In the EPR analysis of this reaction, it is the *total* concentration of nitroxide functionalities, [N], that is physically measured. Each $\mathrm{AN}^\bullet$ species contains one nitroxide functionality, and each ${}^\bullet\mathrm{NN}^\bullet$ species contains two nitroxide functionalities, to give

$$[\mathrm{N}] = [\mathrm{AN}^\bullet] + 2[{}^\bullet\mathrm{NN}^\bullet] \qquad \text{(SI.9)}$$

Taking the derivative of equation SI.9 with respect to time gives

$$\frac{d[\mathrm{N}]}{dt} = \frac{d[\mathrm{AN}^\bullet]}{dt} + 2\frac{d[{}^\bullet\mathrm{NN}^\bullet]}{dt} \qquad \text{(SI.10)}$$

and substituting in equations SI.7 and SI.8 gives

$$\frac{d[\mathrm{N}]}{dt} = 2k_\mathrm{d}[\mathrm{AA}] + k_\mathrm{d}[\mathrm{AN}^\bullet] \qquad \text{(SI.11)}$$

From the stoichiometry of the reaction, $[\mathrm{AA}] = [\mathrm{AA}]_0 - [\mathrm{AN}^\bullet] - [{}^\bullet\mathrm{NN}^\bullet]$, and equation SI.11 can be rewritten as

$$\frac{d[\mathrm{N}]}{dt} = 2k_{\mathrm{d}}([\mathrm{AA}]_0 - [\mathrm{AN}^\bullet] - [{}^\bullet\mathrm{NN}^\bullet]) + k_{\mathrm{d}}[\mathrm{AN}^\bullet] \tag{SI.12}$$

which simplifies to

$$\frac{d[\mathrm{N}]}{dt} = k_{\mathrm{d}}(2[\mathrm{AA}]_0 - [\mathrm{N}]) \tag{SI.13}$$

This first order rate law is integrated to give

$$\ln\left(\frac{2[\mathrm{AA}]_0 - [\mathrm{N}]}{2[\mathrm{AA}]_0}\right) = -k_{\mathrm{d}}t \tag{SI.14}$$

Because each bisalkoxaymine eventually forms two nitroxide moieties, $2[\mathrm{AA}]_0$ is equal to $[\mathrm{N}]_\infty$, and equation SI.14 reduces to the same equation that is used in the plateau method for monoalkoxyamines (equation SI.3) For nitroxides that undergo thermal decomposition, equation SI.14 cannot be used. Instead, equation SI.13 is evaluated at time $t = 0$ to give the initial slope equation for k_{d}.

$$k_{\mathrm{d}} = \frac{\left(\frac{d[\mathrm{N}]}{dt}\right)_{t=0}}{2[\mathrm{AA}]_0} \tag{SI.15}$$

Because 2[AA] is equal to the concentration of *alkoxyamine functionality*, equation SI.15 reduces to the same equation that is used in the initial slope method for monoalkoxyamines (equation SI.4), where $[\mathrm{A}]_0$ = the initial concentration of alkoxyamine functionality.

The above derivation assumes that the dissociation of the second nitroxide moiety occurs at the same rate as the dissociation of the first nitroxide moiety. This may not be the case, and a more general form of the dissociation reaction for a bisalkoxyamine is given by equations SI.16 and SI.17.

$$\mathrm{AA} \xrightarrow{2k_1} \mathrm{AN}^{\bullet} + \mathrm{P}^{\bullet} \tag{SI.16}$$

$$\mathrm{AN}^{\bullet} \xrightarrow{k_2} {}^{\bullet}\mathrm{NN}^{\bullet} + \mathrm{P}^{\bullet} \tag{SI.17}$$

Equation SI.10 can be rewritten as

$$\frac{d[\mathrm{N}]}{dt} = 2k_1[\mathrm{AA}] + k_2[\mathrm{AN}^{\bullet}] \tag{SI.18}$$

and evaluating this equation at $t = 0$ gives

$$k_1 = \frac{\left(\dfrac{d[\mathrm{N}]}{dt}\right)_{t=0}}{2[\mathrm{AA}]_0} \tag{SI.19}$$

because $[\mathrm{AN}^{\bullet}] = 0$ at $t = 0$. Equation SI.19 is the same as equation SI.15, except that the rate constant which is measured by this initial slope method is k_1.