Stable Free Radical Polymerization Process: Kinetic and Mechanistic Study of the Thermal Decomposition of MB-TMP Monitored by NMR and ESR Spectroscopy

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ABSTRACT: A detailed experimental investigation was conducted to study the thermal decomposition of the nitroxide adduct *N*-(1′-methylbenzyloxy)-2,2,6,6-tetramethylpiperidine (MB-TMP) at elevated temperatures using ^{1}H NMR and ESR spectroscopy. At 125 °C, the concentration of TEMPO was followed by ESR spectroscopy, while ^{1}H NMR spectroscopy was employed to monitor MB-TMP and the various byproducts of MB-TMP decomposition: styrene, *N*-hydroxylamine of TEMPO, acetophenone, and *sec*-phenethyl alcohol. A mechanism was developed to describe the formation of these various products. When oxygen is present in the system, even in trace amounts, the inhibiting effect of aerial oxygen via autoxidation preferentially competes with the reversible capping of 1-phenylethyl radical by TEMPO, which produced acetophenone and *sec*-phenethyl alcohol.

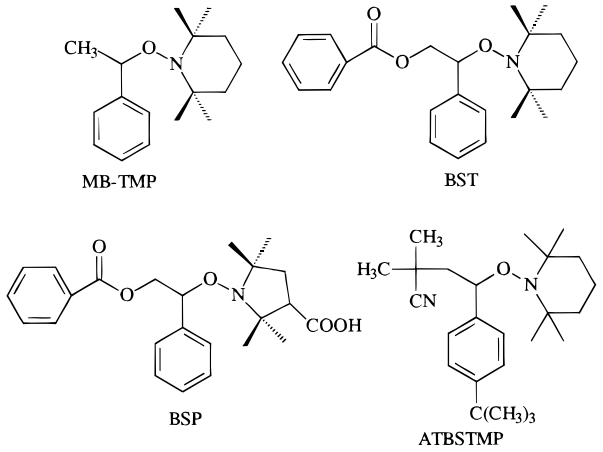
Introduction

Since the initial report by Georges et al.[1] in 1993 on the "living" nitroxide-mediated stable free radical polymerization (SFRP) of styrene, numerous publications employing this controlled polymerization process have been reported. These include key publications on the kinetic and mechanistic studies of chain initiation[2] and methods to control and increase the rate of propagation.[3,4] One method to initiate the SFRP process can be accomplished by employing conventional thermally labile initiators such as benzoyl peroxide (BPO)[1] or azobis(isobutyronitrile) (AIBN). A second approach to initiate SFR polymerization is to employ alkoxyamines, which can be isolated from an oligomeric reaction or synthesized independently from the polymerization using simple organic chemistry. To control the number of initiating species in a SFR polymerization, alkoxyamines are used to provide a clean and simplified initiating system.

Numerous groups have used the alkoxyamine approach to initiate controlled stable free radical polymerization. Veregin et al.[3c] initially reported the synthesis and isolation of unimers BST and BSP. Abrol et al.[5] prepared "one-pot" microgels using the initiating adduct ATBSTMP to polymerize *tert*-butylstyrene and divinylbenzene at 130 °C for 72 h.

Hawker[6] isolated the TEMPO-based initiator BST and used it to initiate an SFR polymerization of styrene to produce block copolymers with *p*-acetoxymethylstyrene. In addition, telechelic[7] and random copolymers[8] were prepared by hydrolyzing the benzoyloxy group of BST with KOH to produce the hydroxyl derivative as the initiator, prior to polymerization. Priddy et al. also utilized the hydroxyl derivative of BST to initiate block copolymer[9] synthesis. Dendritic block copolymers,[10] three-armed polystyrene star polymers,[11] hyperbranched polymers,[12] and various block copolymers[13] have all been prepared utilizing derivatives of BST. In all cases, BST was isolated and purified from the oligomeric reaction mixture of BPO, styrene, and TEMPO.

Independent of the polymerization, alkoxyamines or unimolecular nitroxide adducts were prepared by a variety of different organic reactions. Moffat et al.[14] have used low-temperature conditions to prepare *N*-(1′-methylbenzyloxy)-2,2,6,6-tetramethylpiperidine (MB-TMP) and other adducts[15] from the reaction of tributyltin hydride with alkyl or aryl halides and nitroxides. Braslau et al.[16] reported several different synthetic routes to produce carbon radicals that were subsequently trapped by TEMPO, which included PbO_2 with benzylic radicals and phenylhydrazines. Also, nitroxide adducts were generated from the oxidation reaction of lithium enolates[16] by $CuCl_2$ followed by carbon-centered radical trapping with TEMPO.



Hawker has prepared unimolecular initiators[17] using two different methods. First, benzylic radicals of organometallic reagents were trapped with TEMPO at −78 °C. This reaction required 5 mol equiv of TEMPO to obtain reasonable reaction yields of 86%. If the temperature was increased, the yield of the nitroxide adducts decreased significantly. The second route to MB-TMP, first reported by Priddy and Howell,[18] involved the reaction of ethylbenzene with *tert*-butyl peroxide in the presence of TEMPO at the refluxing temperature of ethylbenzene (136 °C). MB-TMP was used to initiate novel styrenic graft copolymers[19] and block copolymers.[20]

Other adducts, A−T and T−A−T, were prepared from ethylbenzene and di-*tert*-butyl nitroxide by Catala et

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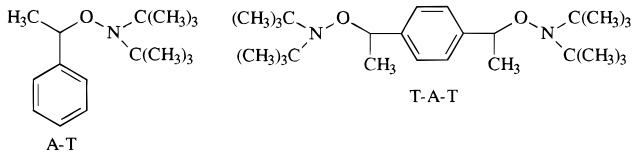
al.[21] and used in their kinetic studies of the SFRP of styrene at 80−100 °C and to initiate the SFRP of styrene in opposing directions. In addition to the small molecule organic preparative methods, photochemical reactions have been used to prepare similar nitroxide adducts as reported by Scaiano.[22]



In addition to initiation of SFR polymerization by nitroxide adducts, these compounds can be used to study potential termination reactions in the polymerization and to identify various chain end functional groups derived from chain termination. Early work by Solomon et al.[23,24] on nitroxides trapping carbon-centered radicals showed that hydrogen abstraction by the nitroxide from MA and MMA occurred. In some cases, the formation of the *N*-hydroxylamine was detected. It was proposed for the SFR polymerization that a similar hydrogen abstraction from the β-carbon of the propagating chain end by another molecule of nitroxide could result in a terminal vinyl group. This reaction would terminate the chain, prevent further chain growth, and produce the *N*-hydroxylamine. Upon exposure to air, the hydroxylamine would then be oxidized to the nitroxyl radical.

Other groups working in the SFRP area have suggested that TEMPO is involved in hydrogen abstraction, but the experimental proof for the formation of the corresponding *N*-hydroxylamine is not conclusive. Connolly and Scaiano[25] heated TEMPO in the presence of toluene, ethylbenzene, or cumene for 12 h and observed the formation of nitroxide adducts produced by initial hydrogen radical abstraction from the benzylic position. They implied that during a SFR polymerization subsequent hydrogen radical abstraction from the benzylic carbon in a polystyrene chain could occur, creating branching points for additional SFR polymerization. Conclusive experimental evidence for branching in polystyrene chains has not been found.

Yoshida and Okada[26] studied the nitroxide radical transformation of a low molecular weight polystyrene (M_n = 2170, MWD = 1.15) in benzene at 130 °C. The starting polystyrene was capped with 4-hydroxy-TEMPO. After 24 h, 80% of the nitroxide chain ends were substitution with 4-methoxy-TEMPO instead of the 4-hydroxy-TEMPO. When pushed further, the degree of substitution decreased with time. This was attributed to hydrogen radical abstraction from the β-carbon by 4-methoxy-TEMPO to produce a terminal vinyl group and the resulting *N*-hydroxylamine of 4-methoxy-TEMPO. The signals discerned at 5.9−6.2 ppm were attributed to one of the vinyl protons. NMR evidence for the hydroxylamine was not reported. The important conclusion from this work is that to produce a terminal vinyl group at the end of a polystyrene chain required very long reaction times (>24 h). These conditions are not normal SFR polymerization conditions.

Li, Howell, and Priddy[27,28] reported a proposed mechanism for the decomposition of MB-TMP involving hydrogen radical abstraction by TEMPO to produce the corresponding *N*-hydroxylamine and styrene as the major reaction products. Additional secondary reactions were included in their mechanism such as the coupling of two 1-phenylethyl radicals to explain the presence of 2,3-diphenylbutane and smaller quantities of ethylbenzene prepared by reacting the 1-phenylethyl radical with a hydrogen radical source, such as *N*-hydroxylamine. To produce 2,3-diphenylbutane, the instantaneous concentration of 1-phenylethyl radicals must be significantly high for this dimer to form. The temperature at which this study was conducted was 140 °C. At 140 °C, the rate constant for homolytic cleavage of the C−ON bond in MB-TMP is higher, thus enabling larger concentrations of 1-phenylethyl radicals which led to the formation of the dimer 2,3-diphenylbutane. Using HPLC and ^{1}H NMR, they monitored the thermal decomposition kinetics of MB-TMP in 1,2,4-trichlorobenzene, DMSO-d_6, and toluene. On the basis of these results, they concluded that the nitroxide-capped polystyrene chain end undergoes a similar decomposition reaction and is likely a major source of polydispersity broadening.

This paper reports our kinetic study on the thermal decomposition of MB-TMP at elevated temperatures using high-temperature ^{1}H NMR and ESR spectroscopy to identify and quantify the various reaction products. In this study, the effect of aerial oxygen is reported and included in a modified mechanism. The differences in this mechanism as compared to that of Li et al.[27,28] for MB-TMP decomposition are also discussed.

Experimental Section

Measurements. All nitroxide adduct solutions were prepared in an Innovative Technology Inc. drybox model system 1DC. The drybox was equipped with moisture and O_2 detectors. The atmosphere in the drybox was anhydrous argon. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on either a 400 MHz Bruker AMX400 or a 300 MHz Bruker DPX300 spectrometer. The ^{1}H NMR spectra were referenced internally to the solvent, either $CDCl_3$, toluene-d_8, or *o*-xylene-d_{10}. The sample temperature was controlled using a Bruker BVT-1000 temperature controller. Electron spin resonance (ESR) spectra were collected using a Bruker ESP300 spectrometer and ER4111 variable temperature accessory.

Materials. All reagents were purchased from Aldrich and used as is. The solvent diethyl ether, anhydrous (Caledon), was dried over 4 Å molecular sieves (Aldrich).

Preparation of N-(1′-Methylbenzyloxy)-2,2,6,6-tetramethylpiperidine (MB-TMP). The synthetic method outlined by Anderson et al.[29] was used to prepare MB-TMP. The reagents (1-bromoethyl)benzene (2.3 g, 12.5 mmol) and TEMPO (3.84 g, 25 mmol), dissolved in anhydrous diethyl ether (100 mL), were added into a 250 mL three-necked round-bottom (RB) flask equipped with an argon purge, reflux condenser, $CaCl_2$ drying tube, dropping funnel, and stirring bar which was cooled in an ice water bath. Using a dropping funnel, tributyltin hydride was added to the TEMPO aryl halide solution at a rate to maintain the reaction temperature below 10 °C. The mixture was stirred for 4 h and then allowed to warm to room temperature. The solution was concentrated with a rotary evaporator to produce an oily crude mixture of MB-TMP. The crude mixture was passed through a column of silica gel using flash chromatography[30] techniques utilizing CH_2Cl_2 as the eluting solvent for the first pass and 2% ethyl actetate/98% CH_2Cl_2 in the second pass. Pure crystalline MB-TMP (2.0 g, 62.4%) was obtained. mp: 48−50 °C (lit.[31] 44.5−45.0 °C, lit.[32] 46−47 °C). MS (CI) *m*/*z* (RI%): 262 (38%), 157 (47%), 142 (100%), 105 (45%). ^{1}H NMR ($CDCl_3$/TMS) [400 MHz] at 243 K: δ 0.635, 1.016, 1.166, 1.308 (each as sharp s, 12H, CH_3), 1.36−1.38 (m, 6H, CH_2), 1.48 (d, J = 7 Hz, 3H, CH(C**H**$_3$)), 4.75 (quartet, J = 7 Hz, 1H, C**H**(CH_3)), 6.21−7.20 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) [100.6 MHz] at 243 K: δ 16.88 (CH_2 at C4 of piperidine ring), 20.11 (2C, anti CH_3 to N lone pair), 23.97 (CH(**C**H$_3$)), 33.83, 34.21 (2C, syn CH_3 to N lone pair), 39.75,

Table 1. Initial TEMPO Concentration and Release Rate of TEMPO for Nitroxide Adduct MB-TMP

$[MB\text{-}TMP]_0$ (M)	temp (°C)	solvent	$[TEMPO]_0$ (M)	rate 1 (s^{-1})	rate 2 (s^{-1})
1.126×10^{-1}	103	toluene-d_8	2.0×10^{-5}	2.64×10^{-2}	4.94×10^{-4}
1.11×10^{-1}	125	*o*-xylene-d_{10}	4.43×10^{-5}	1.21×10^{-2}	1.38×10^{-3}
1.23×10^{-1}	132	*o*-xylene-d_{10}	3.14×10^{-6}	4.43×10^{-2}	3.02×10^{-4}

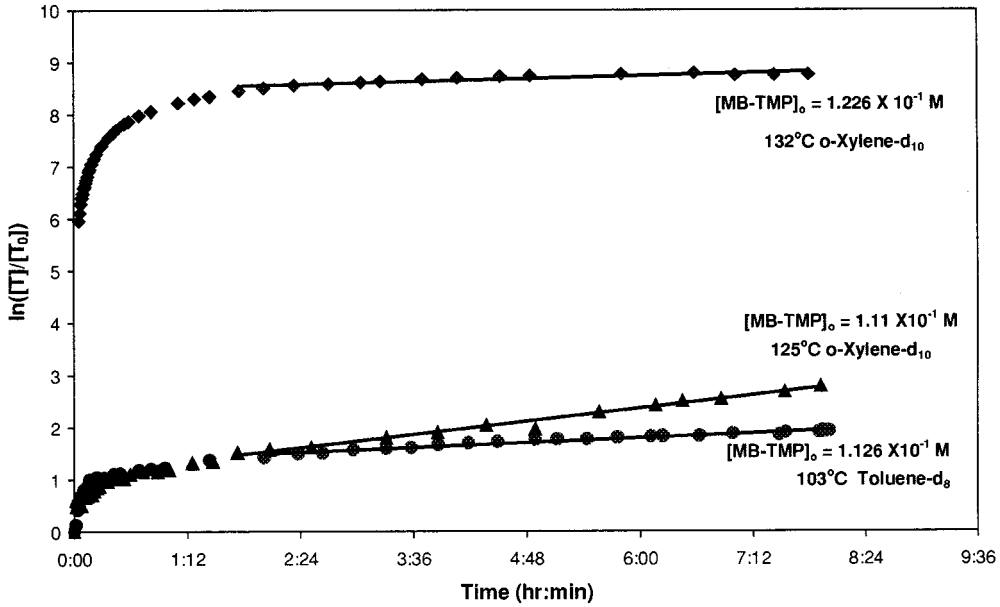


Figure 1. Plot of $\ln([T]/[T]_0)$ vs time for nitroxide adduct MB-TMP at 103, 125, and 132 °C obtained by ESR spectroscopy.

39.78 (2C, CH_2 at C3 and C5 of piperidine ring), 59.37, 59.52 (2C, quaternary C2 and C6 of piperidine ring), 83.08 (**C**H-(CH_3)), 126.32, 126.65, 127.91 (5C, aromatic CH), 145.58 (aromatic quaternary C).

Sample Preparation of MB-TMP for High-Temperature ^{1}H NMR and ESR Experiment. The nitroxide adduct MB-TMP was recrystallized from cold ethanol and dried under vacuum to remove residual solvent and moisture. All sample preparation was performed in a drybox. Into a 50 mL beaker was dissolved 32 mg of MB-TMP in 1 mL of *o*-xylene-d_{10}. Into an 8 in. thin-walled NMR tube, constricted 1 in. from the top of the tube, was added 650 μL of this solution using a syringe, and then the tube was attached to a Wilmad Taperlok NMR valve. Similarly, for the ESR sample, 110 mg of the above solution of MB-TMP in *o*-xylene-d_{10} was added into a NMR tube, and the tube was attached to a Wilmad Taperlok NMR valve. The sealed samples were removed from the drybox and attached to a vacuum line. Using the freeze−pump−thaw (FPT) technique, each sample was degassed 4−5 times to remove molecular oxygen and then sealed under vacuum.

Since the ESR and the ^{1}H NMR experiments were performed on the same adduct solution, the temperatures of the ESR cavity and the NMR sample probe were adjusted to the same temperature, within ±0.5 K. The internal temperature of the ESR cavity was calibrated using a solution of *o*-xylene-d_{10} in a NMR tube containing a thermocouple placed in the solvent. Similarly, the NMR probe was calibrated with ethylene glycol using the procedure outlined by Raiford[33] and Ammann.[34] The ^{1}H NMR spectra were referenced internally to the residual methyl protons in the solvent *o*-xylene-d_{10} which appeared at 2.25 ppm.

Results and Discussion

Thermal Decomposition of MB-TMP Monitored by ESR Spectroscopy. The increase in TEMPO concentration at elevated temperatures during the thermal decomposition of MB-TMP was measured as a function of time by ESR spectroscopy. The initial concentrations of MB-TMP in either toluene-d_8 or *o*-xylene-d_{10} were relatively low—0.113, 0.111, and 0.123 M—so that as the ESR experiment progressed, the unpaired electron concentration would not saturate the signal toward the end of the experiment. Since the same concentration of MB-TMP was used in the NMR experiment, the ^{1}H signals had to be intense enough to enable a short data acquisition time (NS = 16). Prior to heating the samples, the initial concentration of free TEMPO was measured and is reported in Table 1. Even though MB-TMP can be isolated as a very pure solid, upon dissolving it in a solvent, free nitroxide (10^{-6}−10^{-5} M) was readily detected by ESR spectroscopy. Some researchers[35] have reported that a 1:1 stoichiometric ratio of initiating radicals to nitroxide is present when alkoxyamines are employed as initiator for the SFRP process. In solution, this is not completely accurate as reported by Veregin et al.[36] even though under normal stoichiometric ratio considerations a 1:1.00001 molar ratio is essentially a 1:1 molar ratio. There is always a small amount of free nitroxide present in solution with MB-TMP, which has been detected in our ESR studies,[37] and this excess of nitroxide affects the rate of SFR polymerization.

Figure 1 is an ESR kinetic plot of $\ln([T]/[T_0])$ vs time, showing the increase in TEMPO concentration as the thermal decomposition of MB-TMP proceeded. MB-TMP was evaluated at three different temperatures (103, 125, and 132 °C), and as expected, the rate of liberation of free TEMPO is the greatest at the highest temperature. Each curve contains two distinct regimes. In the first and steepest portion of the curve, the observed rate constant is largely controlled by the liberation of free TEMPO that is required to establish the equilibrium with the dormant adduct. The observed rate constants for this region are presented in Table 1 and are denoted as rate 1. All values are approximately 10^{-2} s^{-1}. This rate is quite slow in comparison to the trapping of carbon-centered radicals by the nitroxide,[38] which is close to a diffusion-controlled reaction with a rate

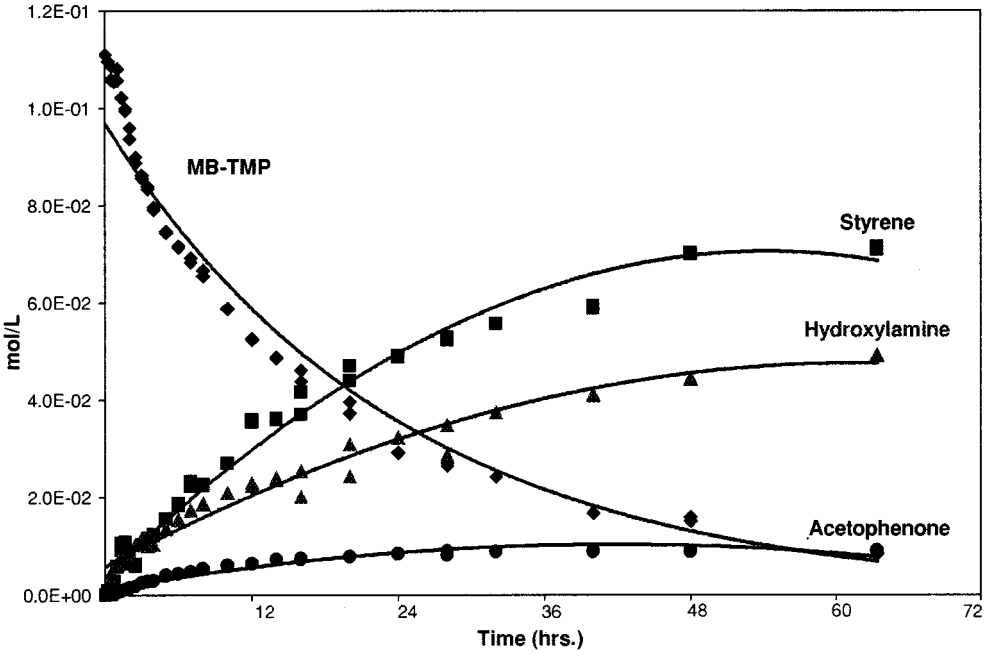


Figure 2. Plot of mol/L of MB-TMP, styrene, the *N*-hydroxylamine derivative of TEMPO, and acetophenone production as a function of reaction time at 125 °C.

constant k_L that approximately equals 10^9 M^{-1} s^{-1}. In *o*-xylene-d_{10}, MB-TMP at 125 °C released TEMPO at a rate of 1.21×10^{-2} s^{-1} while at 132 °C the rate was 4.43×10^{-2} s^{-1}, approximately 4 times faster. At 103 °C in toluene-d_8, free TEMPO was produced at a rate of 2.64×10^{-2} s^{-1}, indicating that the choice of solvent has a secondary effect. The initial steep portion in all three data sets (Figure 1) leveled off after 60 min.

In the second portion of each curve in Figure 1, the increase in free TEMPO has slowed, 10^{-4} to 10^{-3} s^{-1}. At this point in the reaction, not only is the carbon-centered radical of 1-phenylethyl trapped by the nitroxide but other products are formed in significant quantities, and these products continue to grow as the decomposition of the adduct is pushed to completion. These decomposition reactions occur throughout the experiment but are 10−100 times slower than the equilibrium reaction between the dormant capped adduct and the free nitroxide and exposed styryl radical. The experimental evidence to support a faster radical trapping rate constant of 1-phenylethyl radical by TEMPO versus the rate of adduct decomposition is illustrated by the amount of time necessary to completely decompose adduct MB-TMP. At 125 °C, 64 h was required to completely decompose MB-TMP as illustrated in Figure 2. The rate of trapping of the 1-phenylethyl radical by TEMPO is very efficient at close to a diffusion-controlled rate, and it is this fast rate of capture that is responsible for the longevity of MB-TMP at 125 °C. This efficient rate of capture of the 1-phenylethyl radical by TEMPO is key to the SFRP process.

Product Study of Thermal Decomposition of MB-TMP by High-Temperature ^{1}H NMR Spectroscopy. To complement the kinetic ESR experiment, a ^{1}H NMR experiment at 125 °C in *o*-xylene-d_{10} was performed to monitor the formation of byproducts from the decomposition of MB-TMP.

The byproducts of the thermal decomposition of MB-TMP consist of styrene, acetophenone, the *N*-hydroxylamine derivative of TEMPO, and a very small amount of *sec*-phenethyl alcohol. Figures 3 and 4 are high-

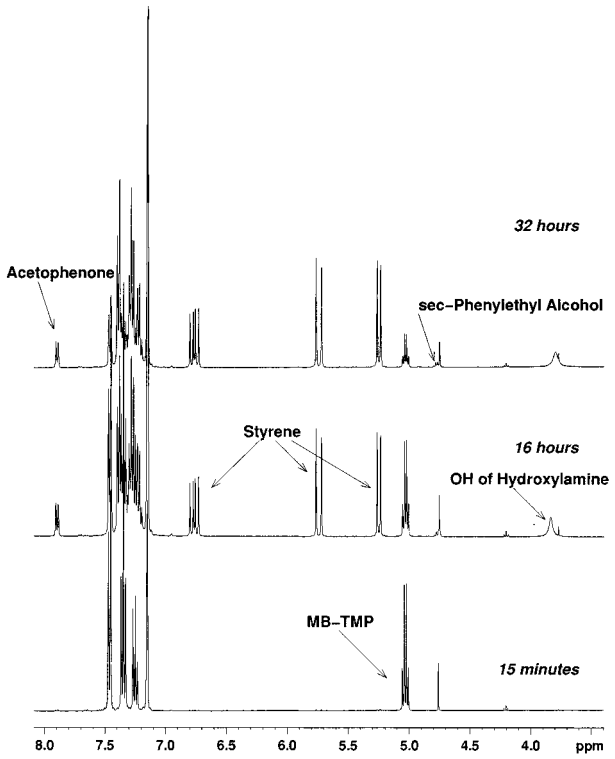


Figure 3. Series of three high-temperature (125 °C) 400 MHz ^{1}H NMR spectra in *o*-xylene-d_{10} at 15 min, 16 h, and 32 h reaction time, illustrating the decomposition of MB-TMP and formation of styrene, the *N*-hydroxylamine of TEMPO, and acetophenone covering 3.5−8.0 ppm.

temperature 400 MHz ^{1}H NMR spectra at 125 °C, taken at different times throughout the experiment. Figure 3 shows the region from 3.5 to 8.0 ppm at 15 min, 16 h, and 32 h. The peaks of interest include the ortho-aromatic protons of acetophenone resonating at 7.90 ppm, which did not increase in intensity going from 16 to 32 h. The characteristic vinyl methine proton of styrene appears as a doublet of doublets at 6.77 ppm, along with the two vinyl methylene protons at δ 5.74

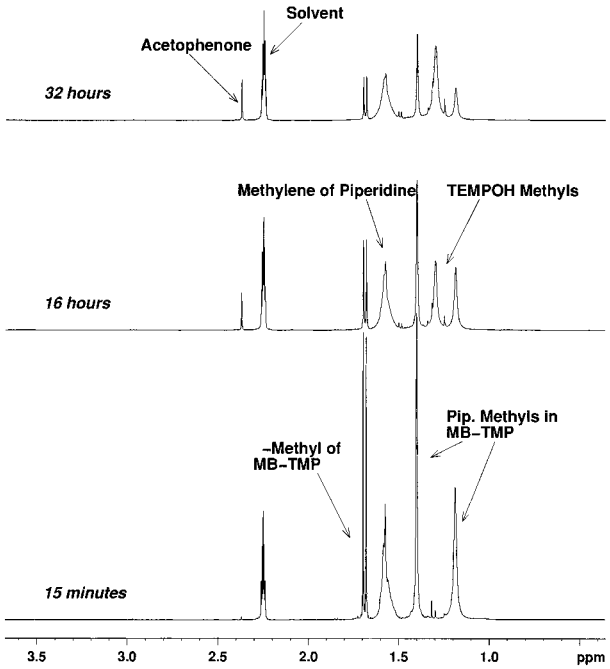


Figure 4. Series of three high-temperature (125 °C) 400 MHz ^{1}H NMR spectra in *o*-xylene-d_{10} at 15 min, 16 h, and 32 h reaction time, illustrating the decomposition of MB-TMP and formation of styrene, the *N*-hydroxylamine of TEMPO, and acetophenone, covering 0.5−3.5 ppm.

and δ 5.25. All three signals grow significantly over the course of the reaction. The quartet at δ 5.03 of the methine proton of MB-TMP decreases in intensity, and by 32 h into the reaction, MB-TMP is only a minor component in the system. At 4.76 ppm is the weak multiplet of the methine proton of *sec*-phenethyl alcohol with a sharp singlet resonating at the same position. The broad singlet at δ 3.91 is characteristic of the alcohol proton of the *N*-hydroxylamine derivative of TEMPO. The identification of the OH proton of the *N*-hydroxylamine of 4-benzoate-TEMPO gave us confidence in assigning the broad singlet at δ 3.91 to TEMPOH which is difficult to confirm through isolation, since it is readily oxidized to TEMPO in air.

The spectral region covered in Figure 4, also at 15 min, 16 h, and 32 h, is from 0.5 to 3.5 ppm. Downfield of the methyl resonance (2.25 ppm) of *o*-xylene-d_{10} are the methyl protons of acetophenone at 2.37 ppm. Contained in the aliphatic region between 1.19 and 1.70 ppm is the doublet at 1.69 ppm due to the methyl group on the asymmetric center of MB-TMP. The ring methylene protons of both TEMPO and the *N*-hydroxylamine derivative of TEMPO are found in the broad peak at 1.57 ppm. The four methyl groups of the piperidine portion of MB-TMP are found at 1.40 and 1.19 ppm, and as the reaction proceeds, these two peaks decrease in intensity as the ring methyls of the *N*-hydroxylamine of TEMPO increase at 1.30 ppm.

Certain characteristic signals for each component of the reaction were integrated and used to determine the concentration of each species formed as the reaction proceeded. All integrated peak areas were divided by the number of protons and normalized to the methyl quintet of the solvent set at 100. The methine proton resonance at δ 5.03 was used to determine the concentration of MB-TMP. The vinyl methine proton of styrene at 6.75 ppm was integrated and monitored. The alcohol proton at δ 3.91 and the 12 methyl protons (1.30 ppm) of *N*-hydroxylamine were followed. The two ortho-aromatic protons at δ 7.90 and three methyl protons resonating at 2.37 ppm in acetophenone were integrated. The methine proton at 4.76 ppm of *sec*-phenethyl alcohol was followed, but accurate integration for this signal was difficult to obtain due to an unknown singlet resonating at the same position.

This unknown singlet was only observed in solution at 125 °C, not at room temperature. Illustrated in Figure 5, for the first 8 h of the reaction, are the increase in concentration of various byproducts and the decrease in MB-TMP concentration. Also added to the plot is the TEMPO concentration data taken from the ESR experiment for the first 8 h.

Unexpectedly, the concentration of TEMPO changed from only 4.4×10^{-5} to 7.2×10^{-4} M, a factor of 16, which is a minor increase in comparison to the other changes in the system. The majority of the TEMPO liberated by the homolytic cleavage of the labile C−ON bond in MB-TMP, which did not reversibly terminate the 1-phenylethyl radical, produced the *N*-hydroxylamine derivative of TEMPO. After 8 h into the decomposition reaction, the distribution of the various products formed and MB-TMP was calculated as shown in Table 2. The initial concentration of MB-TMP was 111.0 mmol/L, and after 8 h, it had decreased to 66.7 mmol/L, which accounts for 58.4% of the initial concentration of MB-TMP. After 8 h at 125 °C, 41.6% of MB-MTP had decomposed into secondary products: styrene (19.8%), free TEMPO (0.6%), the *N*-hydroxylamine derivative of TEMPO (16.3%), acetophenone (4.6%), and minor traces of *sec*-phenethyl alcohol (0.3%).

Based on the ESR and ^{1}H NMR experimental data, a modified mechanism was proposed that accounts for the various products produced in the thermal decomposition of MB-TMP at 125 °C. This mechanism is different from that proposed by Li et al.,[27,28] who used a different approach to study the thermal decomposition of MB-TMP. The mechanism of Li et al. is shown in Scheme 1. Their study identified ethylbenzene and 2,3-diphenylbutane as secondary products of the reaction. These compounds probably formed due to a higher reaction temperature, 140 vs 125 °C, producing a larger instantaneous concentration of 1-phenyethyl radicals that subsequently dimerized to give 2,3-diphenylbutane or reacted with a hydrogen radical source to produce ethylbenzene.

The proposed mechanism based on the high-temperature ^{1}H NMR experiments of this study is shown in Scheme 2. Upon homolytic cleavage of the C−O bond in MB-TMP, the TEMPO radical and the carbon-centered 1-phenylethyl radical are produced, which undergo rapid reversible capping to re-form the dormant adduct MB-TMP. This equilibrium is the dominant reaction, but in the absence of monomer, MB-TMP slowly decomposed to produce five different compounds. After the initial homolytic cleavage to liberate TEMPO and 1-phenylethyl radical, and in the absence of O_2, the nitroxide radical abstracts a hydrogen radical from the β-carbon of 1-phenylethyl radical to form the *N*-hydroxylamine derivative of TEMPO (TEMPOH) and styrene. After 8 h, TEMPOH (16.3%) and styrene (19.8%) account for the majority of the decomposition products produced. This reaction is very fast, and within 15 min at 125 °C the vinyl protons of styrene are just visible by ^{1}H NMR.

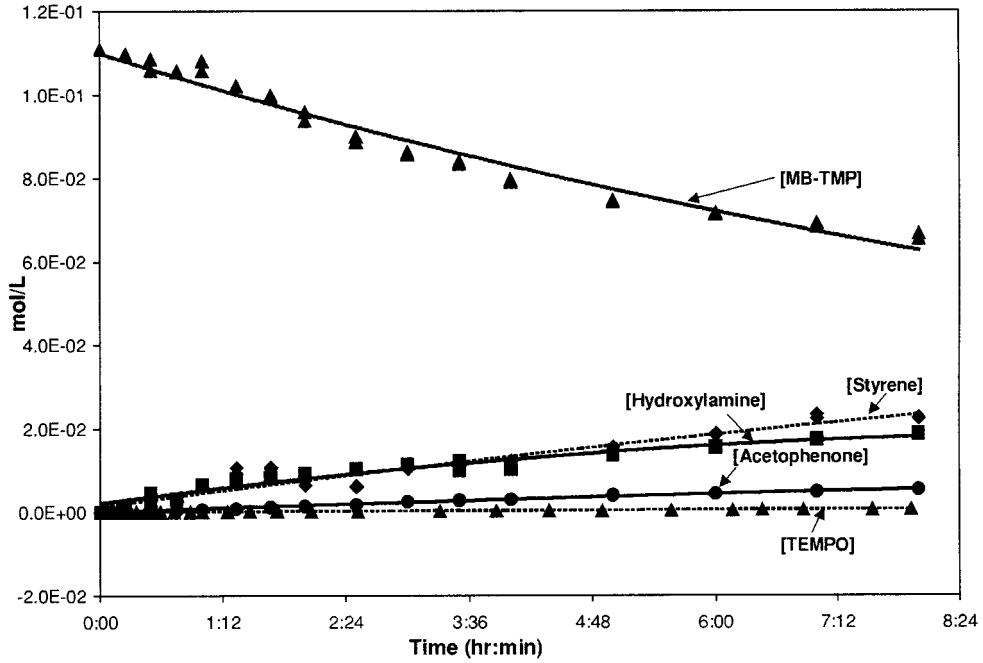


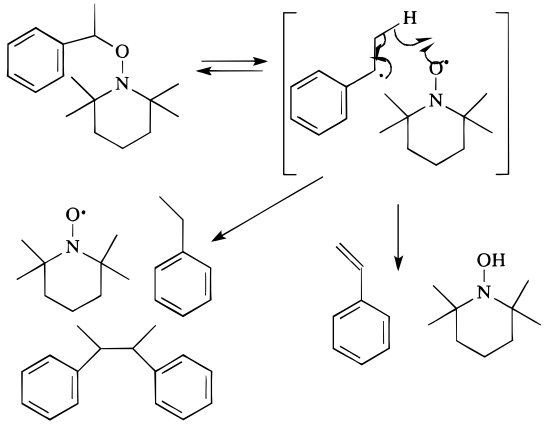
Figure 5. Concentration (mol/L) of the byproducts produced as a function of reaction time during the thermal decomposition of MB-TMP at 125 °C.

Table 2. Product Distribution of the Various Decomposition Components and MB-TMP after 8 h at 125 °C

component	normalized ^{1}H area	conc (mmol/L)	component (%)
MB-TMP (initial)	51	111.0	
MB-TMP	30.65	66.7	58.4
styrene	10.4	22.6	19.8
TEMPO[a]		0.7	0.6
TEMPOH	8.55	18.6	16.3
acetophenone	2.45	5.3	4.6
sec-phenethyl alcohol	0.17	0.4	0.3
total		114.3	100

[a] The concentration of TEMPO was determined from the double integrated area of the unpaired electron density signal of TEMPO measured by ESR spectroscopy.

Scheme 1. A Mechanism Proposed by Li et al.[27,28] for the Thermal Decomposition of MB-TMP at 140 °C



In our experiments we tried to thoroughly degas the samples to remove aerial O_2 by the freeze−pump−thaw technique, but in fact, the samples were not totally oxygen free. The deuterated aromatic solvent strongly retains molecular oxygen. In the presence of trace amounts of oxygen, the biradical oxygen rapidly reacts with the 1-phenylethyl radical to form acetophenone and *sec*-phenethyl alcohol as illustrated in Scheme 2. The formation of acetophenone and *sec*-phenethyl alcohol was not in a 1:1 molar ratio as observed by Cais and Bovey[39] and Bhanu and Kishore[40] where aerial oxygen was copolymerized with styrene at 55 °C. The effect of trace amounts of oxygen on the thermal decomposition of MB-TMP occurring via the proposed reaction mechanism in Scheme 2 is supported by Busfield et al.,[41,42] who concluded that the presence of small amounts of O_2 in free radical polymerization can produce polymers that contain oxygenated end groups.

To further test the mechanism outlined in Scheme 2 and the inhibiting effect of O_2, two additional experiments were performed. In the drybox, two identical samples were prepared containing MB-TMP in *o*-xylene-d_{10}, $[\text{MB-TMP}]_0 = 8.43 \times 10^{-2}$ M. Into one NMR tube was added 650 μL of this solution (sample 1). The same volume of sample was added into a second tube, but this sample was capped with a regular plastic NMR cap, sample 2. Both samples were removed from the drybox, and sample 1 was attached to a vacuum line to degas the solution of oxygen. Ten freeze−pump−thaw cycles were used. This was twice the number of FPT cycles used in the previous experiments, which did not completely remove O_2. The plastic cap of sample 2 was removed, and the MB-TMP solution was purposely exposed to atmospheric moisture and oxygen. The samples were placed in an oil bath set to 125 °C, and after 2 h, the samples were quenched in an ice water bath (15 min). The ^{1}H NMR spectra were obtained at room temperature on the 300 MHz spectrometer. This cycle was continued until approximately 8 h of heating was performed.

Illustrated in Figure 6 is the normalized ^{1}H peak area for each byproduct of the reaction, plotted as a function of time. The rate of decomposition of MB-TMP is faster in the presence of aerial O_2 as compared to the case of the FPT sample. The most dramatic difference is the amount of acetophenone produced. In the aerial O_2 sample (sample 2), three times the amount of acetophenone was generated after 8 h and 45 min of heating, as

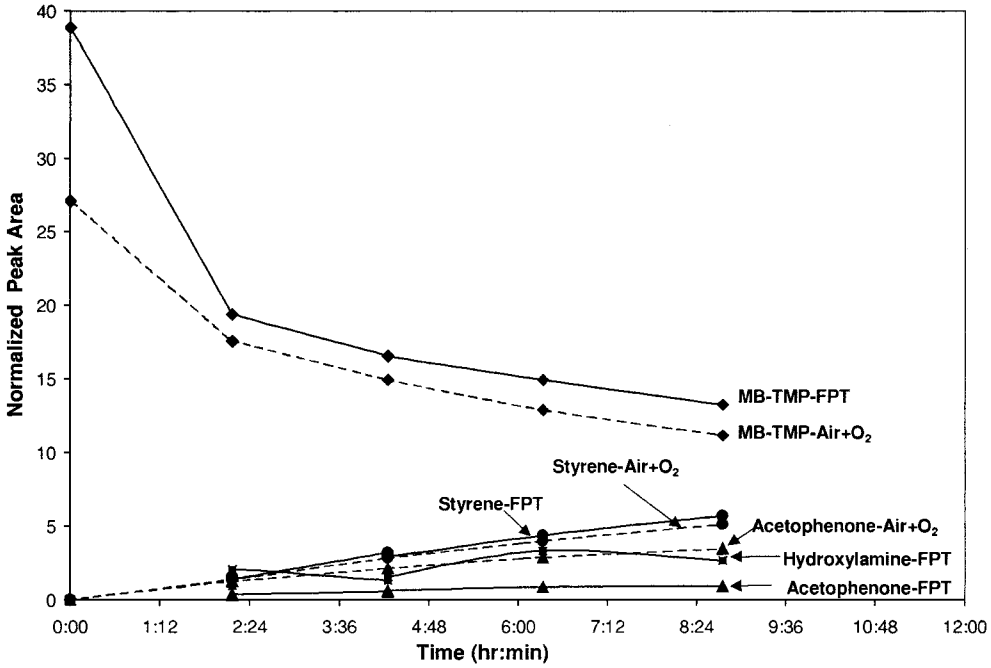
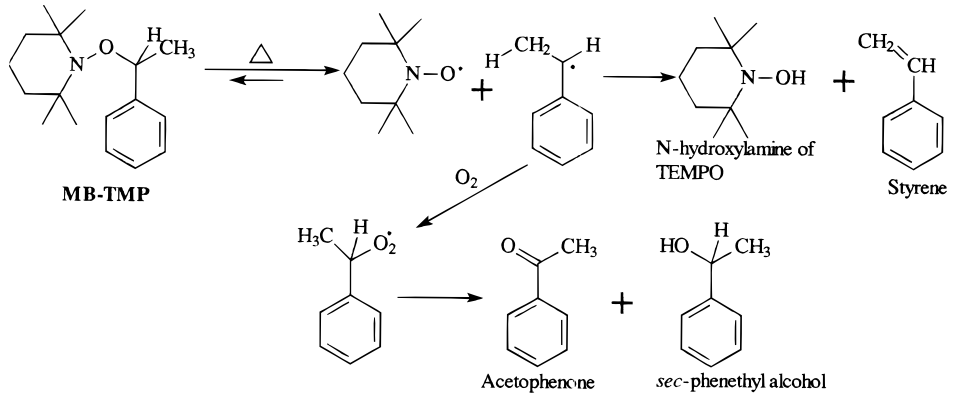


Figure 6. Plot of normalized ^{1}H NMR (300 MHz) resonance peak areas as a function of time, illustrating the effect of O_2 on the products ratios obtained from the thermal decomposition of MB-TMP at 125 °C.

Scheme 2. A Modified Mechanism for the Thermal Decomposition of MB-TMP in *o*-Xylene-d_{10} Produced Styrene, *N*-Hydroxylamine of TEMPO, Acetophenone, and *sec*-Phenylethyl Alcohol at 125 °C



compared to the controlled FPT sample. The rate of production of styrene is similar in both samples. Quantifying the amount of *N*-hydroxylamine produced was more difficult since the spectra were acquired at room temperature. The piperidine ring methylene protons of both MB-TMP and TEMPOH form a very broad peak that prevented baseline peak resolution of the key methyl protons used to integrate the hydroxylamine. This is evident in the ^{1}H NMR spectra of Figure 7 where the spectrum of the starting FPT sample is compared to the spectrum obtained at room temperature after 4 h and 15 min of heating. The sharp singlet at 1.35 ppm was assigned to the four methyls of the *N*-hydroxylamine derivative of TEMPO. Even though 10 FPT cycles were performed on sample 1, acetophenone was still produced, as evident by the peaks at 7.9 ppm. This means that oxygen was still present in the solution.

In this study, the nitroxide adduct MB-TMP has been used to provide valuable experimental data of various potential termination reactions that could occur in the stable free radical polymerization of styrene at 125 °C. In the absence of monomer, the reversible capping of the carbon-centered radical by TEMPO is still the dominant reaction. This was evident by the time required (64 h) to completely decompose adduct MB-TMP at 125 °C in *o*-xylene-d_{10}. Competing with the reversible capping of the 1-phenylethyl radical by TEMPO is the disproportionation reaction, where abstracting the benzylic hydrogen from 1-phenylethyl radical by TEMPO generated TEMPOH and styrene. Under normal SFR polymerization conditions in the presence of styrene monomer and in the total absence of oxygen, this disproportionation reaction could generate a terminal vinyl group at the end of a polystyrene chain. An initial investigation of possible terminal vinyl protons in low molecular weight polystyrene by ^{1}H NMR has not identified such termini. Under more rigorous conditions of long reaction times (24 h) at 130 °C, Yoshida et al.[26] demonstrated in their nitroxide chain end transformation experiment that such conditions were required to show any evidence of terminal vinyl protons.

However, when oxygen is present in the system, even in trace amounts, the inhibiting effect of aerial oxygen via autoxidation reaction preferentially competes with the reversible capping of 1-phenylethyl radical by TEMPO. In this model system, acetophenone and *sec*-phenethyl alcohol were produced as a consequence of these secondary reactions as illustrated in Scheme 2.

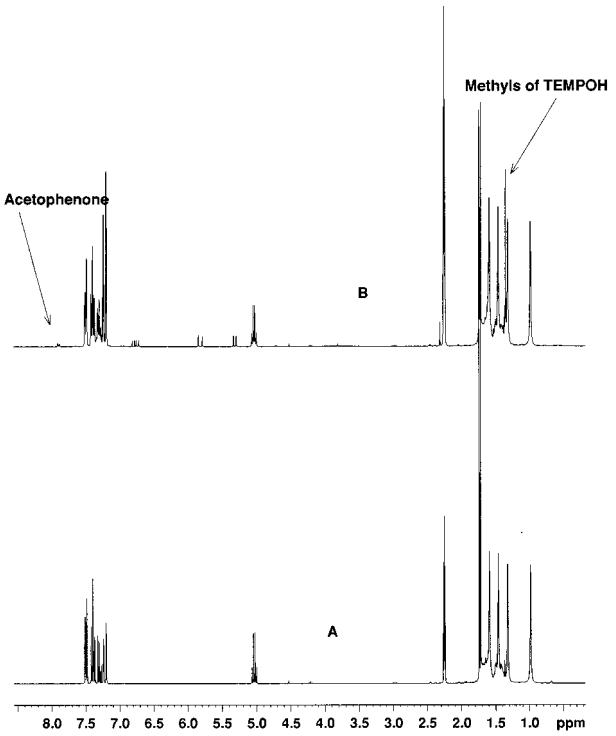


Figure 7. The 300 MHz room temperature ^{1}H NMR spectra of (a) sample 1 (FPT) at time zero and (b) sample 1 after heating at 125 °C for 4 h and 15 min.

This inhibiting effect of aerial oxygen on free radical polymerization is not new. Conventional free radical initiation studies by Busfield[41,42] clearly demonstrated the inhibiting effect O_2 has on the system. In the stable free radical polymerization of styrene, the preferential reaction of O_2 with a carbon-centered radical could produce a terminal phenyl ketone group at the end of the polystyrene chain. The ketone carbonyl would appear as a single resonance in the ^{13}C NMR spectrum, and the two ortho protons of the phenyl ring would resonate near δ 7.90 in the ^{1}H spectrum. This would result in a broader polydispersity due to premature chain termination. Provided the polymerization is under a totally inert atmosphere of N_2 or Ar, the probability of this reaction is greatly reduced. The overall contribution of chain end termination in a SFRP of styrene by the reactions described in Scheme 2 is probably reasonably low, i.e., <5%, but exactly how much these side reactions contribute to the overall polymerization is unclear at this point. Presently, our research efforts are focused on determining how significant these secondary reactions are to the SFRP polymerization process. In a subsequent paper the effect of aerial oxygen in the stable free radical polymerization will be reported.

Conclusions

In conclusion, the nitroxide adduct MB-TMP has been used to provide valuable experimental data of various potential termination reactions that could occur in the stable free radical polymerization of styrene at 125 °C. In the absence of monomer, the reversible capping of the carbon-centered radical by TEMPO is still the dominant reaction. From ESR spectroscopy, at different temperatures (103, 125, 132 °C) and employing two different solvents (toluene-d_8, *o*-xylene-d_{10}) the rate of liberation of free TEMPO was determined. At 125 °C, the complementary ^{1}H NMR study was performed to monitor the formation of various byproducts from the thermal decomposition of MB-TMP. Styrene, *N*-hydroxylamine of TEMPO, acetophenone, and *sec*-phenethyl alcohol were identified from the study, and a modified mechanism was proposed. As demonstrated in this research, when oxygen is present in the system, even in trace amounts, the inhibiting effect of aerial oxygen via autoxidation reaction preferentially competes with the reversible capping of 1-phenylethyl radical by TEMPO, which produced acetophenone and *sec*-phenethyl alcohol. As a consequence, extra care should be taken to thoroughly degas the reaction vessel and monomer in order to produced a well-behaved stable free radical polymerization.

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