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Nitroxide-Mediated Polymerization at Elevated Temperatures

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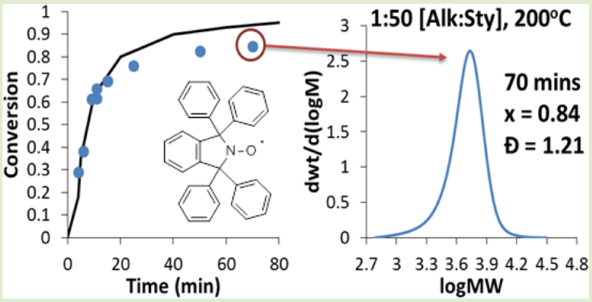
Supporting Information

ABSTRACT: A new alkoxyamine based on a highly thermally stable nitroxide is used for the controlled polymerization of styrene and butyl acrylate at temperatures up to 200 °C. High monomer conversions are reached in a few minutes with a linear increase in polymer chain-length with conversion, a final dispersity (Đ) of ∼1.2, and successful chain-extension of the resulting material. The alkoxyamine concentration was altered to target various chain lengths, with autopolymerization dictating the polymerization rate of styrene regardless of alkoxyamine concentration. Controlled polymerization of methacrylate monomers and acrylic acid was successful with the addition of styrene. The new material opens the possibility to increase the range of specialty products made for applications in coatings, inks, overprint varnishes, and adhesives.



The first mention of nitroxide-mediated polymerization (NMP) was by the group of Solomon and co-workers, whose seminal work with the use of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as a radical trap led to further development by Georges et al. to produce polystyrene (PS) resins with low dispersities.[1−4] As with other RDRP (reversible-deactivation radical polymerization) methods, the mechanism involves the reversible trapping of the propagating radical ($R^\bullet$) by the stable free nitroxide ($Y^\bullet$) to produce the dormant species or (macro)alkoxyamine (R_n-Y). The forward activation (decomposition) reaction is significantly slower than the reverse deactivation (cross-coupling) reaction such that the radical species concentration is lowered, facilitating control over the polymerization due to the suppression of termination and other side reactions. However, some bimolecular termination is unavoidable, leading (in the absence of newly generated radicals) to an excess of the persistent radical ($Y^\bullet$), as described by the persistent radical effect.[5]

The inability for TEMPO to effectively mediate monomers other than styrene was circumvented with the development of other nitroxides such as 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO)[6] and *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN or SG1).[7,8] This inspired a diversity of nitroxides and alkoxyamines (as summarized in the review paper of Nicolas et al.[9]), allowing the successful NMP of methyl methacrylate (MMA),[10,11] *n*-butyl acrylate (BA),[12] and acrylic acid (AA),[13] among other monomers. The need to minimize H-transfer to the nitroxide during the polymerization of methacrylates[10,14,15] has been achieved through copolymerization with styrene or acrylonitrile and by the synthesis of alkoxyamines that have a low dissociation temperature due to long-range polar effects.[10,11,16,17]

While promising developments have been witnessed, the widespread industrial application of NMP has remained elusive due to the need to tailor the alkoxyamine/nitroxide to the reaction conditions.[18] Typical polymerization temperatures for NMP of styrene with TEMPO have not exceeded 125−145 °C due to the elevated rate of alkoxyamine homolysis.[19] Nitroxides in the literature trend toward lower temperatures as a means to limit competitive side reactions and operate under emulsion polymerization conditions.[20−22] To the best of our knowledge, no one has pursued NMP for application at the elevated temperature conditions (>150 °C) used to produce commercial low molecular weight (MW) materials. In particular, continuous processes at elevated temperatures facilitate better temperature control, with high reaction rates allowing the use of small reactors for high output.[23] Providing tailored MW acrylic resins with low viscosity arising from narrow dispersities, as well as novel materials such as macromers and block copolymers, will extend the range of commercial products with applications in coatings, inks, varnishes, and adhesives. Herein, we describe the development and application of alkoxyamines **1** and **2** based on a nitroxide **3** (Scheme 1) to control polymerizations at higher temperatures.

High temperature NMP of bulk styrene: A range of alkoxyamine concentrations were used to generate polystyrene (PS) of target chain lengths (TCL) between 25 and 300 from bulk monomer at 160 °C. Figure 1 plots the monomer conversion profiles and evolution of polymer chain length and dispersity for alkoxyamine-**2**; as shown in Supporting

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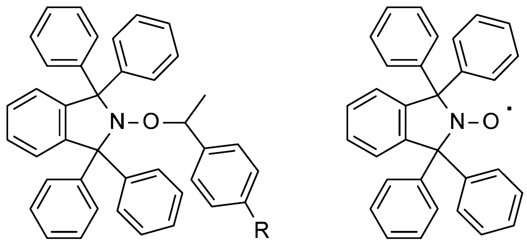
Scheme 1. Alkoxyamines 1 and 2 and the nitroxide 3



1, R = H
2, R = *tert*-Butyl

3

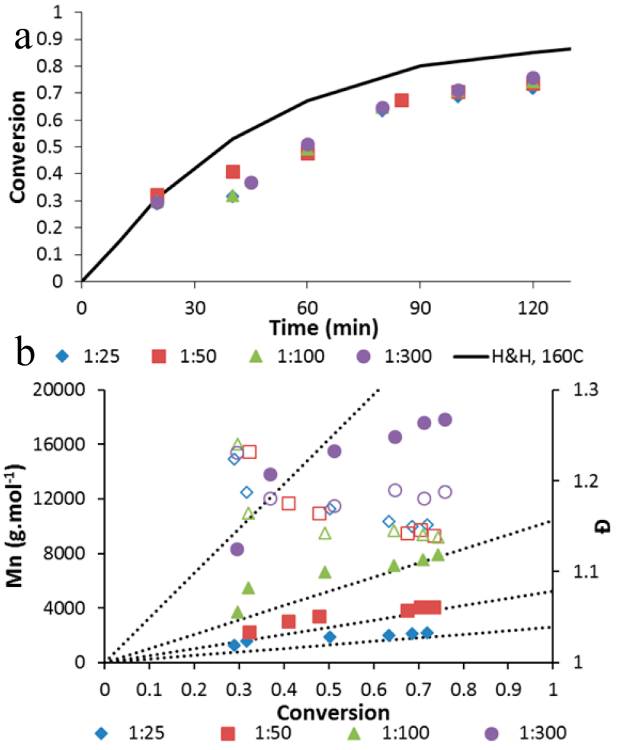


Figure 1. Batch NMP of bulk styrene at 160 °C, with initial alkoxyamine-**2**/styrene molar ratios presented in the legend: (a) conversion vs time and (b) number-average molar mass (M_n, closed symbols) and dispersity (*Đ*, open symbols) vs conversion. Thermal polymerization profile ("H&H" line) included for comparison.[24]

Information, results for alkoxyamine-**1** were similar. There is no appreciable effect of alkoxyamine concentration on the conversion profiles, which closely follow that expected from styrene thermal polymerization in the absence of controlling agent.[24] The control of reaction rate by thermal polymerization is expected from previous literature, where an increase in initiator (alkoxyamine) concentration increases rate only slightly even at high concentrations.[25,26] The measured polymer number-average molar masses (M_n) are in excellent agreement with target values for experiments with TCL of 100 or lower, with final polymer dispersities (*Đ*) of less than 1.2 (Figure 1b) even for PS produced with a TCL of 300.

The efficacy of alkoxyamine-**2** for NMP at elevated temperatures was studied between 140 and 200 °C for a TCL of 50. The polymerization rate is greatly accelerated with increasing temperature, with 70% conversion achieved in 15 min (Figure 2a), still in agreement with the thermal

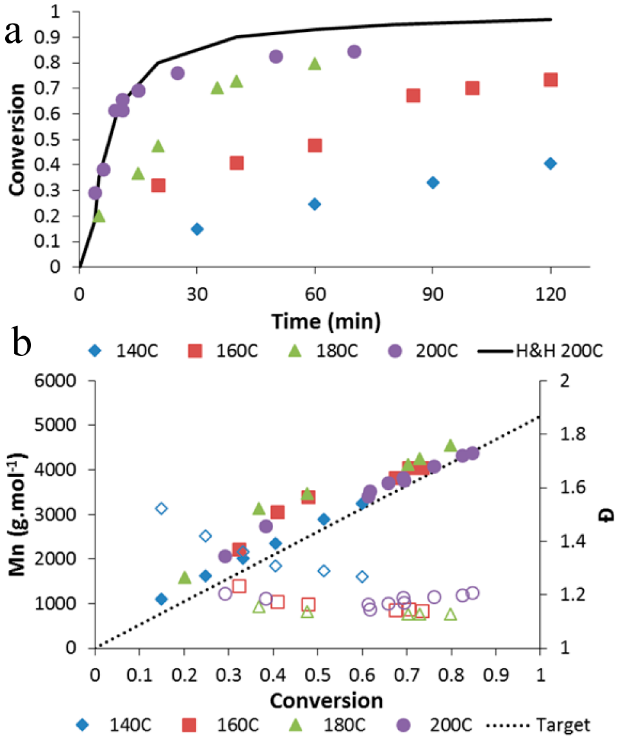


Figure 2. Batch NMP of bulk styrene at various reaction temperatures (see legend), with initial alkoxyamine-**2**/styrene molar ratio of 1:50: (a) conversion vs time and (b) number-average molar mass (M_n, closed symbols) and dispersity (*Đ*, open symbols) vs conversion. Thermal polymerization profile at 200 °C ("H&H" line) included for comparison.[24]

polymerization profiles reproduced from the experimental data of Hui and Hamielec (H&H).[24] The M_n profiles with conversion remain linear with *Đ* values at 1.2 (Figure 2b), indicating that good control is maintained even at 200 °C. Indeed, this unprecedented combination of fast reaction rate and excellent control strongly suggests that this family of alkoxyamines can be used at even higher temperatures, beyond our current experimental capabilities. The unusual thermostability of nitroxide **3** can be explained by its cyclic structure and the presence of the strong aromatic C–H bonds.

Butyl acrylate: The ability of the **3**-based alkoxyamines to mediate *n*-butyl acrylate (BA) has also been investigated. The experiments with alkoxyamine-**1** were conducted in the presence of 50 vol % DMF to overcome the poor solubility of the material in monomer at room temperature (see Supporting Information). However, alkoxyamine-**2** was entirely soluble at room temperature, enabling the study of BA bulk homopolymerization over the same range of conditions examined for styrene. Results at varying temperatures for a constant TCL = 55 are presented in Figure 3, with further results for the variation of TCL included as Supporting Information.

The BA results are very promising, with reaction rates even faster than those of styrene; as shown in Figure 3a, monomer conversion of almost 90% is achieved in 15 min at 200 °C. MW control remains good, with the highest dispersity found at 140 °C (Figure 3b), suggesting the alkoxyamine activation/deactivation kinetics are more favorable for control at higher temperatures, as also seen for styrene. However, final *Đ* values were 1.5–1.6, a result seen in the broader molar mass

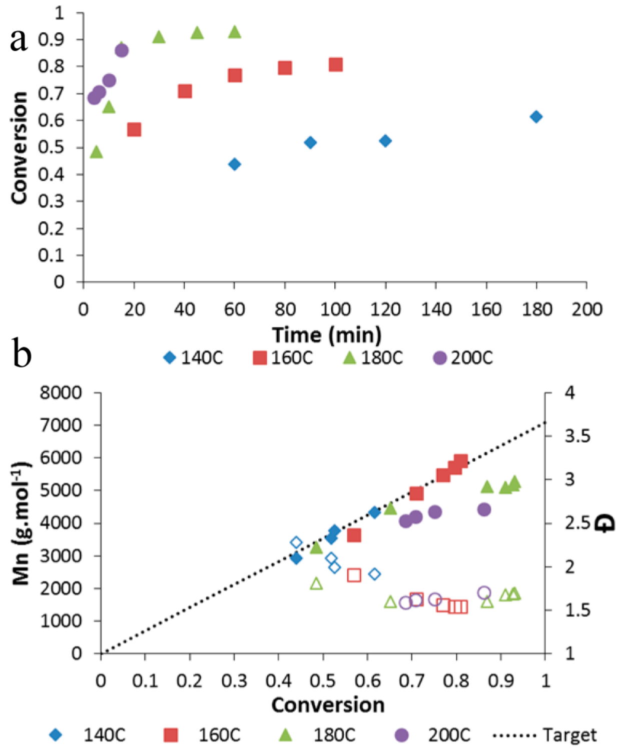


Figure 3. Batch NMP of bulk BA at various reaction temperatures (see legend), with initial alkoxyamine-**2**/BA molar ratio of 1:55: (a) conversion vs time and (b) number-average molar mass (M_n, closed symbols) and dispersity (*Đ*, open symbols) vs conversion.

distributions (MMDs) of poly(BA) compared to PS in Figure 4. This result is likely related to the significantly faster propagation kinetics of BA compared to styrene; in addition, the MMD is broadened by the slower alkoxyamine initiation in the acrylate system, as seen by the slowly disappearing peak at log(MW) = 2.8. Interestingly, no evidence of branching could be detected by ^{13}C NMR, even for the poly(BA) produced at 200 °C (see Supporting Information), a result consistent with other reversible deactivation radical polymerization (RDRP) processes,[27] for which it is hypothesized that fast deactivation reduces the backbiting mechanism compared with conventional free radical polymerization.[28,29]

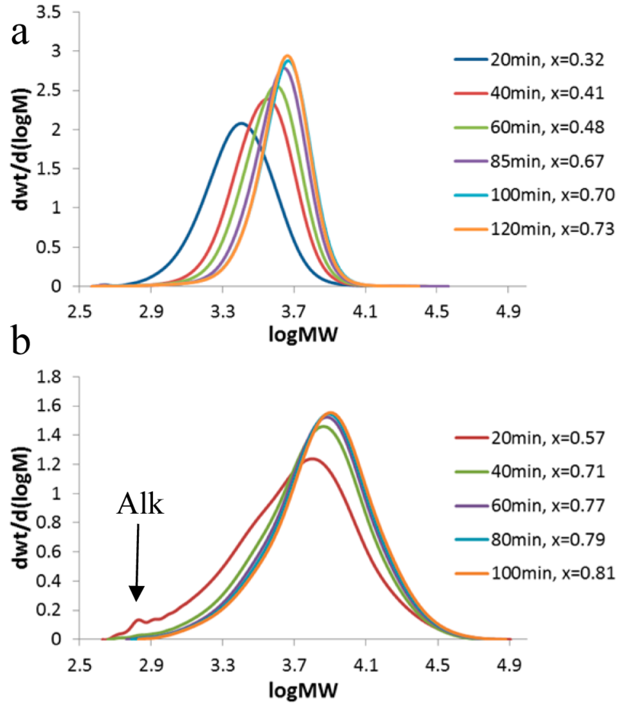


Figure 4. Molar mass distribution resulting from bulk NMP at 160 °C of (a) styrene and (b) butyl acrylate with initial alkoxyamine-**2**/monomer molar ratios of 1:50 (styrene) and 1:55 (butyl acrylate); polymerization time and conversion presented in the legend.

In addition, first experiments have been conducted with other monomers of interest. As detailed in the Supporting Information, excellent control is achieved for copolymerization of acrylic acid with styrene (*Đ* = 1.3 produced with 90% conversion in 60 min at 160 °C), and even some measure of control is achieved at 160 °C for bulk *n*-butyl methacrylate polymerized with 10 mol % styrene.

A chain extension experiment of PS of chain length 39 (produced at 160 °C) extended to 370 was run in order to demonstrate livingness with alkoxyamine-**1**. As shown in Figure 5, over an order-of-magnitude increase in MW was achieved with no obvious low MW tail observed and a *Đ* value of 1.4, thus, demonstrating the high end-group functionality of the polystyrene macromer.

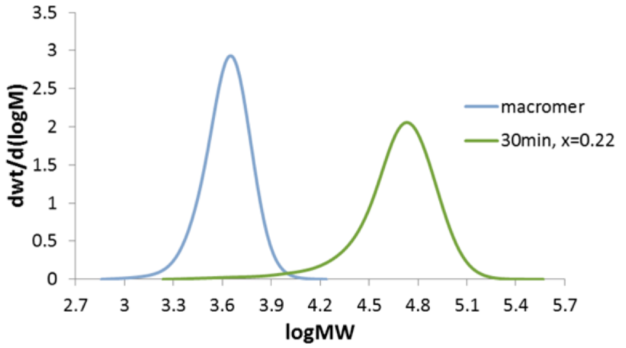


Figure 5. Molar mass distribution resulting from chain extension of PS by bulk NMP at 160 °C of styrene; polymerization time and conversion presented in the legend.

Herein we report the ability of alkoxyamines **1** and **2** based on a highly thermally stable nitroxide **3** to mediate polymerizations at high temperature, providing excellent control of both styrene and BA bulk homopolymerization over a range of TCLs and up to 200 °C, with polymer dispersities of 1.2 for styrene and 1.5 for butyl acrylate. The results indicate that the alkoxyamine should exhibit good control at even higher temperatures, which will further decrease the time required (less than 15 min at 200 °C) to achieve high conversions. Livingness has been verified by chain extension experiments, demonstrating the potential to produce block copolymers in continuous reactors under high temperature conditions.

■ EXPERIMENTAL METHODS

Synthesis of the alkoxyamines: Alkoxyamine-**1** was prepared as described by Hafner et al.[30] The novel alkoxyamine-**2** was made by CuBr promoted radical coupling of the nitroxide **3** with 1-(1-bromoethyl)-4-*tert*-butylbenzene (see Supporting Information).[31,32]

The nitroxide 1,1,3,3-tetraphenylisoindoline-*N*-oxyl **3** was prepared by oxidation of 1,1,3,3-tetraphenylisoindoline with *m*-chloroperbenzoic acid.[30] Alternatively, **3** can be made via oxidation of *N*-benzyl-1,1,3,3-tetraphenylisoindoline with *m*-chloroperbenzoic acid.[33] The nitroxide

3, a red solid, mp 250−253 °C, is remarkably thermally stable, a sample of **3** remaining unchanged (TLC and HPLC) after being heated for 7 h at 200 °C under air.

Polymerization: Styrene (Sigma-Aldrich) was passed through a prepacked column (Aldrich) to remove the 4-*tert*-butylcatechol inhibitor and stored in the freezer prior to reaction. Stock solutions were prepared under nitrogen by adding uninhibited styrene to the alkoxyamine in a ChemGlass AirFree 50 mL round-bottom flask. 0.2 mL of stock solution was added to Low Pressure/Vacuum (LPV) NMR tubes (Wilmad-LabGlass) using a 1 mL glass syringe. For alkoxyamine-**1**, it was necessary to heat the stock solution to 70 °C in a water bath to ensure solubility; no polymerization occurred, as confirmed by ^{1}H NMR. The LPV NMR tubes were subjected to 4 freeze−pump−thaw cycles and sealed under nitrogen (<1 atm) using a Schlenk line and liquid nitrogen, to prevent monomer boiling during reaction at elevated temperature. The tubes were kept refrigerated until use and were suspended in a silicone oil bath to start the polymerization. The reaction was stopped at designated times by removing the tube and immersing in an ice bath for 30 s, with each tube used as an individual sample to reconstruct a complete polymerization profile. Monomer conversions were determined by ^{1}H NMR analysis using a Bruker Avance-400 (400 MHz) instrument after adding deuterated chloroform (Aldrich). Size exclusion chromatography (SEC) was performed as described in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional examples of alkoxyamine performance. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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