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ARTICLE

Nitroxide-Mediated Polymerization of Methyl Methacrylate and Styrene with New Alkoxyamines from 4-Nitrophenyl 2-Methylpropionat-2-yl Radicals

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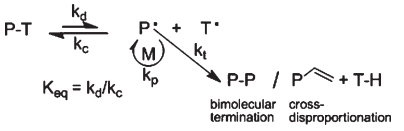
ABSTRACT: The *N*-phenylalkoxyamine *N*-(1-methyl-(1-(4-nitrophenoxy)carbonyl)ethoxy)-*N*-(1-methyl-(1-(4-nitrophenoxy)carbonyl)ethyl)benzenamine (**1**) was prepared by the addition of 4-nitrophenyl 2-methylpropionat-2-yl radicals across the double bond of nitrosobenzene and evaluated as an initiator for nitroxide-mediated polymerization (NMP). *N*-Phenylalkoxyamines have not been extensively studied in NMP, though they have shown promise in controlling methyl methacrylate (MMA) polymerization to moderate conversions. It is thought that delocalization of the nitroxide radical through the *N*-phenyl substituent may minimize cross-disproportionation of the nitroxide with the chain end that has made NMP of MMA difficult. Here, we show that alkoxyamine **1** is capable of controlling the NMP of MMA to 50% conversion while maintaining narrow molecular weight distributions ($M_w/M_n = 1.12-1.30$). Additionally, chain extension from the resulting PMMA macroinitiators with MMA or styrene allows the formation of diblock copolymers. The corresponding *N*-*tert*-butylalkoxyamine, 2,2-dimethyl-3-(1-methyl-(1-(4-nitrophenoxy)carbonyl)ethoxy)-4-methyl-(4-(4-nitrophenoxy)carbonyl)ethyl-3-azapentane (**2**), was synthesized by the addition of 4-nitrophenyl 2-methylpropionat-2-yl radicals across the double bond of 2-methyl-2-nitrosopropane. Polymerization of MMA with alkoxyamine **2** was uncontrolled, which suggests the paramount importance of the *N*-phenyl group for MMA polymerizations.

Introduction

Nitroxide-mediated polymerization (NMP) is one of the most widely employed controlled radical polymerization techniques.[1−6] It operates by the reversible trapping of growing polymer chains with nitroxides and is controlled by the persistent radical effect, which ensures efficient cross-coupling of polymeric radicals with nitroxides instead of terminating with themselves.[7,8] NMP has been utilized to control the polymerization of styrenics, dienes, acrylates, acrylamides, and, to some extent, methacrylates.[9−11,13]

Because methacrylates comprise about 1 billion pounds of polymeric products produced in the United States each year, it is desirable to extend NMP to enable greater control over methacrylate polymerization.[12] This has proven difficult because cross-disproportionation and a large activation−deactivation equilibrium constant, K_{eq} (k_d/k_c, Scheme 1), are two problematic issues with the NMP of methyl methacrylate (MMA).[13,14] Polymerization of MMA with the widely available nitroxide 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) fails because of the cross-disproportionation side reaction, which occurs when TEMPO abstracts a hydrogen atom from the PMMA chain end to form a saturated polymer chain end and a hydroxylamine.[15−18] With newer α-hydrido nitroxides such as 1-(diethoxyphosphinyl)-2,2-dimethylpropyl-1,1-dimethylethylnitroxide (SG1), cross-disproportionation side reactions have not been observed in some studies, and the uncontrolled nature of MMA polymerization has been attributed solely to the large activation−deactivation equilibrium constant (K_{eq}, Scheme 1).[17,19] The large K_{eq} for MMA is attributed to a large k_d due to steric destabilization of the ground state, as well as a small k_c because of steric hindrance as the nitroxide approaches the bulky tertiary propagating radical center.[19] However, cross-disproportionation has been observed during the polymerization of MMA with an excess of SG1,[18] and Charleux and co-workers detected the occurrence of both cross-disproportionation and bimolecular termination in SG1-mediated MMA polymerizations.[14]

Scheme 1. Activation−Deactivation Equilibrium for NMP Where P = Polymer Chain and T = Nitroxide



Because of both cross-disproportionation and the large K_{eq} for MMA, the design of an initiator that can control the homopolymerization of MMA has been difficult. The most successful route for MMA homopolymerization has been the use of *N*-arylnitroxides. It is thought that these nitroxides allow radical delocalization through the *N*-aryl moiety, perhaps preventing the cross-disproportionation side reaction and allowing better control over MMA polymerization.[20,21] An alternative route involves the copolymerization of a small percentage of styrene (4−10%) with MMA to form copolymers dense with methacrylate functionality.[5,21−29] This copolymerization method allows high MMA conversions to afford PMMA-rich copolymers with low polydispersity indices.

Guillaneuf and co-workers utilized 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl (DPAIO)-based alkoxyamines that

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contained either a phenyl 2-methylpropionat-2-yl initiating fragment or a 4-nitrophenyl 2-methylpropionat-2-yl initiating fragment for the polymerization of MMA.[20] Because the DPAIO nitroxide allows delocalization of the free radical through the indolinoxyl ring, it was reasoned that the extent of cross-disproportionation would be minimized, and the polymerization would be better controlled. They observed better control for MMA polymerization with the alkoxyamine containing the 4-nitrophenyl 2-methylpropionat-2-yl initiating fragment and ascribed this result to a long-range polar effect.[20] According to studies based on similar initiating fragments trapped with the nitroxide SG1, the dissociation rate constant, k_d (Scheme 1), was increased for the nitro derivative as a result of the electron withdrawing nature of the nitro group ($t_{1/2} = 120$ s) when compared to the SG1 derivative with the phenyl propionat-2-yl initiating fragment ($t_{1/2} = 197$ s).[20,30,31] They postulated that a faster homolysis rate for the nitrophenyl ester-substituted DPAIO derivative led to faster initiation and better control from the early stages of the polymerization. These results suggest that the more general problem of ensuring that initiation is rapid relative to propagation is also relevant to the NMP of methacrylates.

Previously, we prepared *N*-phenylalkoxyamines by the addition of 1-phenylethyl or phenyl 2-methylpropionat-2-yl radicals to nitrosobenzene that were able to control MMA polymerization to moderate conversions (32−41%) to yield PMMA with narrow molecular weight distributions.[21] In this work, we describe the one-step preparation of a new *N*-phenylalkoxyamine (**1**), analogous to the nitrophenyl ester-based DPAIO initiators reported by Guillaneuf and co-workers,[20] by the addition of 4-nitrophenyl 2-methylpropionat-2-yl radicals across the nitroso group of nitrosobenzene, and evaluate its effectiveness for the polymerization of styrene and MMA. These results indicate that a small structural change in the initiator, such as the addition of *para*-nitro groups on the phenyl rings, can lead to valuable improvements in the polymerization kinetics, affording control to higher conversions (49%) with narrow molecular weight distributions ($M_w/M_n = 1.12-1.30$). In order to assess the effect of the *N*-phenyl moiety on polymerization kinetics, the *N*-*tert*-butyl analog (**2**) of alkoxyamine **1** was also synthesized and evaluated for use in the polymerizations of styrene and MMA.

Experimental Section

Materials. 2-Methyl-2-nitrosopropane, 2-bromo-2-methylpropionyl bromide, 4-nitrophenol, Cu(0), Cu(I)Br, nitrosobenzene, *N*,*N*,*N*′,*N*′,*N*′′-pentamethyldiethylenetriamine (PMDETA), and triethylamine were used as purchased from Fisher Scientific or Sigma-Aldrich. ACS-grade solvents were used as received unless ultrapure solvent was needed in which case it was dried by passage through basic alumina under positive N_2 pressure.[32] Monomers were passed through a column of basic alumina to remove inhibitors before use. Alkoxyamine **3** was synthesized as previously reported.[21] 4-Nitrophenyl 2-bromo-2-methylpropionate (**4**) was synthesized according to a literature procedure.[33]

General. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz Varian Unity spectrometer using $CDCl_3$ or CD_2Cl_2 as solvent with the solvent peak as reference. Monomer conversion was calculated by ^{1}H NMR by comparison of the integration values for monomer peaks to polymer peaks using the following equation: p = [mol polymer]/[mol monomer + mol polymer].

Size exclusion chromatography (SEC) was performed at 40 °C with HPLC-grade tetrahydrofuran (THF) as eluent at a flow rate of 1.0 mL/min on a system consisting of a K-501 pump (Knauer), a K-3800 Basic Autosampler (Marathon), a set of two PLgel 5 μm Mixed-D columns (300 × 7.5 mm^2, rated for molecular weights from 200 to 400 000 g/mol, Polymer Laboratories), and a PL-ELS 1000 Evaporative Light Scattering Detector (Polymer Laboratories). SEC data were acquired through a PL Datastream unit (Polymer Laboratories) and analyzed with Cirrus GPC software (Polymer Laboratories) calibrated with narrow molecular weight polystyrene standards with molecular weights in the range of 580−400 000 g/mol (EasiCal PS-2, Polymer Laboratories). All reported $M_{n,SEC}$ values are based upon comparison to polystyrene standards. Initiating efficiencies for polystyrene samples were calculated based on the following formula: $I_{eff} = M_{n,th}/M_{n,SEC}$.[34] Elemental analysis data were obtained from Schwarzkopf Microanalytical Laboratory and Galbraith Laboratories, Inc.

Synthesis of *N*-(1-Methyl-(1-(4-nitrophenoxy)carbonyl)ethoxy)-*N*-(1-methyl-(1-(4-nitrophenoxy)carbonyl)ethyl)benzenamine (1). In a nitrogen-filled glovebox, 4-nitrophenyl 2-bromo-2-methylpropionate (**4**) (8.00 g, 27.7 mmol) was combined with nitrosobenzene (1.78 g, 16.6 mmol) and dissolved in toluene (8 mL) in a Schlenk tube equipped with a magnetic stir bar. CuBr (0.993 g, 6.90 mmol), Cu(0) (1.80 g, 28.4 mmol), and PMDETA (1.20 g, 6.9 mmol) were added sequentially to form a dark green heterogeneous mixture. The tube was sealed under N_2, removed from the glovebox, and placed in an oil bath at 60 °C. The mixture was allowed to stir for 24 h and was then flushed through a column of basic alumina. The solution was concentrated to a dark brown oil and placed on the Schlenk line for further drying, which resulted in a dark powder. The material was recrystallized from methanol to afford alkoxyamine **1** as a fine white powder (2.60 g, 36%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.29 (d, $J = 7$ Hz, Ar-*H*, 2H); 8.15 (d, $J = 7$ Hz, Ar-*H*, 2H); 7.41−7.22 (m, Ar-*H*, 7H); 6.84 (d, $J = 7$ Hz, Ar-*H*, 2H); 1.63 (s, C*H*$_3$, 3H); 1.57 (s, C*H*$_3$, 3H); 1.54 (s, C*H*$_3$, 3H); 1.50 (s, C*H*$_3$, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.27, 170.60, 155.83, 155.40, 147.68, 145.51, 145.40, 128.44, 127.11, 126.15, 125.43, 125.08, 122.49, 122.26, 82.11, 69.05, 24.94, 24.87, 24.11, 21.75. Elem. Anal. Calcd. for $C_{26}H_{25}N_3O_8$: C, 59.68%; H, 4.97%; N, 8.03%. Found: C, 59.53%; H, 5.08%, N, 7.84%.

Synthesis of 2,2-Dimethyl-3-(1-methyl-(1-(4-nitrophenoxy)-carbonyl)ethoxy)-4-methyl-(4-(4-nitrophenoxy)carbonyl)ethyl-3-azapentane (2). A Schlenk tube with a magnetic stir bar was charged with 4-nitrophenyl 2-bromo-2-methylpropionate (**4**) (1.93 g, 6.67 mmol) and 2-methyl-2-nitrosopropane (0.350 g, 4.00 mmol) in anhydrous toluene (10 mL). CuBr (0.240 g, 1.67 mmol), Cu(0) (0.430, 6.84 mmol), and PMDETA (0.290 g, 1.67 mmol) were added to the tube sequentially. The contents of the tube were degassed by three freeze−pump−thaw cycles and backfilled with N_2. The tube was placed in an oil bath at 60 °C and allowed to stir for 42 h. The contents of the tube were passed through a plug of basic alumina and then purified by flash chromatography (SiO_2, 12.34: 1 hexanes-ethyl acetate) to afford alkoxyamine **2** as bright yellow needles (0.17 g, 10% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.33 (d, Ar-*H*, 4H); 7.36 (d, $J =$ 9 Hz, Ar-*H*, 4H); 1.80 (s, C*H*$_3$, 3H); 1.76 (s, C*H*$_3$, 3H); 1.65 (s, C*H*$_3$, 3H); 1.60 (s, C*H*$_3$, 3H); 1.30 (s, C*H*$_3$, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.12, 172.94, 156.05, 155.85, 145.69, 145.51, 125.58, 125.55, 122.51, 122.27, 83.31, 68.06, 62.59, 30.45, 28.78, 25.65, 23.61, 21.85. Elem. Anal. Calcd. for $C_{24}H_{29}N_3O_9$: C, 57.27%; H, 5.77%; N, 8.35%. Found: C, 56.32%; H, 5.89%, N, 8.13%.

Polymerization of Styrene. In a typical procedure, alkoxyamine **2** (0.018 g, 0.036 mmol) and styrene (0.75 g, 0.082 mL, 7.2 mmol) were sealed in a Schlenk tube, degassed by three freeze−pump−thaw cycles, backfilled with N_2 and placed in an oil bath set at 125 °C for 7.5 h. After the specified amount of time, the polymerization was stopped by placing the tube in an ice bath. The contents of the tube were dissolved in CH_2Cl_2 and purified by precipitation into methanol. The solution was decanted yielding the white polymer, which was subsequently dried and analyzed by ^{1}H NMR and SEC ($M_{n,NMR} = 8.5$ kg mol^{-1}, conversion = 39%; $M_{n,SEC} = 9.0$ kg mol^{-1}, $M_w/M_n = 1.11$).

Polymerization of MMA. In a typical procedure, alkoxyamine **1** (0.022 g, 0.042 mmol) and MMA (1.26 g, 1.35 mL, 12.6 mmol) were sealed in a side arm Schlenk tube, degassed by three freeze−pump−thaw cycles, and placed under N_2. The tube was placed

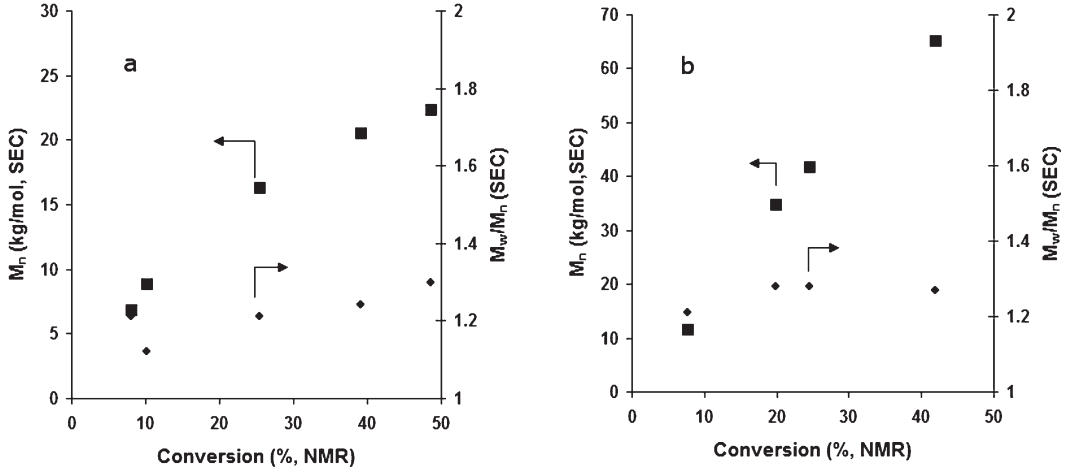
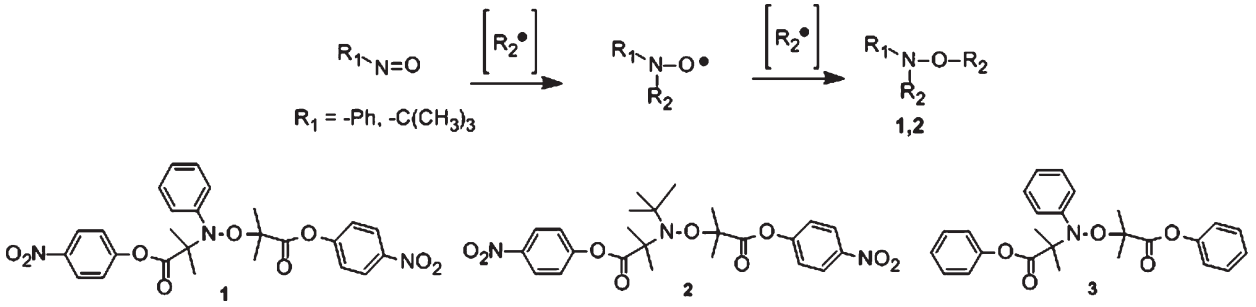


Figure 1. (a) Evolution of M_n and M_w/M_n with conversion for [MMA]:[**1**] = 300:1 at 125 °C; (b) Evolution of M_n and M_w/M_n with conversion for [MMA]:[**1**] = 1000:1 at 125 °C. The molecular weights for PMMA are relative to polystyrene standards used in SEC.

Scheme 2. Synthesis of Alkoxyamines 1 and 2



in an oil bath thermostatted at 125 °C for 5 h, and then the polymerization was quenched by placing the tube in an ice bath. The contents of the tube were dissolved in CD_2Cl_2, and an aliquot was withdrawn for ^{1}H NMR and SEC analyses. The remainder of the material was purified by precipitation into hexanes and analyzed by SEC against polystyrene standards. ($M_{n,NMR}$ = 15.1 kg mol^{-1}, conversion = 49%; $M_{n,SEC}$ = 22.4 kg mol^{-1}, M_w/M_n = 1.30).

Results and Discussion

Synthesis of Alkoxyamines. Alkoxyamine **1** was synthesized by the addition of 4-nitrophenyl 2-methylpropionat-2-yl radicals generated from 4-nitrophenyl 2-bromo-2-methylpropionate[33] across the double bond of nitrosobenzene and obtained as a white powder in 36% overall yield after recrystallization (Scheme 2). We postulated that alkoxyamine **1** might provide better control over the polymerization of MMA than was achieved with the phenyl ester-functional alkoxyamine *N*-(1-methyl-1-(phenoxycarbonyl)ethoxy)-*N*-(1-methyl-1-(phenoxycarbonyl)ethyl)benzenamine **3**[21] (Scheme 2) due to a potentially larger initiating dissociation rate constant, k_d, for alkoxyamine **1** than for **3** because of the presence of the *para*-nitro groups in **1**. The *N*-*tert*-butyl analog of initiator **1**, 2,2-dimethyl-3-(1-methyl-(1-(4-nitrophenoxy)carbonyl)ethoxy)-4-methyl-(4-(4-nitrophenoxy)carbonyl)ethyl-3-azapentane (**2**), was also investigated in order to make a direct comparison between the two different *N*-substituents for both styrene and MMA polymerization. Alkoxyamine **2** was isolated as bright yellow needles after the addition of 4-nitrophenyl 2-methylpropionat-2-yl radicals across the nitroso group of 2-methyl-2-nitrosopropane (Scheme 2).

Polymerization of MMA. Alkoxyamine **1** was used to initiate the polymerization of MMA (300 equiv). The molecular weights increased with conversion to the highest observed conversion of 49%, and the polydispersity indices remained low throughout the polymerization (M_w/M_n = 1.12−1.30) (Figure 1a). However, the highest observed conversion for these polymerizations was 49%. The ^{1}H NMR spectrum of PMMA synthesized from alkoxyamine **1** revealed vinylic resonances (δ 6.2 and 5.5 ppm) indicative of alkene-terminated chain ends, suggesting that cross-disproportionation occurred during the course of the polymerization. This process leads to dead polymer chains and to the build up of free nitroxide, both of which would contribute to halting the polymerization at lower conversion. On the basis of the kinetic data (Figure 1a), initiator **1** appears to be better than alkoxyamine **3** as an initiator for the polymerization of MMA, as it shows a faster rate of polymerization and gives slightly narrower molecular weight distributions (Table 1).

The preparation of higher molecular weight PMMA was examined by polymerizing MMA (1000 equiv) with alkoxyamine 1. The molecular weights of the polymers increased with conversion to the highest observed conversion of 42% at 6 h (Figure 1b). The molecular weight distributions remained narrow during the polymerizations (M_w/M_n = 1.21−1.28), and molecular weights as high as 65 kg/mol (against polystyrene standards) were observed at 42% conversion with M_w/M_n = 1.27, indicating good control with alkoxyamine **1**.

Since alkoxyamine **1** was an efficient initiator for the homopolymerization of MMA, the effect of the *N*-phenyl group was probed by exchanging the phenyl moiety for the *t*-butyl group (**2**; Scheme 2). Alkoxyamine **2** was utilized in the polymerization of 300 equiv of MMA, and the effect of this structural change was quite pronounced. There was no control exhibited over MMA polymerization using initiator **2**. The polymerizations stopped at low conversions (19−27%

Table 1. Comparison of Alkoxyamines 1 and 3 for the Polymerization of MMA[a]

entry	alkoxyamine	time/h	conv.[b]/%	M_w/M_n[c]
1	**3**	4	31	1.29
2	**1**	4	39	1.24
3	**3**	6	38	1.34
4	**1**	5	49	1.30

[a] Polymerizations run at 125 °C under N_2 atmosphere. [MMA]/[**1** or **3**] = 300:1. [b] Conversion determined by ^{1}H NMR. [c] Determined by SEC against polystyrene standards.

Table 2. Polymerization of Styrene with Alkoxyamine 1[a]

entry	time/h	conv.[b]/%	$M_{n,theor}$[c]/kg/mol	$M_{n,SEC}$[d]/kg/mol	M_w/M_n[d]
1	4.5	4.3	1.4	7.2	1.50
2	7	23.5	5.4	11.5	1.57
3	15	40	8.9	15.1	1.43

[a] Polymerizations run at 125 °C under N_2 atmosphere. [Styrene]/[**1**] = 200:1. [b] Conversion determined by ^{1}H NMR. [c] Calculated based on conversion. [d] Determined by SEC against polystyrene standards.

conversion) with most chains appearing to have undergone irreversible termination reactions in less than 1 h, and the molecular weight distributions remained broad for the different times examined (M_w/M_n = 1.58−1.63). This suggests that the *N*-phenyl group plays an important role in the successful homopolymerization of MMA.

Polymerization of Styrene. Polymerization of styrene (200 equiv) with **1** was uncontrolled, with large discrepancies observed between the theoretical and calculated molecular weights and broad molecular weight distributions (M_w/M_n = 1.43−1.57) (Table 2). We have previously observed similar results with the arylnitroxide-based alkoxyamine **3**, which produced polystyrene with broad molecular weight distributions over the conversion range studied (conversion = 20−66%; M_w/M_n = 1.36−1.50), along with inconsistent theoretical and calculated molecular weights.[21] The polymerization of styrene with alkoxyamine **1** proceeded more slowly than with alkoxyamine **3**, although initiating efficiencies were similar for **1** (I_{eff} = 0.47−0.59) and **3** (I_{eff} = 0.50−0.53) for conversions from 20 to 40%. Molecular weight distributions were also slightly broader for polystyrene prepared from **1** (M_w/M_n = 1.43−1.57) than polystyrene prepared from **3** (M_w/M_n = 1.36−1.50).

Initiator **2** was also employed in the polymerization of styrene (200 equiv). While alkoxyamine **2** was not able to control the homopolymerization of MMA, presumably due to steric and electronic effects of the *N*-*t*-butyl moiety, it was able to effect a controlled polymerization of styrene. The molecular weights evolved linearly with conversion, up to the highest observed conversion of 73%, and the theoretical and calculated molecular weights correlated well to at least 66% conversion. The molecular weight distributions remained narrow throughout the polymerization (M_w/M_n = 1.08−1.22) suggesting a controlled process (Figure 2a). The pseudo-first-order kinetic plot exhibited a smooth consumption of monomer over time (Figure 2b).

Nitroarenes, while known to be relatively innocuous additives in the radical polymerization of MMA, are known to retard the polymerization of styrene.[35] However, the ability of alkoxyamine **2** to control styrene polymerizations suggests that the lack of control observed with alkoxyamine **1** and styrene results largely from the *N*-aryl substituent and not the nitro group.

Chain Extension Studies. Chain extension polymerizations from a PMMA macroinitiator made from alkoxyamine **1** were conducted with both MMA and styrene. Macroinitiator **PMMA-1** ($M_{n,SEC}$ = 11.4 kg/mol; M_w/M_n = 1.28) was

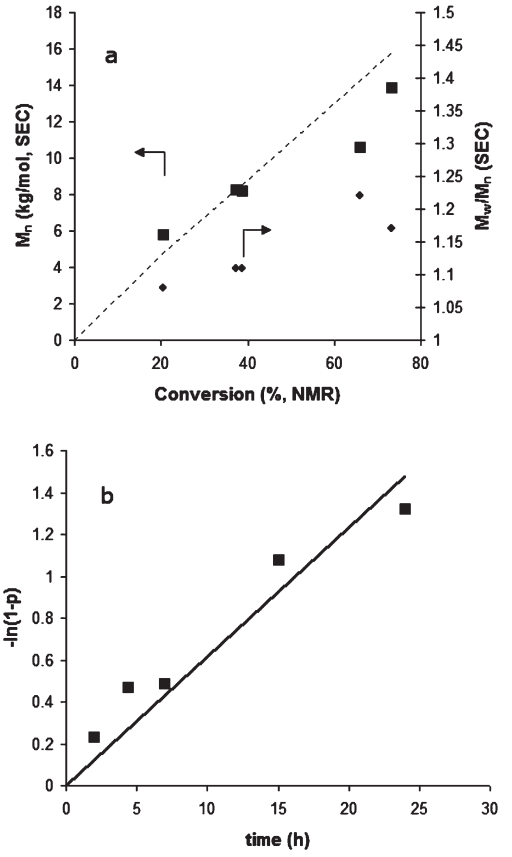


Figure 2. (a) Evolution of M_n and M_w/M_n with conversion; (- - -) = theoretical M_n and (b) pseudo-first-order kinetic analysis for [styrene]:[**2**] = 200:1 at 125 °C; (—) = best fit line.

prepared by the polymerization of MMA (300 equiv) from alkoxyamine **1** to 17% conversion. For MMA chain extension, purified **PMMA-1** was redissolved in MMA (2000 equiv) and allowed to react at 125 °C for 6 h. The resulting **PMMA−PMMA-1** showed a slightly higher molecular weight ($M_{n,SEC}$ = 14.0 kg/mol) and broader molecular weight distribution (M_w/M_n = 1.37) (Figure 3). This indicates that the macroinitiator **PMMA-1** had living chain ends that could be extended with additional MMA, although chain extension to high enough molecular weights to show significant shifts in SEC traces was not achieved.

Macroinitiator **PMMA-1** was also employed for chain extension with styrene to examine the feasibility of diblock copolymer formation. **PMMA-1** macroinitiator was dissolved in styrene (2000 equiv) and allowed to react at 125 °C for 6 h to 24% conversion. The resulting PMMA-PS diblock (**PMMA-PS-1a**; Figure 4a) had a substantially higher molecular weight by SEC (M_n = 61.8 kg/mol). The molecular weight distribution was significantly broadened, however, from homopolymer to the diblock (M_w/M_n = 1.28 for **PMMA-1a**; M_w/M_n = 1.97 for **PMMA-PS-1a**). This result is not unusual since *N*-phenyl initiators, such as alkoxyamine **1**, do not appear to be capable of controlling the polymerization of pure styrene. The substantial increase in molecular weight seen in this polymerization shows that there is a low molecular weight shoulder present in the SEC trace of the diblock, which was not visible in the MMA chain extension experiments (Figure 3) and most likely results from dead homopolymer that was not able to chain extend with styrene (Figure 4a).

After precipitation of **PMMA-PS-1a**, the resultant diblock (**PMMA-PS-1b**, Figure 4b) showed a higher molecular weight

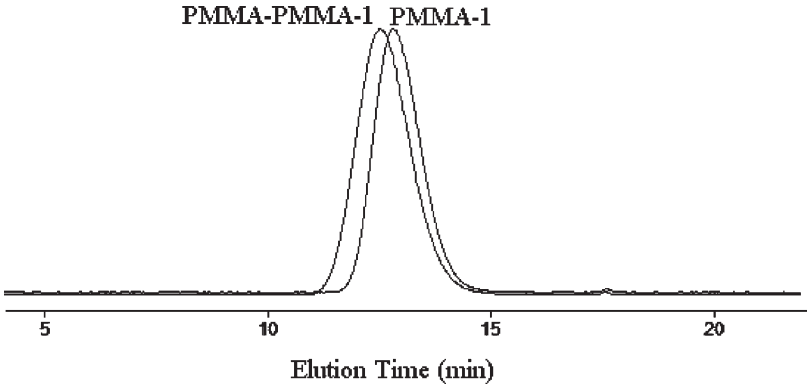


Figure 3. Chain extension from PMMA made from **1** with MMA. **PMMA-1**: reaction time 2.5 h; ^{1}H NMR: $M_n = 5.6$ kg/mol, conversion = 17%; SEC: $M_n = 11.4$ kg/mol, $M_w/M_n = 1.28$; **PMMA−PMMA-1**: reaction time 6 h; SEC: $M_n = 14.0$ kg/mol, $M_w/M_n = 1.37$. The polymer was precipitated once into hexanes from dichloromethane before SEC analysis.

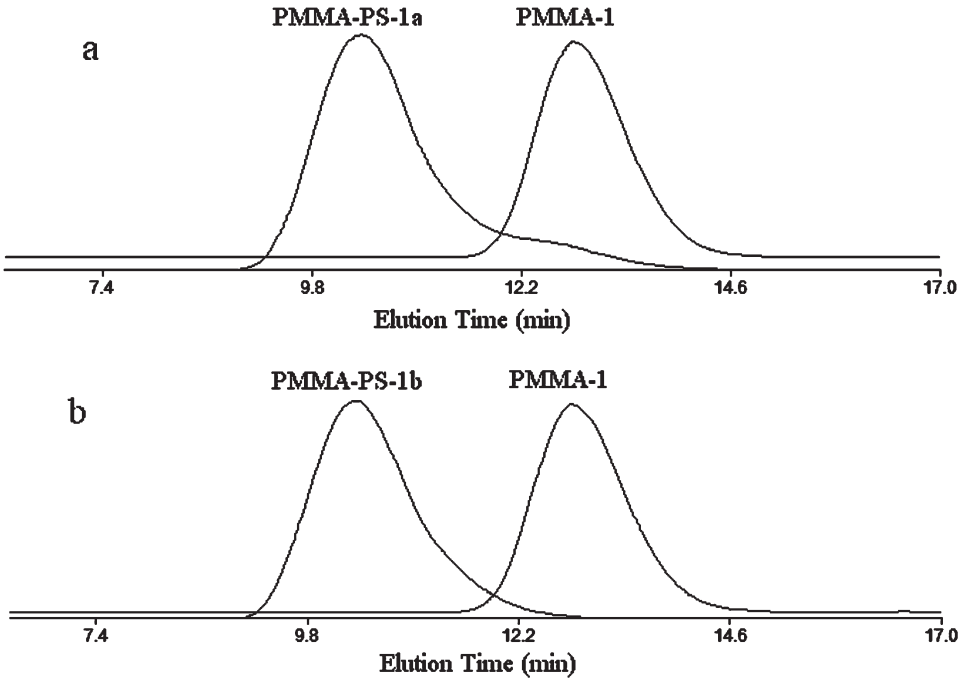


Figure 4. Chain extension from PMMA made from **1** with styrene. (a) **PMMA-1**: reaction time 2.5 h; ^{1}H NMR: $M_n = 5.6$ kg/mol, conversion = 17%; SEC: $M_n = 11.4$ kg/mol, $M_w/M_n = 1.28$; **PMMA-PS-1a**: reaction time 6 h; ^{1}H NMR: $M_n = 60.8$ kg/mol, conversion = 24%; SEC: $M_n = 61.8$ kg/mol, $M_w/M_n = 1.97$. The polymer was not precipitated prior to SEC analysis. (b) **PMMA-1**: reaction time 2.5 h; ^{1}H NMR: $M_n = 5.6$ kg/mol, conversion = 17%; SEC: $M_n = 11.4$ kg/mol, $M_w/M_n = 1.28$; **PMMA-PS-1b**: reaction time 6 h; ^{1}H NMR: $M_n = 60.8$ kg/mol, conversion = 24%; SEC: $M_n = 94.3$ kg/mol, $M_w/M_n = 1.42$. The polymer was precipitated once into methanol from dichloromethane before SEC analysis.

($M_{n,SEC} = 94.3$ kg/mol) than that seen with the unprecipitated **PMMA-PS-1a** diblock copolymer ($M_{n,SEC} = 61.8$ kg/mol), and the molecular weight distribution was narrower for the precipitated polymer as a result of fractionation of shorter polymer chains ($M_w/M_n = 1.42$ for **PMMA-PS-1b** compared to $M_w/M_n = 1.97$ for **PMMA-PS-1a**). The ^{1}H NMR spectrum of the precipitated diblock **PMMA-PS-1b** showed incorporation of both PS and PMMA blocks, which, in conjunction with the monomodal SEC trace, corroborates formation of the diblock.

Conclusion

Alkoxyamine **1** was synthesized to ascertain the effect of the *para*-nitrophenyl ester substituents on the polymerization of MMA and styrene. Alkoxyamine **1** was able to control the polymerization of MMA (300−1000 equiv) at conversions up to 50% and molecular weights up to 65 kg/mol (vs PS standards) with narrow molecular weight distributions ($M_w/M_n = 1.12-1.30$) and appeared to allow greater control over MMA polymerization than the previously examined phenyl ester-functional alkoxyamine **3**. As had previously been observed with other arylnitroxide-based alkoxyamines,[21] PS prepared with alkoxyamine **1** showed large discrepancies between the theoretical and calculated molecular weights and broad molecular weight distributions, suggesting that *N*-phenylalkoxyamines are not broadly applicable to a wide range of monomers for NMP. However, they are able to control MMA polymerization to moderate conversions and allow chain extension for the formation of block copolymers. A recent report also suggests that *N*-arylalkoxyamines can also afford some degree of control over the polymerization of acrylate monomers.[36]

The effect of the *N*-phenyl group of initiator **1** was probed by the synthesis of the corresponding *N*-alkylnitroxide-based initiator **2**, which contained an *N*-*tert*-butyl group. Alkoxyamine **2** was not able to control the polymerization of MMA, but controlled the polymerization of styrene. These findings are corroborated by our previous work, which showed that arylnitroxides are not

capable of controlling the polymerization of styrene, but are successful at controlling MMA polymerizations to moderate conversions, while the corresponding *N*-*tert*-butylnitroxides control styrene polymerization but not methacrylate polymerization.[21] This indicates that the steric and electronic effects afforded by the *N*-phenyl moiety in alkoxyamine **1** are paramount to achieving success with the NMP of MMA.

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