Supporting Information

Novel Alkoxyamines for the Successful Controlled Polymerization of Styrene and Methacrylates

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Conversion Determination for Polymerization of Styrene in the Presence of Alkoxyamine

\[
\text{Conversion} = \frac{m_{\text{monomer}} + m_{\text{alkoxyamine}} + m_{\text{solvent}}}{m_{\text{monomer}} + m_{\text{alkoxyamine}}} \times \frac{m_{\text{dry capsule}} - m_{\text{tare}}} {m_{\text{wet capsule}} - m_{\text{tare}}}
\]

Equation (1)

Polymerization of Styrene in the Presence of Alkoxyamine (B)

In a typical procedure, Alkoxyamine (B) (857 mg, 2.52 mmol), styrene (87.6 g, 333 equiv, 75 wt.%) and tert-butylbenzene (29.5 g) were charged into a three-neck 250-mL RBF fitted with a stirring bar, thermometer and rubber seals. The mixture was stirred and deoxygenated with nitrogen for 30 minutes and subsequently placed in a pre-heated oil bath at 136 °C. The solution was left to polymerize at 126 °C for at least 5 hours. Samples for conversion and SEC analysis were carefully taken from the polymerization mixture via a deoxygenated syringe. Monomer conversion was calculated from gravimetric analysis using Equation 1.

After polymerization, the solution was diluted in THF, precipitated in MeOH and dried under vacuum to yield a white solid.
Influence of temperature when using Alkoxyamine (B)

Figure S1. Polymerization of styrene ([Alkoxyamine (B)]:[M] 1:333 with a monomer concentration of 75 wt.% in tert-butylbenzene), at different temperatures (110, 126 and 136 °C). Evolution of Ln([M]₀/[M]) versus time (bottom) and evolutions of observed molecular weight ($M_n$, SEC-MALS, dotted lines corresponding to the theoretical evolutions) and dispersity values ($D$) with monomer conversion (top).
Influence of $DP_n$, when Using Alkoxyamine (A)

For comparison, polymerization of styrene for a targeted $DP_n = 333$ was also conducted at 50 wt.% monomer in tert-butylbenzene (Figure S2).

**Figure S2.** Polymerization of styrene ([Alkoxyamine]:[M] 1:333 with a monomer concentration of 50 wt.% in tert-butylbenzene), at 126 °C. Evolution of $\ln([M]_0/[M])$ versus time (bottom) and evolutions of observed molecular weight ($M_n$, SEC-MALS, dotted lines corresponding to the theoretical evolutions) and dispersity values ($D$) with monomer conversion (top).
Figure S3. Polymerization of styrene ([Alkoxyamine (A)]:[M]:[Ac₂O]= 1:999:2 with a monomer concentration of 50 wt.% in tert-butylbenzene) at 126 °C. Evolution of Ln([M]₀/[M]) versus time (bottom) and evolutions of observed molecular weight ($M_n$, SEC-MALS, dotted lines corresponding to the theoretical evolutions) and dispersity values ($D$) with monomer conversion (top).

Polymerization of Styrene in the Presence of BlocBuilder

In a typical procedure, BlocBuilder (439 mg, 1.14 mmol), styrene (40 g, 333 equiv, 75 wt.%) and tert-butylbenzene (13.3 g) were charged into a three-neck 250-mL RBF fitted with a stirring bar, thermometer and rubber seals. The mixture was stirred and deoxygenated with nitrogen for 30 minutes and subsequently placed in a pre-heated oil bath at 136 °C. The solution was left to polymerize at 126 °C for at least 5 hours. Samples for conversion and SEC analysis were carefully taken from the polymerization mixture via a deoxygenated syringe. Monomer conversion was calculated from gravimetric analysis using Equation 1.

After polymerization, the solution was diluted in THF, precipitated in MeOH and dried under vacuum to yield a white solid.
Polymerization of Styrene in the Presence of Alkoxyamine (C)

In a typical procedure, Alkoxyamine (C) (662 mg, 2.52 mmol), styrene (87.6 g, 333 equiv, 75 wt.%) and tert-butyl benzene (29.5 g) were charged in a three-neck 250-mL RBF fitted with a stirring bar, thermometer and rubber seals. The mixture was stirred and deoxygenated with nitrogen for 30 minutes and subsequently placed in a pre-heated oil bath at 136 °C. The solution was left to polymerize at 126 °C for at least 5 hours. Samples for conversion and SEC analysis were carefully taken from the polymerization mixture via a deoxygenated syringe. Monomer conversion was calculated from gravimetric analysis using Equation 1.

After polymerization, the solution was diluted in THF, precipitated in MeOH and dried under vacuum to yield a white solid.

Nitroxide Exchange for a Polystyrene Macro-alkoxyamine (A) with TEMPO

![Figure S4. SEC (THF) traces of poly(styrene) macro-alkoxyamine with Alkoxyamine (A) functionality before (blue) and after (orange) nitroxide exchange with TEMPO.](image)
Figure S5. DOSY NMR (CDCl$_3$, 400 MHz) of poly(styrene) mediated by Alkoxyamine (A).

Figure S6. DOSY NMR (CDCl$_3$, 400 MHz) of poly(styrene) mediated by Alkoxyamine (A) after nitrooxide exchange with TEMPO.
Chain Extension for a Poly(styrene) Macro-alkoxyamine (B) with Styrene (moderate conversion of styrene for the macro-alkoxyamine)

A poly(styrene) macro-alkoxyamine (B) (242 mg, 1 equiv, $M_n = 2700$ g.mol$^{-1}$), prepared via the pre-detailed procedure (target $DP_n = 50$ stopped at 60% conversion) was added to a 50-mL RBF fitted with rubber seals. Styrene (3g, 19 mmol, 200 equiv) and tert-butylbenzene (3 g) were added to the RBF with a magnetic stirring bar and the contents were left to stir and deoxygenate with nitrogen for 30 minutes. Subsequently, the mixture was placed in a pre-heated oil bath at 136 °C (in order to have an internal temperature of 126 °C) and left to polymerize overnight. Then, a sample was isolated for gravimetric analysis, whilst the remaining solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid.
Figure S8. SEC traces (THF eluent) of chain extension of poly(styrene) mediated by Alkoxyamine (B) with styrene ([Macro-alkoxyamine (B)]:[M] 1:200 with a monomer concentration of 50 wt.% in tert-butylbenzene at 126 °C).

Chain Extension for a Poly(styrene) Macro-alkoxyamine (B) with Styrene (high conversion of styrene for the macro-alkoxyamine)

A poly(styrene) macro-alkoxyamine (B) (242 mg, 1 equiv, $M_n = 2000 \text{ g.mol}^{-1}$), prepared via the pre-detailed procedure (target $DP_n = 50$ stopped at >95% conversion) was added to a 50-mL RBF fitted with rubber seals. Styrene (2g, 19 mmol, 200 equiv) and tert-butylbenzene (2 g) were added to the RBF with a magnetic stirring bar and the contents were left to stir and deoxygenate with nitrogen for 30 minutes. Subsequently, the mixture was placed in a pre-heated oil bath at 136 °C (in order to have an internal temperature of 126 °C) and left to polymerize overnight. Then, a sample was isolated for gravimetric analysis, whilst the remaining solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid.

Figure S9. SEC traces (THF eluent) of chain extension of poly(styrene) mediated by Alkoxyamine (B) with styrene. (Left) ([Macro-alkoxyamine (B)]:[M] 1:200 with a monomer concentration of 50 wt.% in tert-butylbenzene at 126 °C).
Nitroxide Exchange for a Poly(styrene) Macro-alkoxyamine (B) with TEMPO

Alkoxyamine (B) (651 mg, 2.52 mmol), styrene (10 g, 50 equiv, 75 wt.%) and tert-butylbenzene (3.3 g) were charged into a 2-neck 50-mL RBF fitted with a stirring bar, thermometer and rubber seals. The mixture was stirred and deoxygenated with nitrogen for 30 minutes and subsequently placed in a pre-heated oil bath at 136 °C. The solution was left to polymerize at 126 °C for 4 hours. Monomer conversion (95 %) was calculated from gravimetric analysis using Equation 1.

After polymerization, the solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid. Subsequently, the nitroxide exchange was performed in a similar fashion as for Alkoxyamine (A).

Figure S10. 13C NMR (CDCl₃, 100 MHz) of poly(styrene) mediated by Alkoxyamine (B) before (left) and after (right) nitroxide exchange with TEMPO.

Chain Extension for a Poly(styrene) Macro-alkoxyamine (B) with Methyl Methacrylate

A poly(styrene) macro-alkoxyamine (B) (1.5 g, 1 equiv), prepared via the pre-detailed procedure, was added to a 50-mL RBF fitted with rubber seals. MMA (2.5 g, 19.9 mmol, 400 equiv) and tert-butylbenzene (4.5 g) were added to the RBF with a magnetic stirring bar and the contents were left to stir and deoxygenate with nitrogen for 30 minutes. Subsequently, the mixture was placed in a pre-heated oil bath at 96 °C (in order to have an internal temperature of 90 °C) and left to polymerize overnight. Then, a sample was isolated for gravimetric analysis,
whilst the remaining solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid.

**Figure S11.** SEC traces (THF eluent) of chain extension of poly(styrene) mediated by Alkoxyamine (B) with methyl methacrylate ([Macro-alkoxyamine]:[M] 1:400 with a monomer concentration of 25 wt.% in tert-butylbenzene at 90 °C).

**Chain extension for a Polystyrene Macro-alkoxyamine (B) with n-Butyl Methacrylate**

A poly(styrene) macro-alkoxyamine (B) (1.2 g, 1 equiv), prepared via the pre-detailed procedure ($M_n^{\text{target}} = 35000 \text{ g.mol}^{-1}$, 78% conversion), was added to a 50-mL RBF fitted with rubber seals. BMA (5 g, 35 mmol, 800 equiv) and tert-butylbenzene (5 g) were added to the RBF with a magnetic stirring bar and the contents were left to stir and deoxygenate with nitrogen for 30 minutes. Subsequently, the mixture was placed in a pre-heated oil bath at 136 °C (in order to have an internal temperature of ca. 126 °C) and left to polymerize overnight. Then, a sample was isolated for gravimetric analysis, whilst the remaining solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid.

In order to have a better insight of the end group fidelity, a similar procedure was employed, using a poly(styrene) macro-alkoxyamine (B) (250 mg, $7.0 \times 10^{-5}$ mol, $M_n = 2800 \text{ g.mol}^{-1}$) and BMA (500 mg, 3.5 mmol, 50 eq). The resulting polymer ($M_n = 4400 \text{ g.mol}^{-1}$) was analysed by $^1$H NMR, COSY, HSQC and SEC analyses.
Figure S12. $^1$H NMR (CDCl$_3$, 400 MHz) of poly(styrene) mediated by Alkoxyamine (B), $M_n$ = 2800 g.mol$^{-1}$.

Figure S13. HSQC (CDCl$_3$) of poly(styrene) mediated by Alkoxyamine (B), $M_n$ = 2800 g.mol$^{-1}$. 
In Figure S13, the correlation between the CH₂-CH₂-CH₂ peaks at 0.98 ppm and the CH₂-CH₂-CH₂ peaks at 26 ppm, as well as the correlation between the C(CH₃)₂CN peaks at 1.18 ppm and the C(CH₃)₂CN peaks at 28 ppm highlights the presence of the α,ω-end groups of Alkoxyamine (B) on the poly(styrene) chain.

Figure S14. ¹H NMR (CDCl₃, 400 MHz) of PS-b-PBMA, $M_n^{th}$ = 4400 g.mol⁻¹.
Figure S15. COSY NMR (CDCl₃, 400 MHz) of PS-\textit{b}-PBMA, $M_n^{\text{th}} = 4400$ g.mol\textsuperscript{-1}.

The $^1$H-$^1$H correlations observed in Figure S15 support the proton assignments of PS-\textit{b}-PBMA in Figure S14.
Figure S16. HSQC NMR (CDCl₃, 400 MHz) of PS-\textit{b}-PBMA, $M_{n}^{\text{th}}=4400$ g.mol⁻¹.

The $^1$H-$^13$C correlations observed in Figure S16 support the carbon assignments of PS-\textit{b}-PBMA in Figure S17.

Figure S17. $^{13}$C NMR (CDCl₃, 100 MHz) of PS-\textit{b}-PBMA, $M_{n}^{\text{th}}=4400$ g.mol⁻¹.
Polymerization of Methyl Methacrylate in the Presence of Alkoxyamine (B)

In a typical procedure, Alkoxyamine (B) (169 mg, 1 equiv), MMA (5 g, 49.9 mmol, 100 equiv, 50 wt.%) and toluene (5 g) were charged into a 50-mL RBF fitted with a stirring bar and rubber seal. The mixture was stirred and deoxygenated with nitrogen for 30 minutes and subsequently placed in a pre-heated oil bath at 96 °C. The solution was left to polymerize at 90 °C for 4h, reaching a monomer conversion of 70 %.

After polymerization, the solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid.

Chain Extension for a Poly(methyl methacrylate) Macro-alkoxyamine (B) with Styrene

A poly(MMA) macro-alkoxyamine (B) (523 mg, 1 equiv), prepared via the pre-detailed procedure, was added to a 50-mL RBF fitted with rubber seals. Styrene (3 g, 28.8 mmol, 400 equiv) and tert-butylbenzene (3 g) were added to the RBF with a magnetic stirring bar and the contents were left to stir and deoxygenate with nitrogen for 30 minutes. Subsequently, the mixture was placed in a pre-heated oil bath at 136 °C (in order to have an internal temperature of 126 °C) and left to polymerize overnight. Then, a sample was isolated for gravimetric analysis, whilst the remaining solution was diluted in THF, precipitated twice in MeOH and dried under vacuum to yield a white solid.