

## Supporting Information

### Novel Alkoxyamines for the Successful Controlled Polymerization of Styrene and Methacrylates

*Alexandre Simula,<sup>1</sup> Miren Aguirre,<sup>1</sup> Nicholas Ballard,<sup>1</sup> Antonio Veloso,<sup>1</sup> José R. Leiza,<sup>1</sup> Steven van Es<sup>1,2</sup> and José M. Asua<sup>1,\*</sup>*

<sup>1</sup>*POLYMAT and Kimika Aplikatua Saila, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018, Donostia/San Sebastián, Spain*

<sup>2</sup>*Dispoltec BV, PO Box 331, 6160 AH Geleen, The Netherlands*

#### Conversion Determination for Polymerization of Styrene in the Presence of Alkoxyamine

Equation (1)

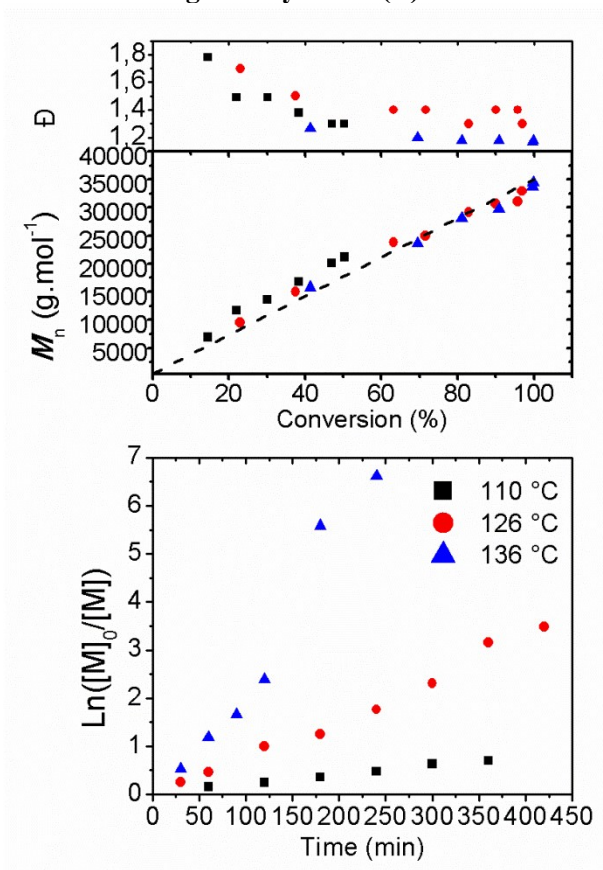
$$\text{Conversion} = \frac{m_{\text{monomer}} + m_{\text{alkoxyamine}} + m_{\text{solvent}}}{m_{\text{monomer}} + m_{\text{alkoxyamine}}} \times \frac{m_{\text{capsule}}^{\text{dry}} - m_{\text{capsule}}^{\text{tare}}}{m_{\text{capsule}}^{\text{wet}} - m_{\text{capsule}}^{\text{tare}}}$$

#### 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.

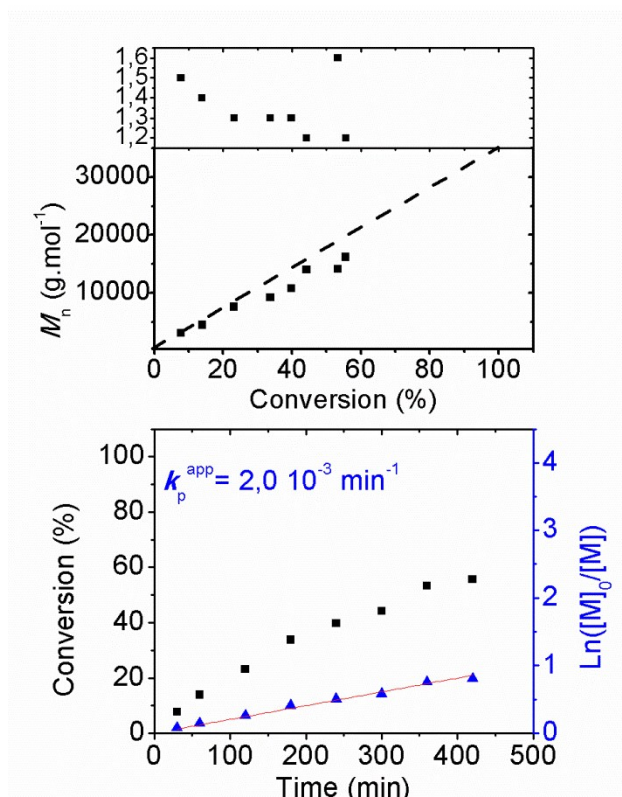
### Influence of temperature when using Alkoxyamine (B)



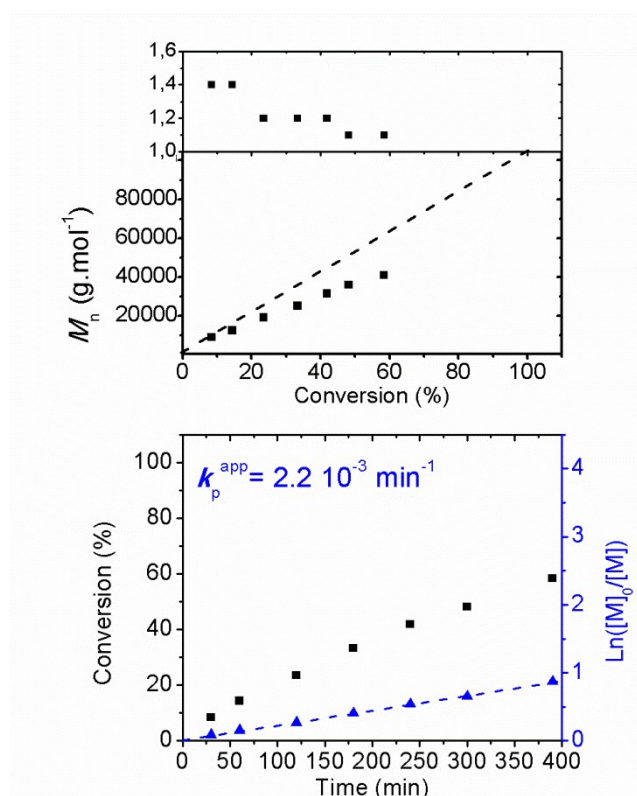
**Figure S1.** Polymerization of styrene ( $[\text{Alkoxyamine (B)}]:[\text{M}]$  1:333 with a monomer concentration of 75 wt.% in *tert*-butylbenzene), at different temperatures (110, 126 and 136 °C). Evolution of  $\text{Ln}([M]_0/[M])$  versus time (bottom) and evolutions of observed molecular weight ( $M_n$ , SEC-MALS, dotted lines corresponding to the theoretical evolutions) and dispersity values ( $\bar{D}$ ) 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 ( $\bar{D}$ ) with monomer conversion (top).



**Figure S3.** Polymerization of styrene ([Alkoxyamine (A)]:[M]:[Ac<sub>2</sub>O]= 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 ( $\bar{D}$ ) 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.

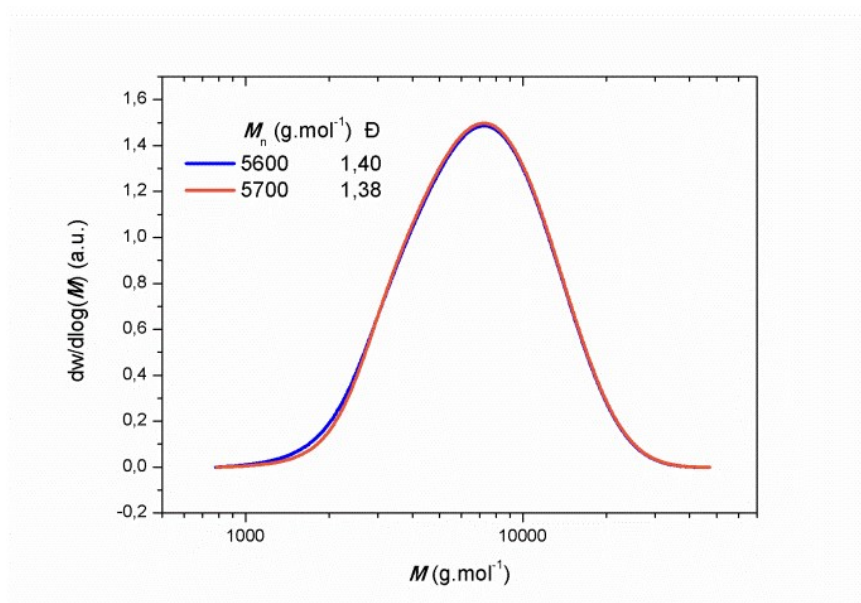
After polymerization, the solution was diluted in THF, precipitated in MeOH and dried under vacuum to yield a white solid.

### Polymerization of Styrene in the Presence of Alkoxyamine (C)

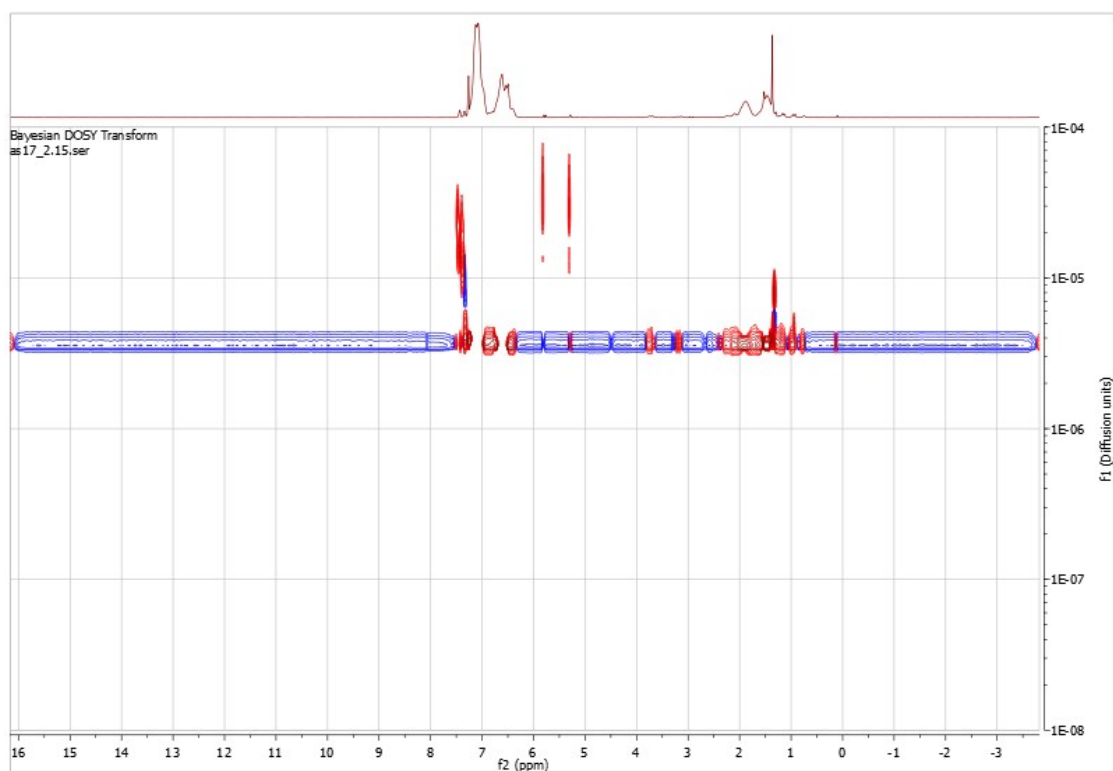
In a typical procedure, Alkoxyamine (C) (662 mg, 2.52 mmol), styrene (87.6 g, 333 equiv, 75 wt.%) and *tert*-butylbenzene (29.5 g) were charged in a three-neck 250-mL RBF fitted with a stirring bar, thermometer and rubber seals. The mixture was stirred and deoxygenated with nitrogen for 30 minutes and 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.

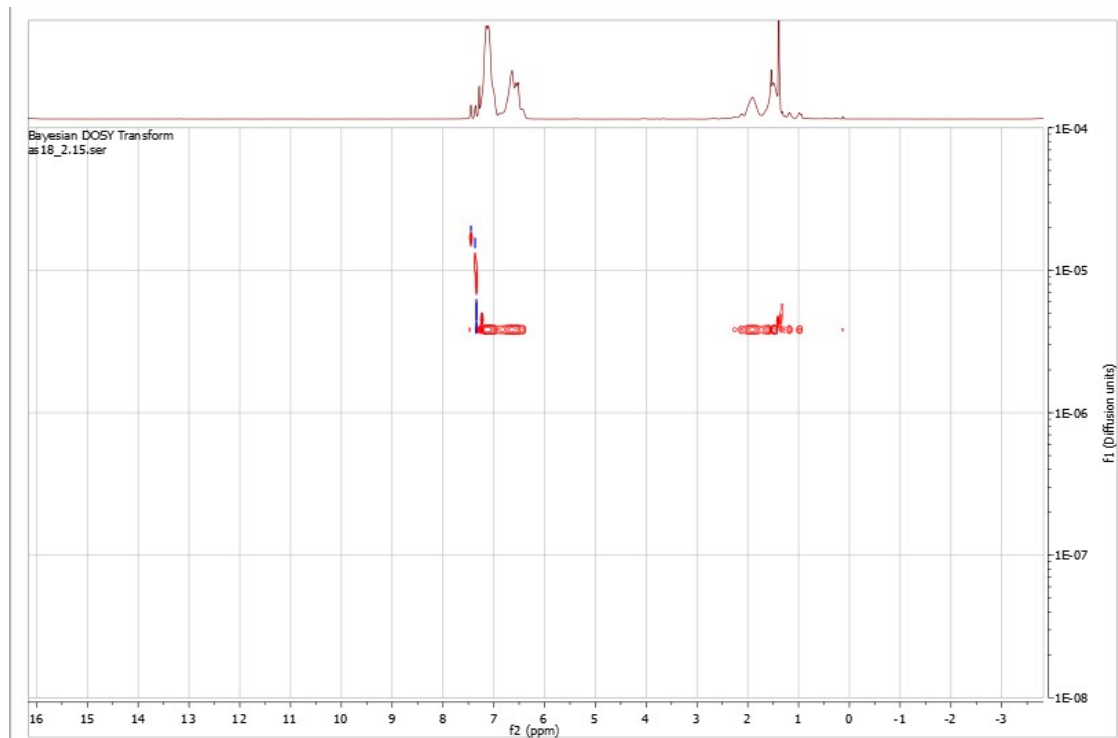
### Nitroxide Exchange for a Polystyrene Macro-alkoxyamine (A) with TEMPO



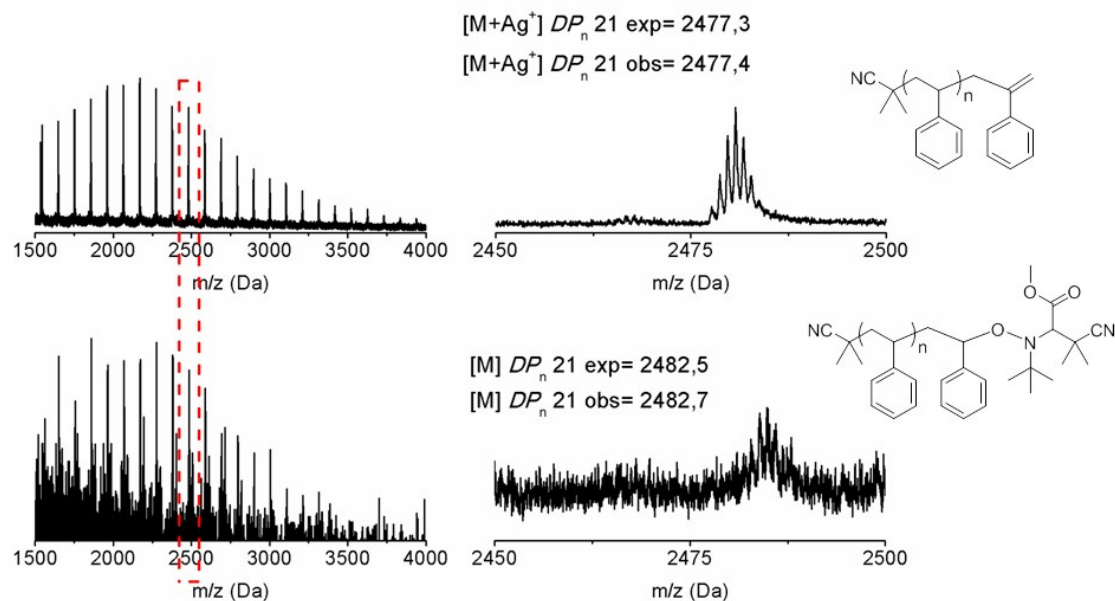
**Figure S4.** SEC (THF) traces of poly(styrene) macro-alkoxyamine with Alkoxyamine (A) functionality before (blue) and after (orange) nitroxide exchange with TEMPO.



**Figure S5.** DOSY NMR ( $\text{CDCl}_3$ , 400 MHz) of poly(styrene) mediated by Alkoxyamine (A).



**Figure S6.** DOSY NMR ( $\text{CDCl}_3$ , 400 MHz) of poly(styrene) mediated by Alkoxyamine (A) after nitroxide exchange with TEMPO.

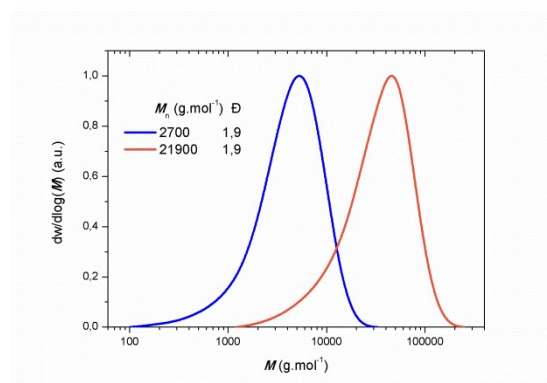


**Figure S7.** Mass spectra (MALDI-ToF MS) of poly(styrene) mediated by Alkoxyamine (A) obtained with DCTB with AgTFA (top) and DHB (bottom) matrices.

**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,  $M_n = 2700 \text{ g.mol}^{-1}$ ), 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.

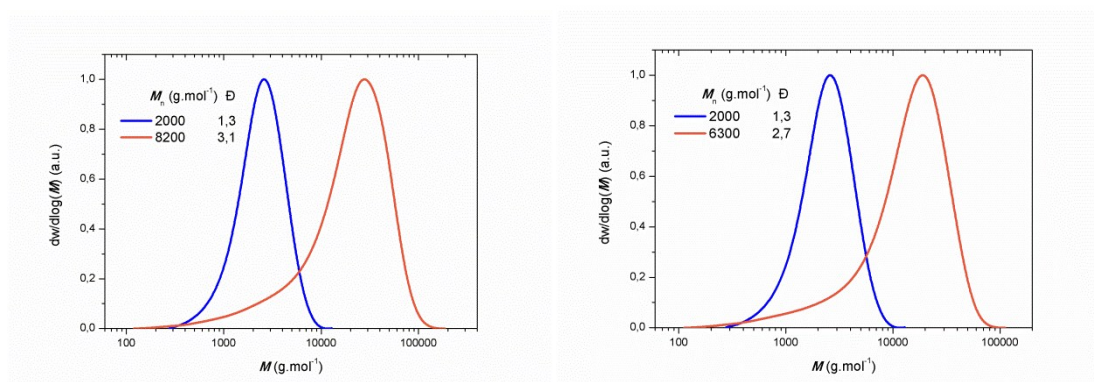




**Figure S8.** SEC traces (THF eluent) of chain extension of poly(styrene) mediated by Alkoxyamine (B) with styrene ([Macro-alkoxyamine (B)]:[M] 1:200 with a monomer concentration of 50 wt.% in *tert*-butylbenzene at 126 °C).

### 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

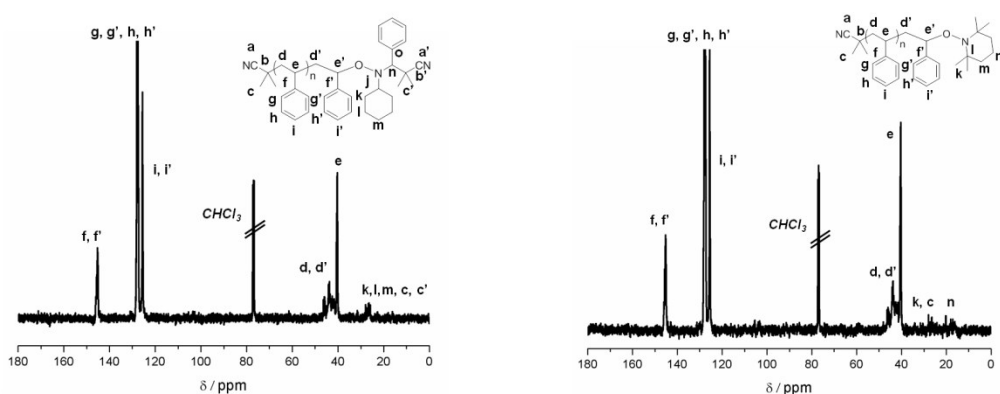


concentration of 50 wt.% in *tert*-butylbenzene at 126 °C). (Right) ([Macro-alkoxyamine (B)]:[M] 1:100 with a monomer concentration of 50 wt.% in *tert*-butylbenzene at 126 °C).

### 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 at 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).

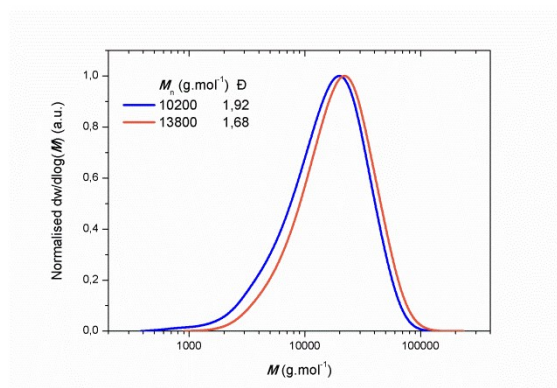


**Figure S10.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of poly(styrene) mediated by Alkoxyamine (B) before (left) and after (right) nitroxide exchange with TEMPO.

### 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.

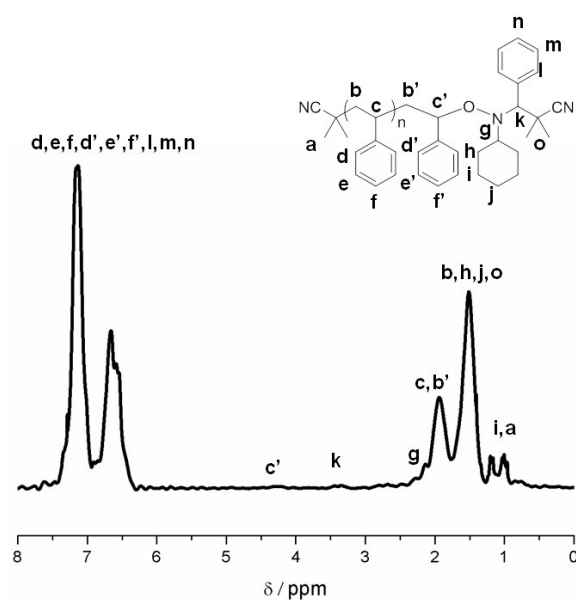


**Figure S11.** SEC traces (THF eluent) of chain extension of poly(styrene) mediated by Alkoxyamine (B) with methyl methacrylate ([Macro-alkoxyamine]:[M] 1:400 with a monomer concentration of 25 wt.% in *tert*-butylbenzene at 90 °C).

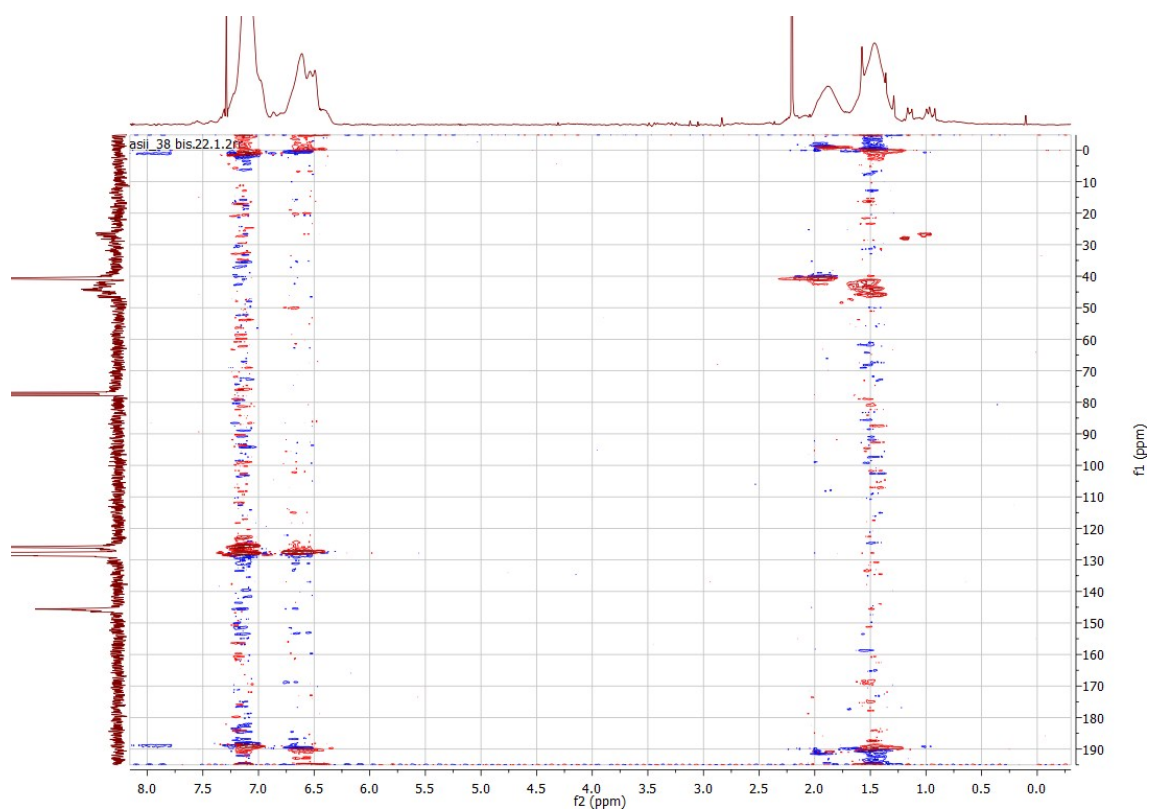
#### Chain extension for a Polystyrene Macro-alkoxyamine (B) with *n*-Butyl Methacrylate

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,  $7.0 \cdot 10^{-5} \text{ mol}$ ,  $M_n = 2800 \text{ g.mol}^{-1}$ ) and BMA (500 mg, 3.5 mmol, 50 eq). The resulting polymer ( $M_n = 4400 \text{ g.mol}^{-1}$ ) was analysed by <sup>1</sup>H NMR, COSY, HSQC and SEC analyses.

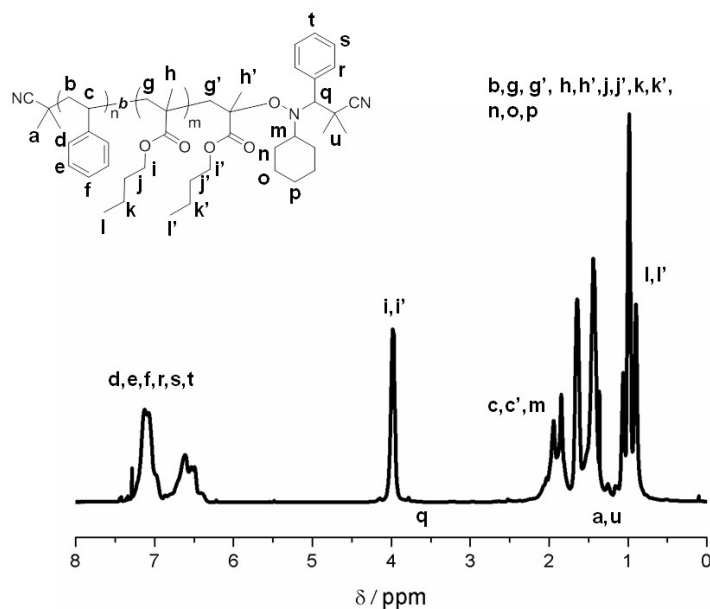


**Figure S12.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of poly(styrene) mediated by Alkoxyamine (B),  $M_n^{\text{th}} = 2800 \text{ g.mol}^{-1}$ .

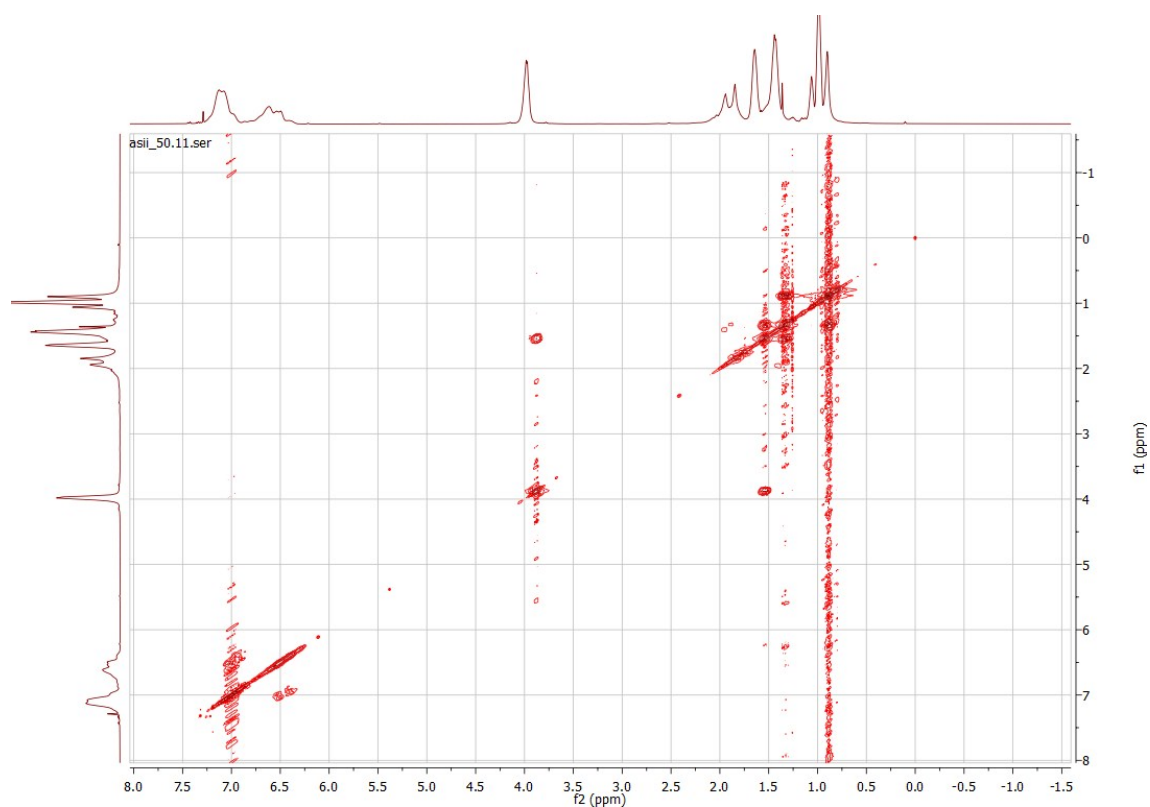


**Figure S13.** HSQC ( $\text{CDCl}_3$ ) of poly(styrene) mediated by Alkoxyamine (B),  $M_n^{\text{th}} = 2800 \text{ g.mol}^{-1}$ .

In Figure S13, the correlation between the  $\text{CH}_2\text{-CH}_2\text{-CH}_2$  peaks at 0.98 ppm and the  $\text{CH}_2\text{-CH}_2\text{-CH}_2$  peaks at 26ppm, as well as the correlation between the  $\text{C}(\text{CH}_3)_2\text{CN}$  peaks at 1.18 ppm and the  $\text{C}(\text{CH}_3)_2\text{CN}$  peaks at 28 ppm highlights the presence of the  $\alpha,\omega$ -end groups of Alkoxyamine (B) on the poly(styrene) chain.

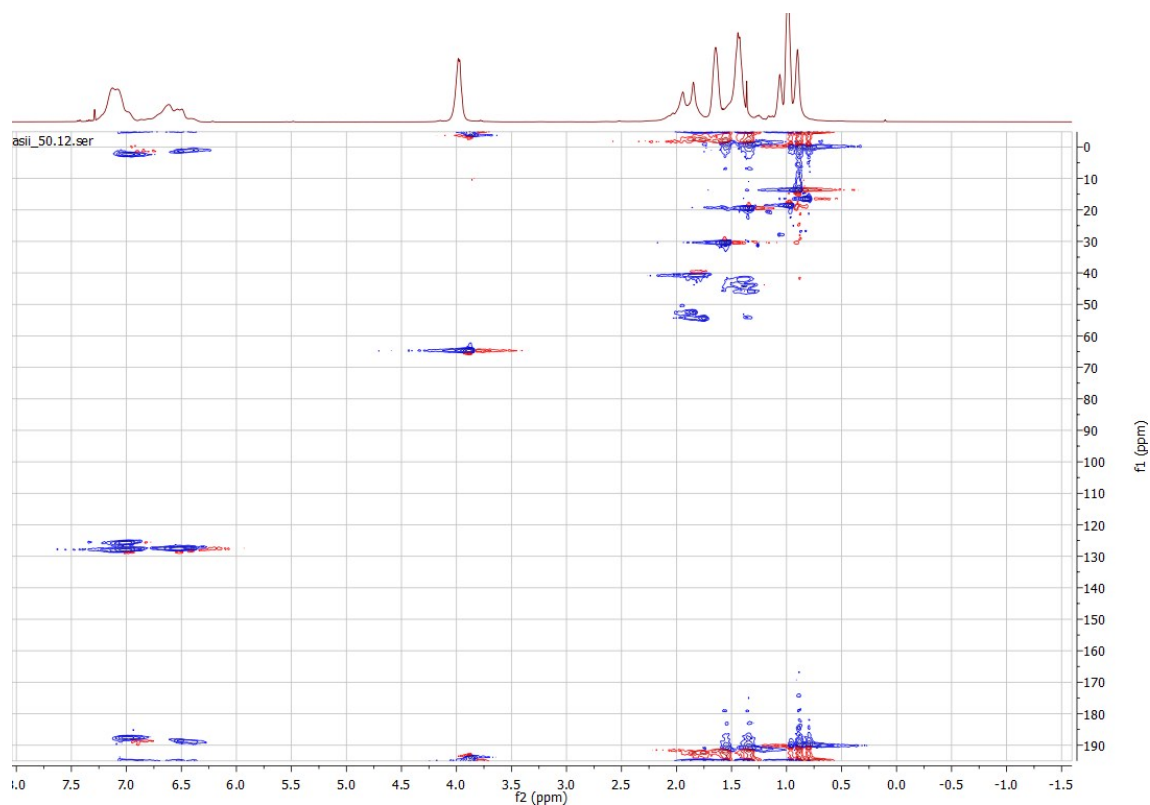


**Figure S14.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz) of  $\text{PS-}b\text{-PBMA}$ ,  $M_n^{\text{th}} = 4400 \text{ g.mol}^{-1}$ .



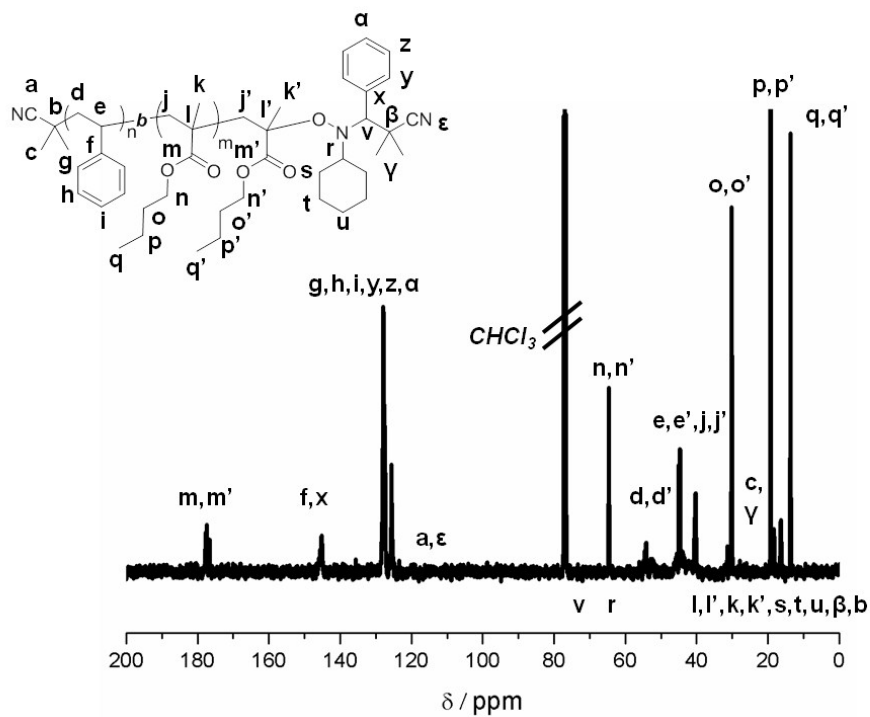
**Figure S15.** COSY NMR (CDCl<sub>3</sub>, 400 MHz) of PS-*b*-PBMA,  $M_n^{\text{th}} = 4400 \text{ g.mol}^{-1}$ .

The <sup>1</sup>H-<sup>1</sup>H correlations observed in Figure S15 support the proton assignments of PS-*b*-PBMA in Figure S14.



**Figure S16.** HSQC NMR ( $\text{CDCl}_3$ , 400 MHz) of PS-*b*-PBMA,  $M_n^{\text{th}} = 4400 \text{ g.mol}^{-1}$ .

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



**Figure S17.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) of PS-*b*-PBMA,  $M_n^{\text{th}} = 4400 \text{ g.mol}^{-1}$ .

### **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.