SUPPORTING INFORMATION for

High Molar Mass Segmented Macromolecular Architectures by Nitrooxide Mediated Polymerisation

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Polyether macroalkoxyamines

Synthesis:

Polyether-TEMPO macroinitiators were prepared by coupling monohydroxyl P(EO-co-PO) polymers with the functional alkoxyamine Cl-BzEt-TEMPO, as shown in Scheme S1. Polyethers with different molar masses were used as starting products: $M_n = 3,000$ g/mol for MI-1a in Table 1 and $M_n = 18,700$ g/mol for entries MI-1b and MI-1c in Table 1 ($M_n$ was determined by SEC calibrated with PS).

![Scheme S1](image)

Scheme S1 Functionalisation of P(EO-co-PO) with Cl-BzEt-TEMPO alkoxyamine.

In a typical experiment (MI-1b, Table 1), 3.340 g (2.27 x 10⁴ mol) of P(EO-co-PO) ($M_n = 18,700$ g/mol) was dried by azeotropic distillation with toluene (alternatively, the polyether could also be dried under vacuum at 150 °C for several hours until bubbles were
not observed anymore). Afterwards, it was dissolved in 3 mL of dried toluene (alternatively dried THF could also be used), cooled to 0 °C and 3 eq. of NaH (0.01636 g, 6.82 x 10^{-4} mol.) compared to the polyether were added under a gentle flow of nitrogen. After 30 min, 0.8 eq. of Cl-BzET-TEMPO alkoxyamine (0.694 mL of a 0.262 mol/L solution in dry toluene) compared to the polyether were added. The reaction was left to proceed overnight at room temperature. Subsequently, the excess of NaH was neutralised with methanol at 0 °C and the solvent was evaporated under reduced pressure.

*Characterisation:*

![NMR spectrum](image)

**Figure S1** ¹H NMR (300 MHz) for P(EO-co-PO)₂₀₀₀ functionalised with the Cl-BzEt-TEMPO alkoxyamine (MI-1a, Table 1).
Figure S2 $^1$H NMR (300 MHz) for P(EO-co-PO)$_{12000}$ functionalised with the Cl-BzEt-TEMPO alkoxyamine (MI-1b, Table 1).
Figure S3 $^1$H NMR (300 MHz) for P(EO-co-PO)$_{12000}$ functionalised with the Cl-BzEt-TEMPO alkoxyamine (MI-1c, Table 1).
**α-Methylstyrene polyether macromonomers**

*Synthesis:*

Polyether macromonomers bearing α-methyl styrene end-groups were prepared by coupling monohydroxyl P(EO-co-PO) polymers with 3-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI), as shown in Scheme S2. Polyethers with different molar masses were used as starting products: $M_n = 6,400 \text{ g/mol}$ for MM-1a in Table 1 and $M_n = 18,700 \text{ g/mol}$ for entries MM-1b in Table 1 ($M_n$ was determined by SEC calibrated with PS).

![Scheme S2](image)

**Scheme S2** Functionalisation of P(EO-co-PO) with 3-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI).

In a typical experiment (MM-1a, Table 1), 50 g of linear monohydroxy P(EO-co-PO) ($M_n = 6,400 \text{ g/mol}, 1.10 \times 10^{-2} \text{ mol}$) was dried for one day under high vacuum. Subsequently, 2.75 mL of TMI ($1.39 \times 10^{-2} \text{ mol}$ (1 eq. compared to –OH groups)) followed by 3 µL of DBTDL ($\approx 0.1 \text{ wt% compared to TMI}$) were added to the polyether under nitrogen. The reaction was then heated at 55 °C and left to react for 2 h.

Note: 0.8 eq. of the TMI compound compared to –OH groups were used to synthesise MM-1b (Table 1).
Characterisation:

Figure S4 $^1$H NMR (300 MHz) for P(EO-co-PO)$_{4000}$ functionalised with 3-isopropenyl-$\alpha,\alpha$-dimethylbenzyl isocyanate (TMI) (entry MM-1a, Table 1).
Figure S5 $^1$H NMR (300 MHz) for P(EO-co-PO)$_{12000}$ functionalised with 3-isopropenyl-$\alpha,\alpha$-dimethylbenzyl isocyanate (TMI) (entry MM-1b, Table 1).
**Styrene functionalised polyether macromonomer**

**Synthesis:**

A polyether macromonomer bearing a styrene end-group (MM-3, Table 1) was prepared by coupling a monohydroxyl P(EO-co-PO) polymer with 4-vinylbenzyl chloride, as shown in Scheme S3.

![Scheme S3](image)

**Scheme S3** Functionalisation of P(EO-co-PO) with 4-vinylbenzyl chloride.

30.815 g of linear monohydroxy P(EO-co-PO) ($M_n = 6,400$ g/mol, $8.56 \times 10^{-3}$ mol) was dried by azeotropic distillation with toluene. Subsequently, the polyether was dissolved in 30 mL of dry toluene and 3 eq. of NaH (0.61630 g, $2.57 \times 10^{-2}$ mol.) compared to the –OH groups were added at 0 °C. The mixture was then stirred for 30 min at 25 °C and turned orange. At this point 0.8 eq. of 4-vinylbenzyl chloride compared to the –OH groups was added. The reaction was then left to proceed overnight under stirring at 25 °C. The excess of NaH was neutralised by adding methanol to the system. Afterwards, toluene was removed under vacuum and the polymer was dissolved in CH$_2$Cl$_2$. NaCl was removed from the solution by filtration over silica gel and the polymer was dried under vacuum.
Characterisation:

Figure S6 $^1$H NMR (300 MHz) for P(EO-co-PO)$_{4000}$ functionalised with 4-vinylbenzyl chloride (entry MM-3, Table 1).
Polystyrene Macroinitiators

PS-TEMPO macroalkoxyamine (MI-2, Table 1).

15 mL of styrene (1.31 x 10^{-1} mol), 0.00764 g of AIBN (4.52 x 10^{-5} mol) and 0.01102 g of TEMPO (7.05 x 10^{-5} mol) ([TEMPO]/[AIBN] = 1.5) were mixed together and poured in a Schlenk flask. Oxygen was removed by three freeze-pump-thaw cycles. Subsequently, the flask was placed in an oil bath heated at 125 °C for 5 h, after which the reaction was quenched in ice. The polymer was then precipitated in cold methanol, filtered off, dissolved in THF, precipitated in cold methanol a second time and filtered off again. Consequently, the polymer was dried at 40 °C for 72 h under vacuum. The polystyrene obtained had a $M_n$ of 66,300 g/mol and a PDI of 1.26. The styrene conversion was 40.1%.

![Figure S7 Molar mass distribution of PS-TEMPO (MI-2, Table 1).](image-url)
PS-SG1 macroalkoxyamine (MI-3a, Table 1).

45 mL of styrene (3.93 x 10^{-1} mol.), 0.03359 g of AIBN (2.05 x 10^{-4} mol.) and 0.15050 g of SG1 (5.12 x 10^{-4} mol.) ([SG1]/[AIBN] = 2.5) were mixed together and poured in a Schlenk flask. Oxygen was removed by three freeze-pump-thaw cycles. Subsequently, the flask was placed in an oil bath heated at 120 °C for 5 h, after which the reaction was quenched in ice. The polymer was then precipitated in cold methanol, filtered off, dissolved in THF, precipitated in cold methanol a second time and filtered off again. Afterwards, the polymer was dried at 40 °C for 72 h under vacuum. The polystyrene obtained had a $M_n$ of 50,000 g/mol and a PDI of 1.18. The styrene conversion was 45.2%.

![Figure S8 Molar mass distribution of PS-SG1 (MI-3a, Table 1).](image)

PS-SG1 macroalkoxyamine (MI-3b, Table 1).

50 mL of styrene (4.35 x 10^{-1} mol.) and 0.49369 g of MAMA-SG1 (1.29 x 10^{-3} mol.) were mixed together and poured in a two-neck flask. Oxygen was removed by bubbling nitrogen through the mixture for 20 min. Subsequently, the flask was placed in an oil bath heated at 120 °C for 4 h, after which the reaction was quenched in ice. The polymer was then precipitated in cold methanol, filtered off and dried at 25 °C for 72 h under vacuum. The polystyrene obtained had a $M_n$ of 21,500 g/mol and a PDI of 1.14. The styrene conversion was 52.5%.
**Figure S9** Molar mass distribution of PS-SG1 (MI-3b, Table 1).

**Block Copolymers**

**Figure S10** Molar mass distribution before (left) and after (right) NMP of styrene with a P(EO-co-PO) macroalkoxyamine (block copolymer, entry 1, Table 4).
**Figure S11** LCxSEC analysis for P(EO-co-PO)-b-PS block copolymer (entry 1, Table 4). Top chromatogram: RI detection; bottom chromatogram: UV detection.

**Figure S12** Molar mass distribution before (left) and after (right) NMP of styrene with a P(EO-co-PO) macroalkoxyamine (block copolymer, entry 2, Table 4).
Figure S13 LCxSEC analysis for P(EO-co-PO)-b-PS block copolymer (entry 2, Table 4). Top chromatogram: RI detection; bottom chromatogram: UV detection.

Graft and Star-Grafted Copolymers

Figure S14 Molar mass distribution before (left) and after (right) copolymerisation of styrene and a P(EO-co-PO) macromonomer (MM-1b, Table 1) by NMP (graft copolymer, entry 4, Table 5).
**Figure S15** Molar mass distribution before (left) and after (right) copolymerisation of styrene and a P(EO-co-PO) star macromonomer (MM-2, Table 1) by NMP (star-grafted copolymer, entry 5, Table 5).

**Palm Tree Copolymers**

**Figure S16** Palm tree copolymer (entry 7, Table 6): molar mass distribution before (left) and after (right) NMP of a P(EO-co-PO) macromonomer (MM-3, Table 1) initiated with a PS macroalkoxyamine (MI-2, Table 1). The macromonomer peak is visible on the left.
**Figure S17** LCxSEC analysis for PS-\textit{b}-(PS-\textit{comb}-P(EO-\textit{co}-PO)) palm tree copolymer (entry 7, Table 6). Top chromatogram: RI detection; bottom chromatogram: UV detection.

**Figure S18** Palm tree copolymer (entry 8, Table 6): molar mass distribution before (left) and after (right) NMP of a P(EO-\textit{co}-PO) macromonomer (MM-3, Table 1) initiated with a PS macroalkoxyamine (MI-3a, Table 1). The macromonomer peak is visible on the left.
Figure S19 LCxSEC analysis for PS-\(b\)-(PS-comb-P(EO-co-PO)) palm tree copolymer (entry 8, Table 6). Top chromatogram: RI detection; bottom chromatogram: UV detection.