

## SUPPORTING INFORMATION for

# High Molar Mass Segmented Macromolecular Architectures by Nitroxide Mediated Polymerisation

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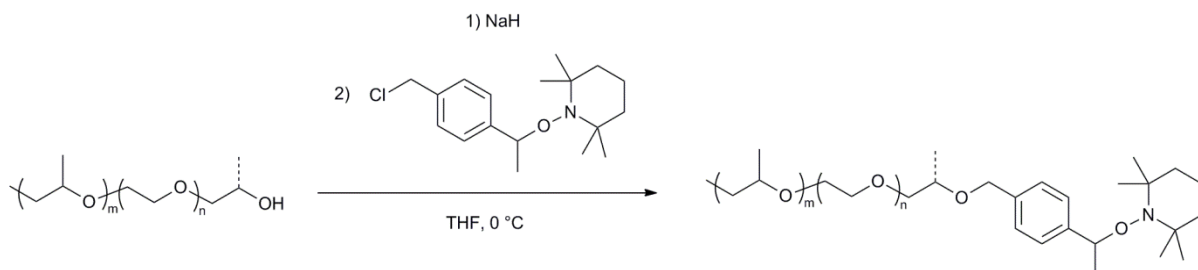
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### Polyether macroalkoxyamines

#### 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).

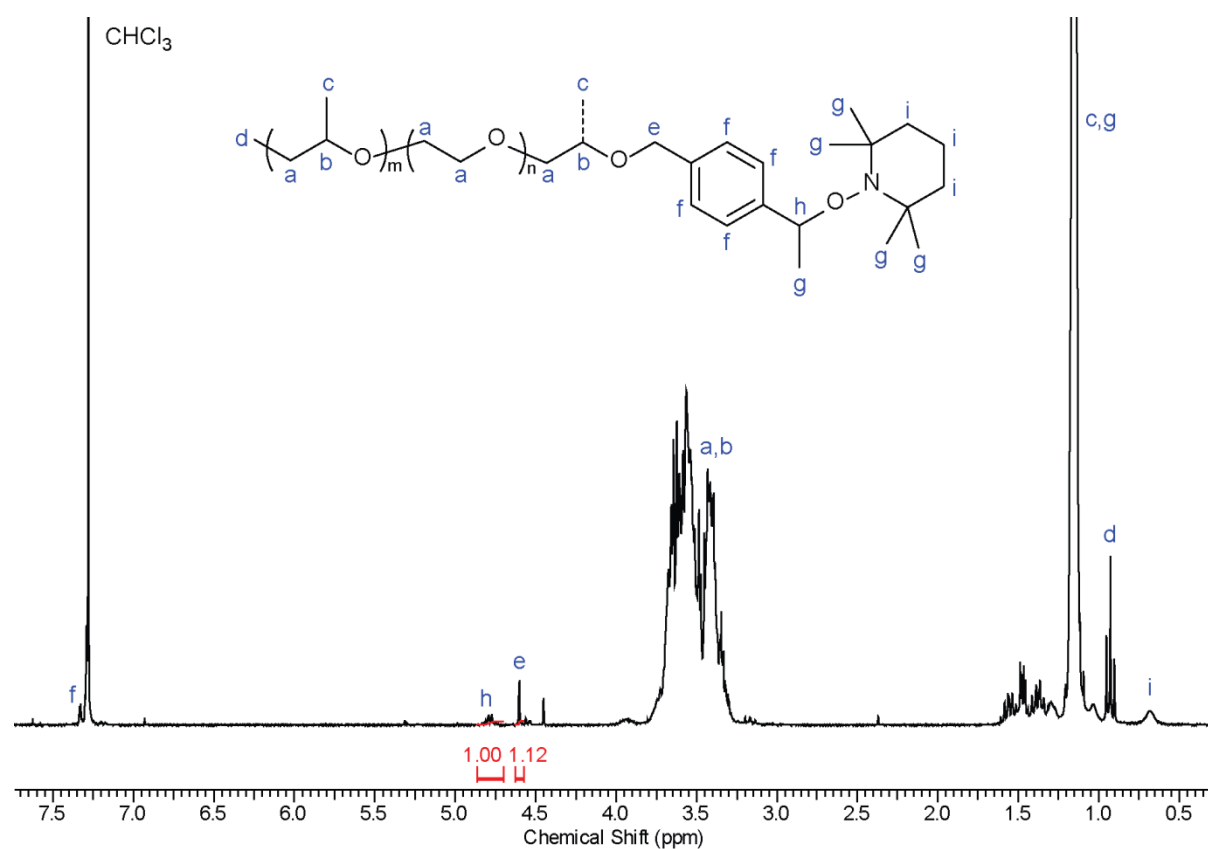


**Scheme S1** Functionalisation of P(EO-*co*-PO) with Cl-BzEt-TEMPO alkoxyamine.

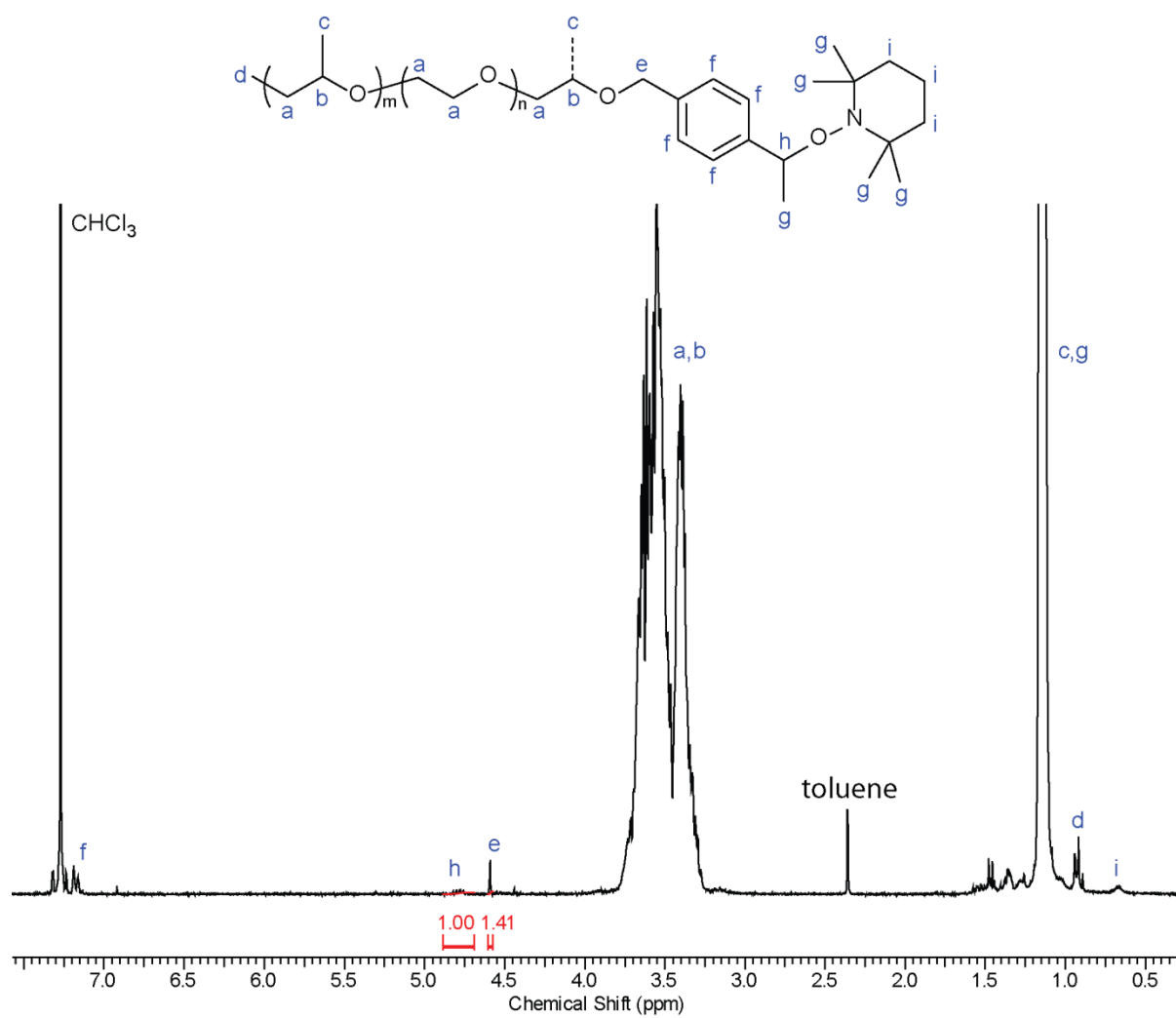
In a typical experiment (MI-1b, Table 1), 3.340 g ( $2.27 \times 10^{-4}$  mol) of P(EO-*co*-PO) ( $M_n = 18,700$  g/mol) was dried by azeotropic distillation with toluene (alternatively, the polyether could also be dried under vacuum at 150 °C for several hours until bubbles were

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<sup>-4</sup> 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.

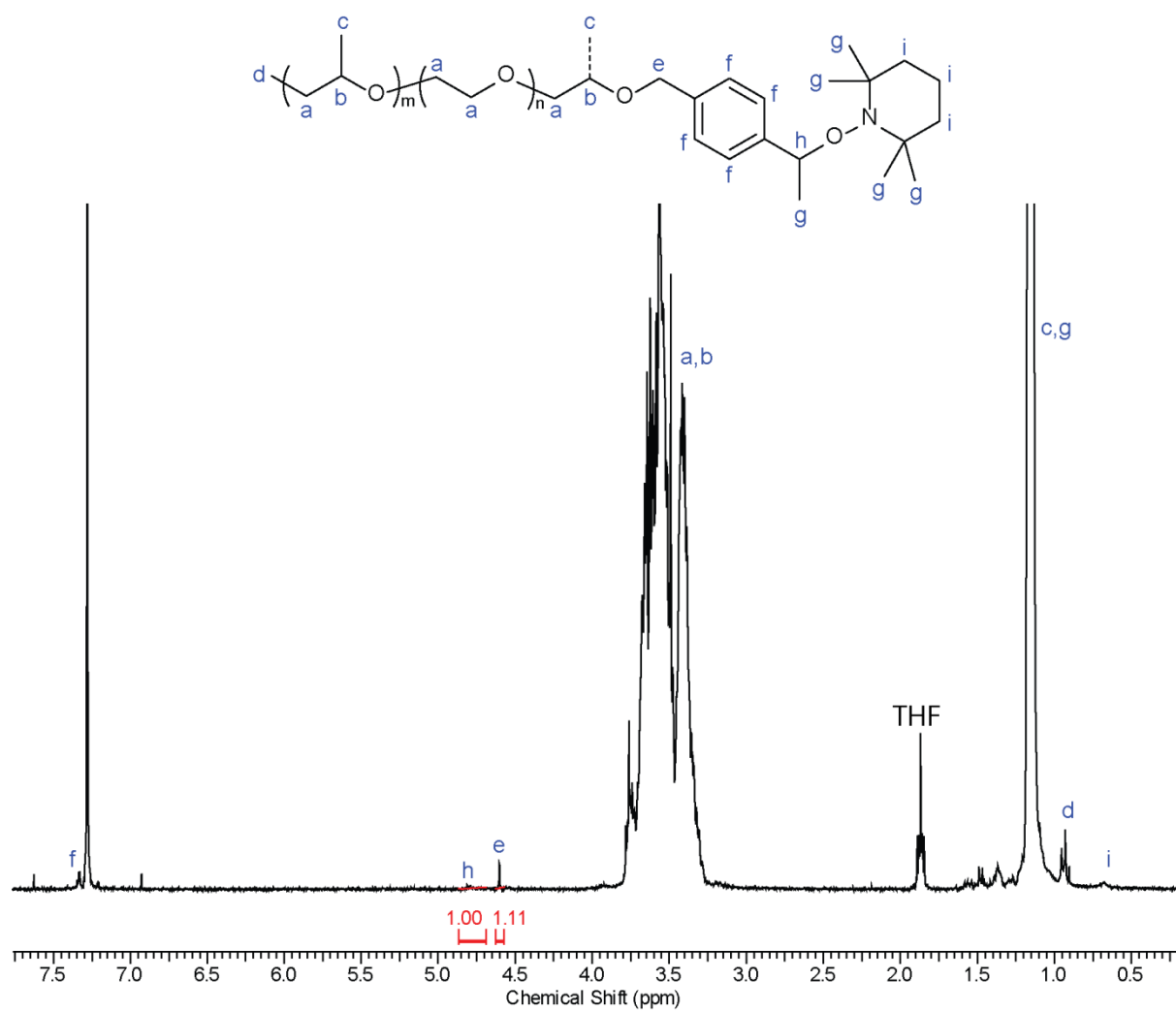
Characterisation:



**Figure S1** <sup>1</sup>H NMR (300 MHz) for P(EO-co-PO)<sub>2000</sub> functionalised with the Cl-BzEt-TEMPO alkoxyamine (MI-1a, Table 1).



**Figure S2** <sup>1</sup>H NMR (300 MHz) for P(EO-*co*-PO)<sub>12000</sub> functionalised with the Cl-BzEt-TEMPO alkoxyamine (MI-1b, Table 1).

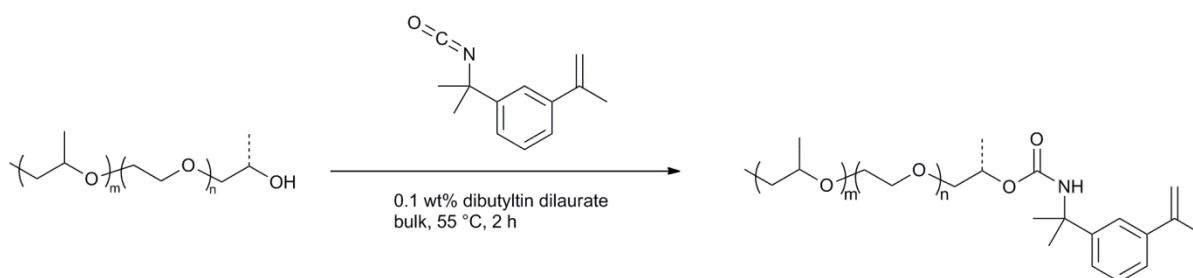


**Figure S3** <sup>1</sup>H NMR (300 MHz) for P(EO-co-PO)<sub>12000</sub> functionalised with the Cl-BzEt-TEMPO alkoxyamine (MI-1c, Table 1).

## $\alpha$ -Methylstyrene polyether macromonomers

### Synthesis:

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

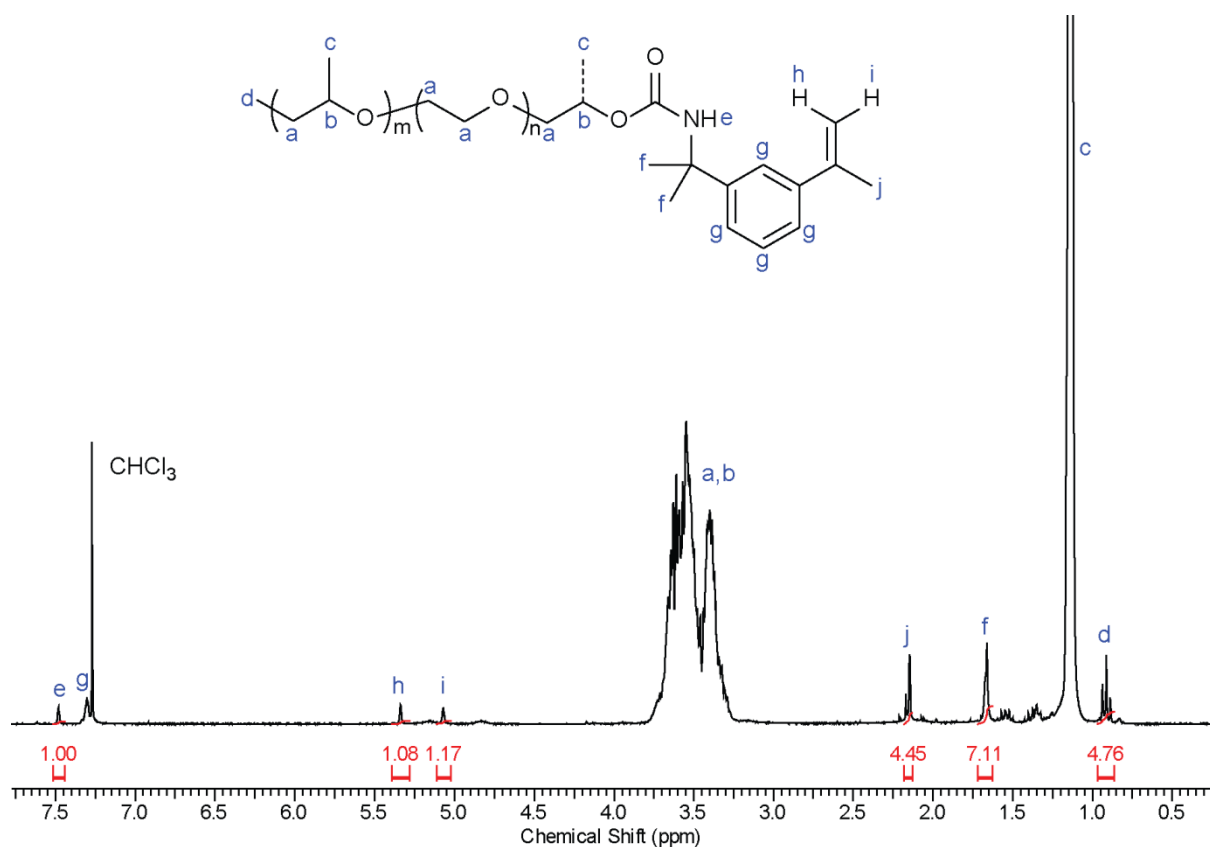


**Scheme S2** Functionalisation of P(EO-*co*-PO) with 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate (TMI).

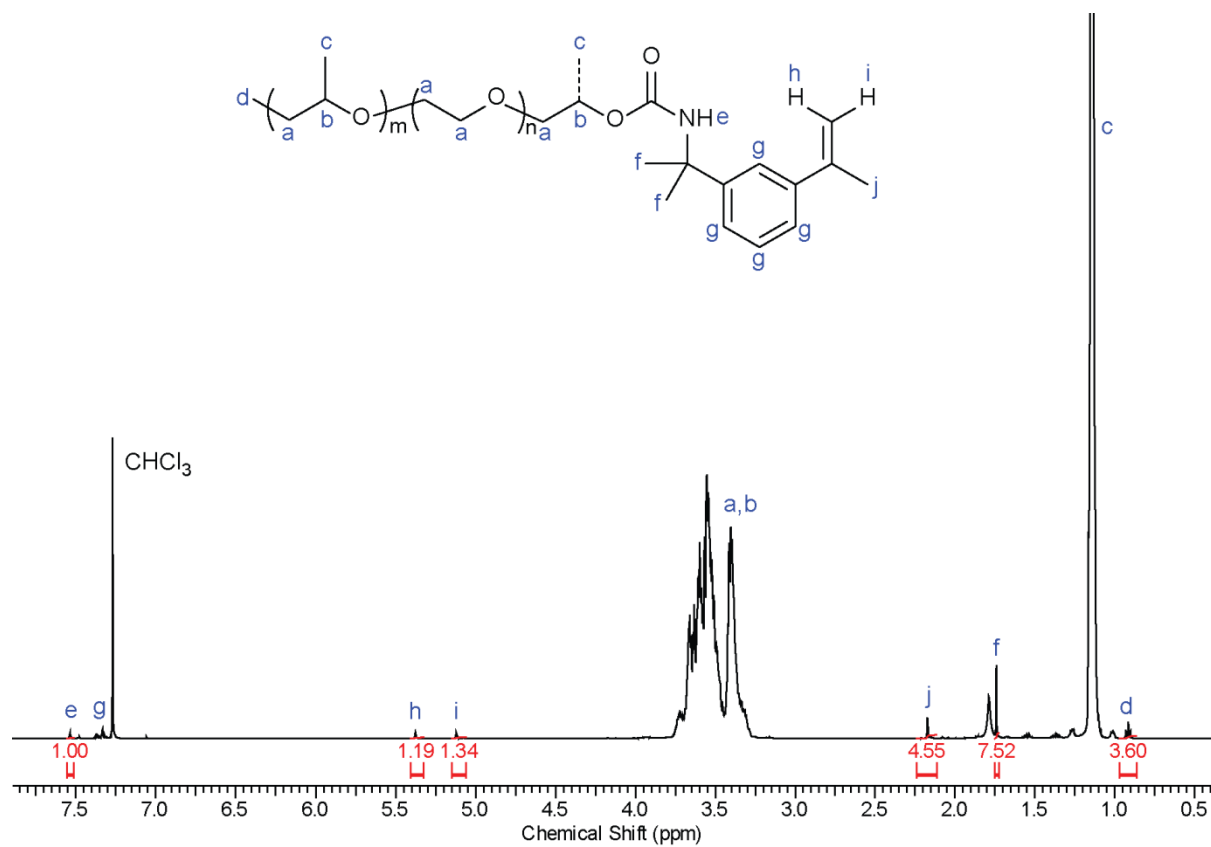
In a typical experiment (MM-1a, Table 1), 50 g of linear monohydroxy P(EO-*co*-PO) ( $M_n = 6,400$  g/mol,  $1.10 \times 10^{-2}$  mol) was dried for one day under high vacuum. Subsequently, 2.75 mL of TMI ( $1.39 \times 10^{-2}$  mol (1 eq. compared to  $-\text{OH}$  groups)) followed by 3  $\mu\text{L}$  of DBTDL ( $\approx 0.1$  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  $-\text{OH}$  groups were used to synthesise MM-1b (Table 1).

Characterisation:



**Figure S4** <sup>1</sup>H NMR (300 MHz) for P(EO-co-PO)<sub>4000</sub> functionalised with 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate (TMI) (entry MM-1a, Table 1).

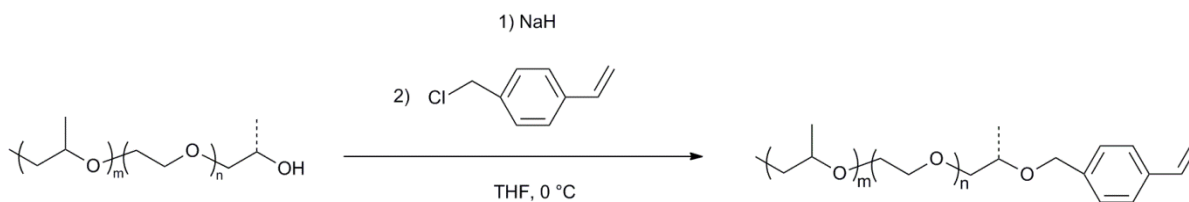


**Figure S5** <sup>1</sup>H NMR (300 MHz) for P(EO-co-PO)<sub>12000</sub> functionalised with 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate (TMI) (entry MM-1b, Table 1).

## **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.

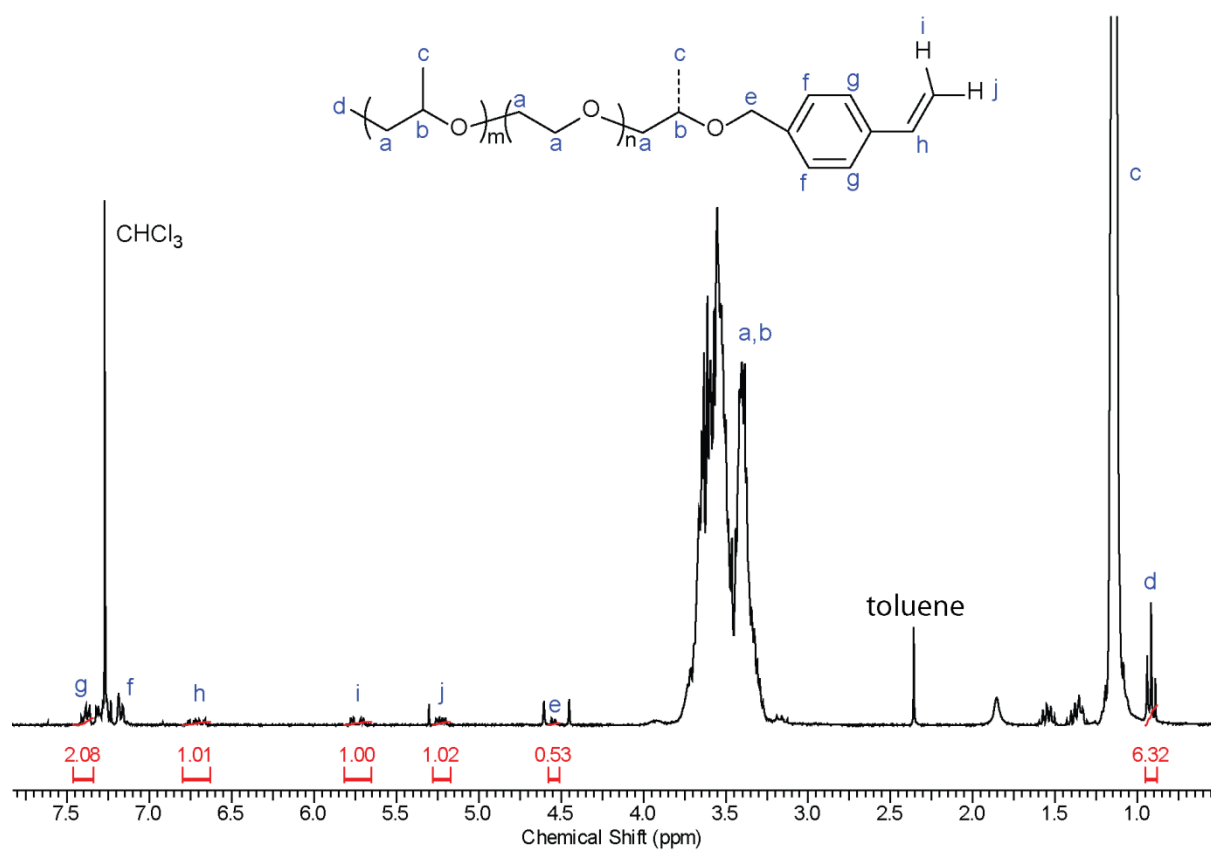


**Scheme S3** Functionalisation of P(EO-*co*-PO) with 4-vinylbenzyl chloride.

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  $\text{CH}_2\text{Cl}_2$ . NaCl was removed from the solution by filtration over silica gel and the polymer was dried under vacuum.



Characterisation:

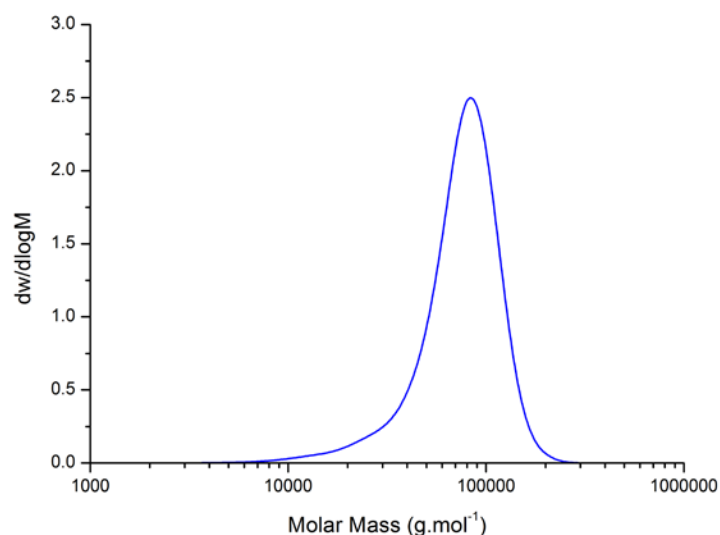


**Figure S6** <sup>1</sup>H NMR (300 MHz) for P(EO-co-PO)<sub>4000</sub> functionalised with 4-vinylbenzyl chloride (entry MM-3, Table 1).

## Polystyrene Macroinitiators

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

15 mL of styrene ( $1.31 \times 10^{-1}$  mol), 0.00764 g of AIBN ( $4.52 \times 10^{-5}$  mol) and 0.01102 g of TEMPO ( $7.05 \times 10^{-5}$  mol) ( $[\text{TEMPO}]/[\text{AIBN}] = 1.5$ ) 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).

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

45 mL of styrene ( $3.93 \times 10^{-1}$  mol.), 0.03359 g of AIBN ( $2.05 \times 10^{-4}$  mol.) and 0.15050 g of SG1 ( $5.12 \times 10^{-4}$  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%.

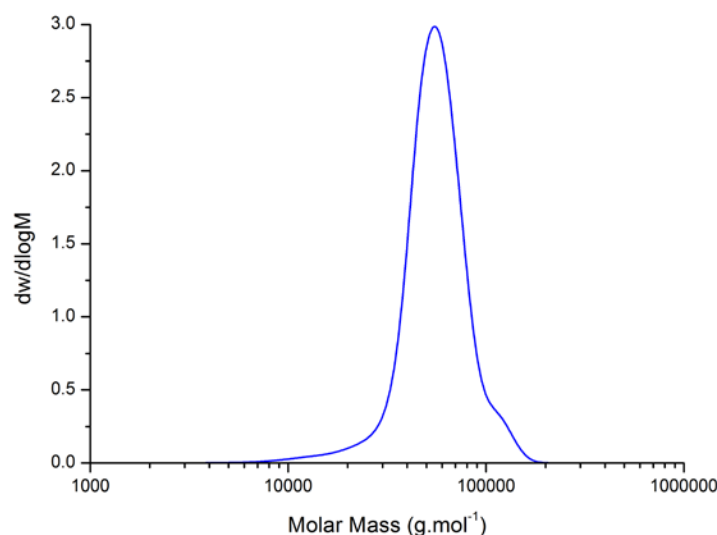
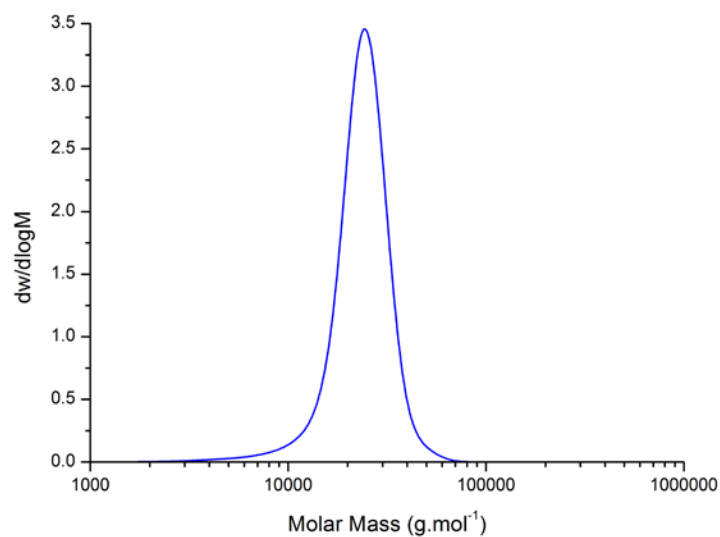


Figure S8 Molar mass distribution of PS-SG1 (MI-3a, Table 1).

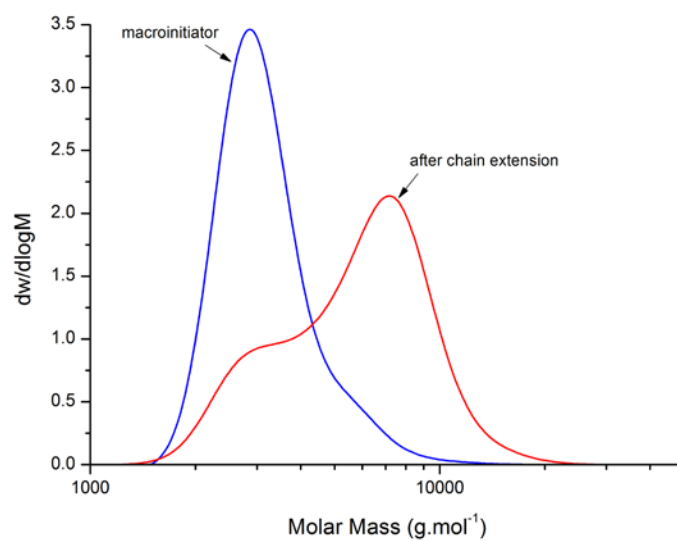
### PS-SG1 macroalkoxyamine (MI-3b, Table 1).

50 mL of styrene ( $4.35 \times 10^{-1}$  mol.) and 0.49369 g of MAMA-SG1 ( $1.29 \times 10^{-3}$  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%.

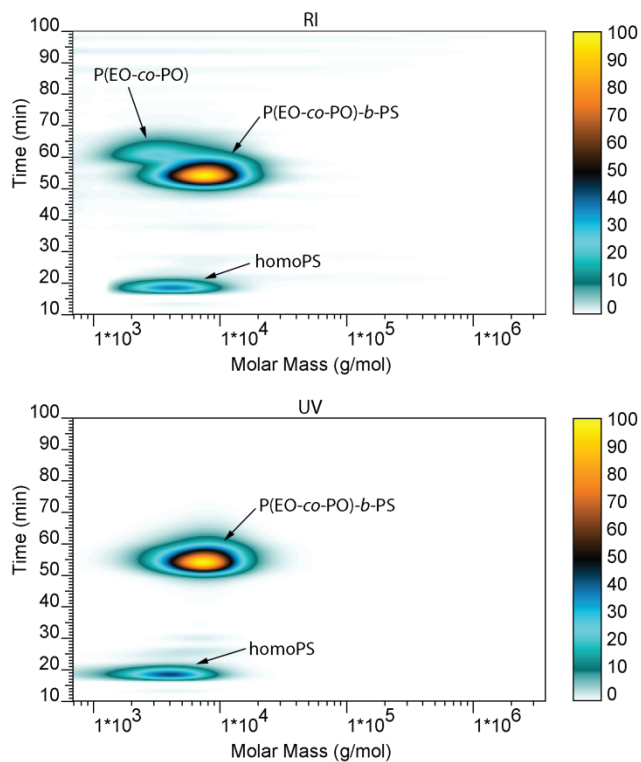


**Figure S9** Molar mass distribution of PS-SG1 (MI-3b, Table 1).

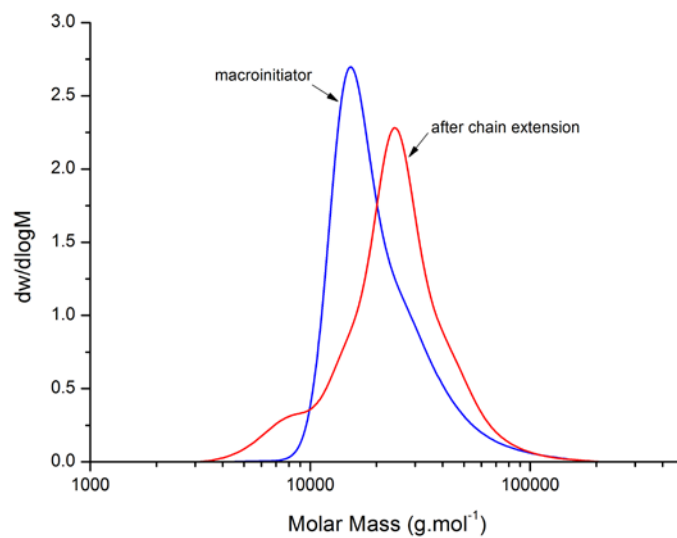
### **Block Copolymers**



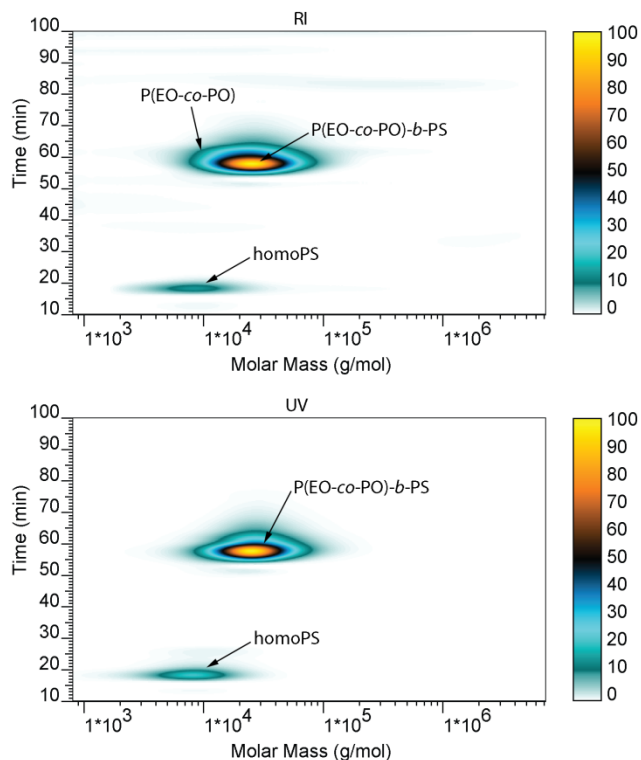
**Figure S10** Molar mass distribution before (left) and after (right) NMP of styrene with a P(EO-co-PO) macroalkoxyamine (block copolymer, entry 1, Table 4).



**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.

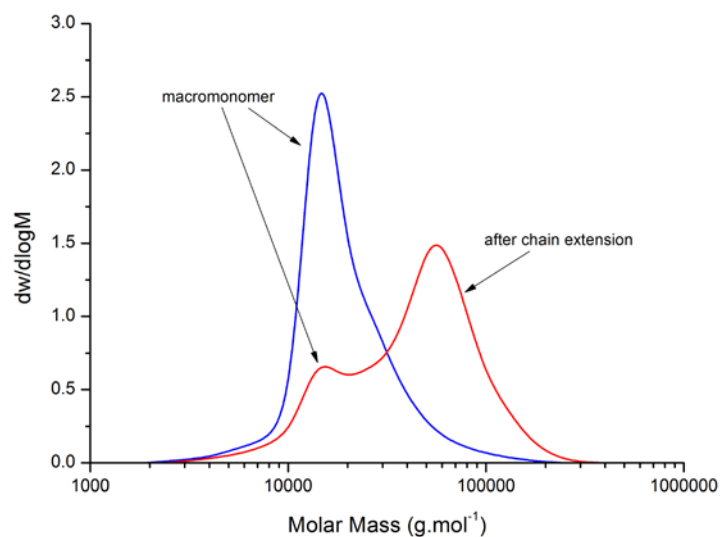


**Figure S12** Molar mass distribution before (left) and after (right) NMP of styrene with a P(EO-co-PO) macroalkoxyamine (block copolymer, entry 2, Table 4).

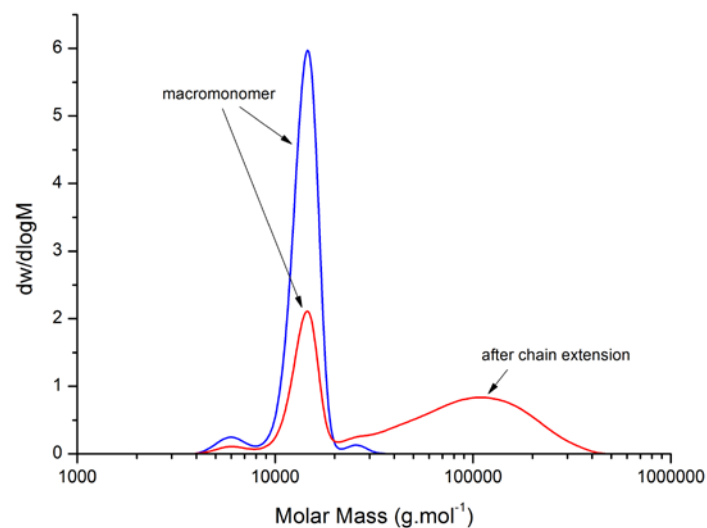


**Figure S13** LCxSEC analysis for P(EO-co-PO)-b-PS block copolymer (entry 2, Table 4). Top chromatogram: RI detection; bottom chromatogram: UV detection.

### Graft and Star-Grafted Copolymers

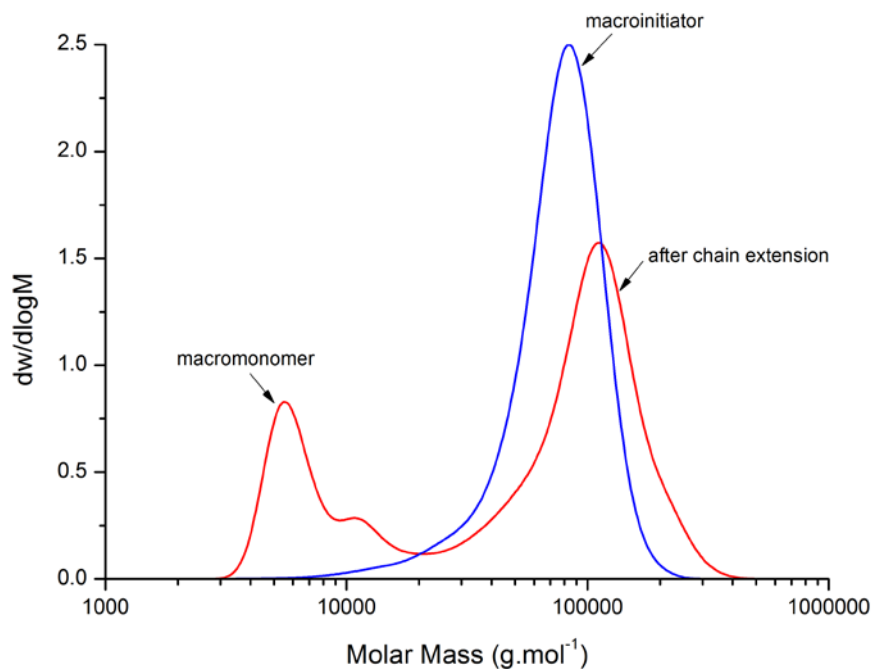


**Figure S14** Molar mass distribution before (left) and after (right) copolymerisation of styrene and a P(EO-co-PO) macromonomer (MM-1b, Table 1) by NMP (graft copolymer, entry 4, Table 5).

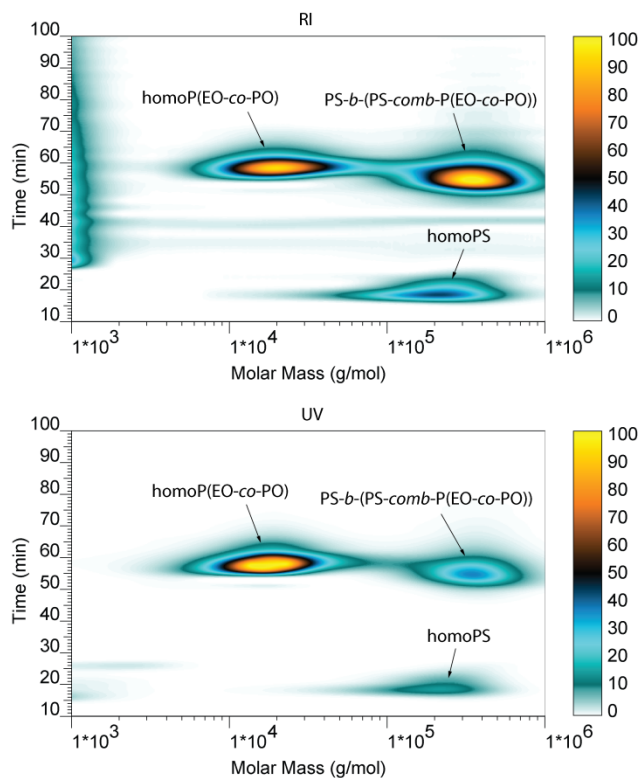


**Figure S15** Molar mass distribution before (left) and after (right) copolymerisation of styrene and a P(EO-*co*-PO) star macromonomer (MM-2, Table 1) by NMP (star-grafted copolymer, entry 5, Table 5).

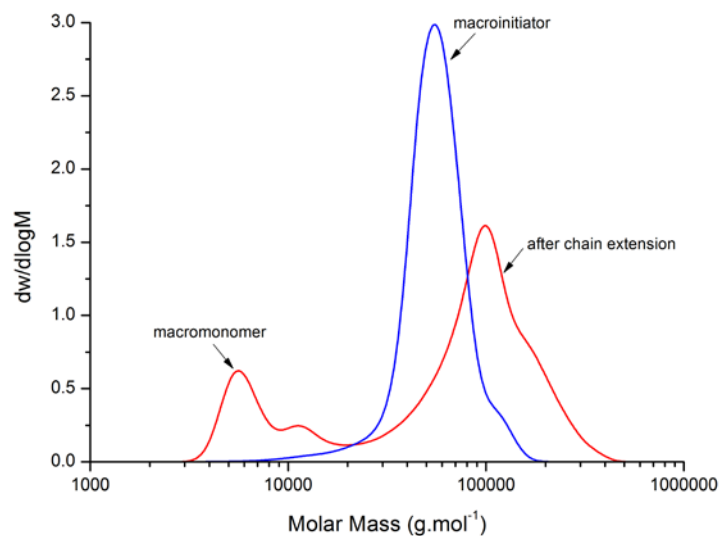
### Palm Tree Copolymers



**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.

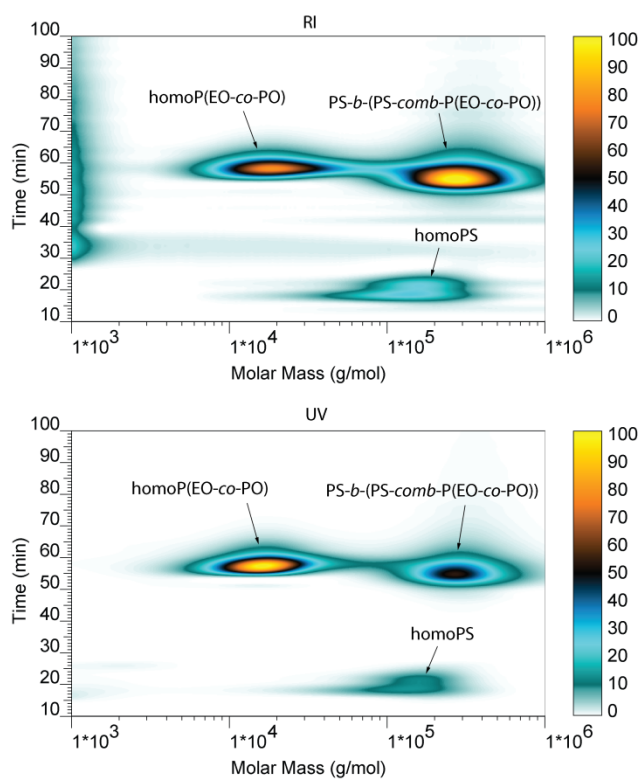


**Figure S17** LCxSEC analysis for PS-*b*-(PS-*comb*-P(EO-*co*-PO)) palm tree copolymer (entry 7, Table 6). Top chromatogram: RI detection; bottom chromatogram: UV detection.



**Figure S18** Palm tree copolymer (entry 8, Table 6): molar mass distribution before (left) and after (right) NMP of a P(EO-*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.