High Molar Mass Segmented Macromolecular Architectures by Nitroxide Mediated Polymerisation

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ABSTRACT: A straightforward synthetic pathway based on nitroxide mediated polymerisation (NMP) for the synthesis of a variety of high molar mass segmented copolymers comprising both polystyrene (PS) and polyether segments is reported. First, various precursors such as linear or star-shaped polyether macromonomers, containing either α-methylstyrene or styrene functions at one polymer terminus, as well as PS and polyether macroalkoxyamines bearing either 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) end-groups were prepared. In a second step, these prepolymers were used to design different copolymer architectures such as block, graft, star-grafted, toothbrush and palm tree structures, in which PS constituted the backbone and polyether the side chains. Block copolymers were obtained by NMP of styrene initiated with polyether macroalkoxyamines. Copolymerisation of styrene with linear and star-shaped polyethers macromonomers by NMP resulted in graft and star-grafted copolymers, respectively. A toothbrush copolymer was produced in a similar way at the exception of the initiator, which was a PS macroalkoxyamine. Likewise, palm tree architectures were obtained by homopolymerising polyether macromonomers initiated by PS macroinitiators. Advanced characterisation of the different polymer structures was performed, including 2D chromatography.

INTRODUCTION

In order to obtain a predetermined copolymer in terms of topology or functionality, it is often necessary to combine different synthetic methods. This has been greatly facilitated since controlled radical polymerisation (CRP) methods[1] such as atom transfer radical polymerisation (ATRP)[2], reversible addition-fragmentation chain transfer (RAFT) polymerisation[3] and nitroxide mediated polymerisation (NMP)[4, 5], which allowed for an exponential development of macromolecular engineering, emerged. The underlying principle of these techniques, in comparison to anionic polymerisation where an equilibrium is reached between unreactive aggregated ion-pairs and reactive dissociated ion species[6], is based on reversible termination of the radical polymerisation process[1]. Hence, the concentration of

propagating radicals is lowered to such an extent compared to free radical polymerisation that termination is virtually eliminated. Also, a fast initiation ensures that all the polymer chains propagate at the same time, which results in a homogeneous end-product[1]. NMP was the first CRP method to be reported by Georges et al. in 1993[7] and relies on the use of a stable radical, usually a nitroxide, to reversibly terminate the reaction and provide control over the polymerisation. It is well suited for the polymerisation of styrenic monomers in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) while the use of more efficient nitroxides such as N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1)[8] or 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO)[9] also allows for the polymerisation of acrylates[10], acrylamides[11], acrylonitrile[9], 1,3-dienes[12] and methacrylates under specific conditions[13]. The NMP process is governed by the persistent radical effect[14], which means that the cross-coupling reaction between transient radicals (initiating or propagating radicals) and persistent radicals (nitroxides) is favoured over the self-reaction of the former if the different radicals are generated at an equal rate. The latter requirement is ensured in NMP by the reversible cleavage of the -C-O- bond. At the beginning of the polymerisation, termination of the transient radicals occurs, leading to a relative increase in the persistent radical concentration, which will ultimately drive the process towards the cross-coupling reaction and ensure a rapid end-capping of the polymer chains with the nitroxide. As a result, NMP is a controlled process as well as a versatile tool for macromolecular engineering, which has successfully been applied to the synthesis of polymer architectures such as block, graft or star copolymers for example, as further exemplified[4].

Block copolymers are probably the most studied of all segmented copolymers, applied for advanced applications such as surfactants[15], dispersants[16], sensors[17], drug delivery systems[18] and nanolithography templates[19], to name a few. The synthetic pathways involved are usually straightforward and based on the successive polymerisation of two different monomers. This is clearly facilitated for monomers amenable to polymerisation with the same method. However, in the case where two different polymerisation techniques must be applied, an additional functionalisation step is usually required. For example, Hawker et al. described the synthesis of functional alkoxyamines[9, 20] that could be applied to the functionalisation of hydroxyl-terminated polymers and subsequent formation of copolymers such as poly(ethylene oxide)-*b*-polystyrene by NMP[21]. Similarly, Perrin et al. coupled an SG1-based alkoxyamine containing a carboxylic acid function with a hydroxyl terminated poly(ethylene glycol) (PEG) through esterification and eventually polymerised styrene to

form PS-*b*-PEG-*b*-PS triblock copolymers[22]. Wegrzyn et al. reported the esterification of a monomethyl ether poly(ethylene oxide) (PEO) with 2-bromopropionyl bromide, followed by the copper-mediated replacement of the terminal bromine with TIPNO[23]. Consequently, NMP of isoprene was performed leading to poly(ethylene oxide)-*b*-poly(isoprene) copolymers. Recently, our group reported the in situ bromination of polymers synthesised by NMP with CBr_4 and their subsequent chain extension by ATRP as a platform towards novel block copolymers[24].

For the synthesis of graft copolymers on the other hand, 'grafting from', 'grafting onto' and 'grafting through' are the main strategies[25]. As an example of the 'grafting from' method, Grubbs et al. copolymerised styrene and 4-vinylbenzyl chloride by NMP after which the pendent chlorine atoms have been reacted with an –OH terminated alkoxyamine through a substitution reaction[26]. Finally, the grafted arms were polymerised directly from the backbone by NMP of styrene.

In the 'grafting onto' method, the polymer segments, constituting both the backbone and the grafted chains, are synthesised separately before being covalently linked together, often by means of click chemistry methods[27].

The third method, 'grafting through', relies on the copolymerisation of a monomer, which will be incorporated in the backbone, with a premade macromonomer[28]. The advantage of this method is that it can be applied to production on large scale and that high molar masses can be reached[29]. Following this methodology, Hawker et al. reported the use of macromonomers for the synthesis of graft copolymers by NMP in the presence of an alkoxyamine based on TEMPO[30]. They copolymerised styrene in bulk with a range of macromonomers: methacrylate terminated polycaprolactone, poly(D,L)lactide, poly(ethylene glycol) or acrylate terminated polyethylene. Ryan et al. also synthesised graft copolymers by SG1 mediated NMP of styrene in the presence of PS macromonomers bearing two different 2-carboalkoxy-2-propenyl ω-end-groups[31]. Likewise, Andruzzi et al. synthesised graft copolymers by initiating the polymerisation of styrenic monomers containing oligo(ethylene glycol) moieties from a TEMPO-based alkoxyamine anchored on a silicon wafer[32]. A similar method was employed by Lessard et al. to synthesise comb-like homopolymers from poly[(ethyl glycol) acrylate] macromonomers ($M_n \approx 450$ g/mol) by NMP with MAMA-SG1, followed by chain extension with styrene in dimethylformamide or anisole in order to obtain amphiphilic block copolymers[33].

The latter structure is in fact more akin to a palm tree copolymer (also designated as brush-block-linear or brush-coil copolymer in literature[34]), which possesses a linear polymeric segment linked to a densely grafted polymer brush as previously described by our group[35], than to a block copolymer. A variation to the palm tree structure is the toothbrush copolymer in which the pendent polymer chains are more loosely grafted[36]. Finally, another complex type of graft copolymer is a star-grafted copolymer, which is prepared by copolymerisation of star or hyperbranched macromonomers with a comonomer and, as a result, possesses star-like or hyperbranched structures along its backbone[37].

In this paper, a synthetic platform based on NMP for the synthesis of a broad range of complex macromolecular architectures of high molar mass, comprising of polystyrene (PS) and poly(ethylene oxide-*co*-propylene oxide) (P(EO-*co*-PO)) segments is reported. The described structures are block, graft, star-grafted, toothbrush and palm tree copolymers, all based on the same type of segments. Although their application is beyond the scope of the current study and will be addressed in a future paper, it should be noted that such a wide set of segmented macromolecular structures is unique in terms of comparing their properties in any area where segmented structures are typically used for. Moreover, a detailed characterisation of the structures was performed by LCxSEC 2D chromatography in order to assess the exact composition of the copolymers.

EXPERIMENTAL

Materials. *Synthesis:* Styrene (S, Acros) was stripped from inhibitor by passing over basic alumina before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purchased from Merck and recrystallised twice from methanol before use. 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) (Acros) was purified by sublimation. 2-Methyl-2-[*N*-*tert*-butyl-*N*-(1-diethoxyphosphoryl-2,2-dimethylpropyl)aminoxy] propionic acid alkoxyamine (MAMA-SG1) and N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) were kindly supplied by Prof. Richard Hoogenboom (Ghent University). N-(1-((4-chloromethyl)phenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (Cl-BzEt-TEMPO) was synthesised according to a known procedure[38]. HPLC grade toluene (Aldrich) was dried over living polystyryl lithium and distilled before use. HPLC grade tetrahydrofuran (THF) (Aldrich) was distilled over sodium benzophenone. *o*-xylene (Aldrich), HPLC grade dichloromethane (CH_2Cl_2) (Aldrich) and technical methanol (Fisher) were used as received.

3-Isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) (Aldrich), dibutyltin dilaurate (DBTDL) (Acros) and sodium hydride (dry 95%, Aldrich) were used as received. 4-Vinylbenzyl chloride (Acros) was stripped from inhibitor by passing over silica gel with petroleum ether as eluent. Flash chromatography was performed over silica gel 60Å, 0.032-0.063 mm (Biosolve). The linear monohydroxy poly(ethylene oxide-*co*-propylene oxide) (P(EO-*co*-PO)) copolymers containing 87.5 mol% PO and 12.5 mol% EO (theoretical M_n: 2,000, 4,000 and 12,000 g/mol, which are referred to as P(EO-*co*-PO)$_{2000}$, P(EO-*co*-PO)$_{4000}$ and P(EO-*co*-PO)$_{12000}$, respectively) were provided by Dow Chemical. The star-shaped (6 arms) P(EO-*co*-PO) macromonomer (theoretical M_n: 12,000 g/mol; 10 wt% of EO) bearing an α-methylstyrene function onto one arm end (MM-2, Table 1) was also provided by Dow Chemical as a mixture with unfunctionalised star-shaped P(EO-*co*-PO) (61.6 wt%).

LCxSEC characterisation: HPLC quality hexane, dichloromethane, and THF were obtained from Lab-Scan (Dublin, Ireland). Polystyrene narrow standards (580 g/mol – 675,000 g/mol) were purchased from Polymer Laboratories (Church Stretton, UK). Broad PS 1683 is a broad polystyrene material obtained from Dow Chemical (M_n: 100,000 g/mol, M_w: 250,000 g/mol).

Synthesis:

Precursors. The macromonomers and macroinitiators used for the synthesis of the different structures are represented in

158 Table 1 below. Further details on the synthesis of these precursors can be found in the
159 electronic supporting information (ESI).

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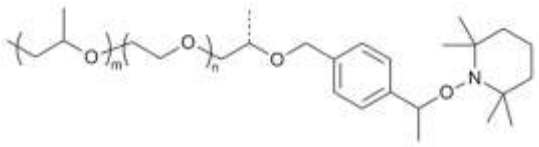
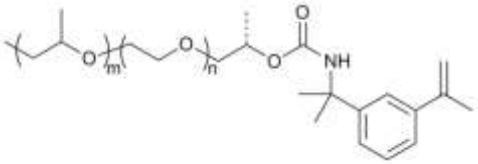
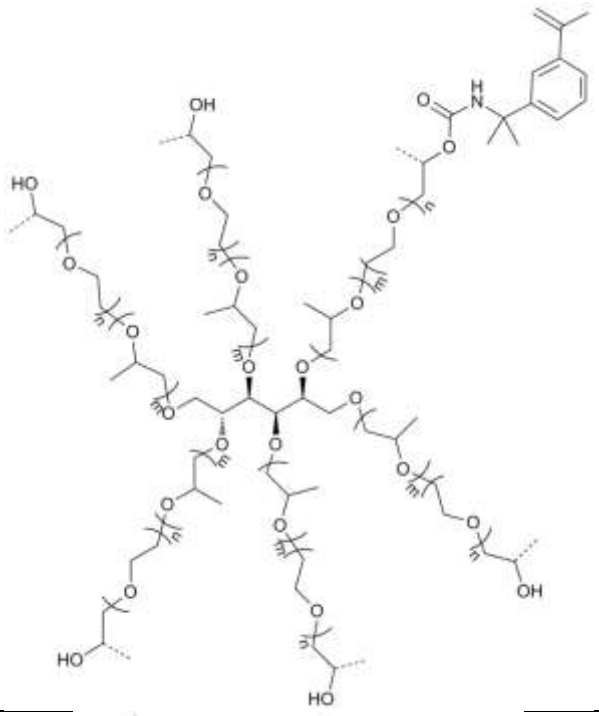
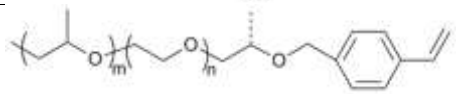
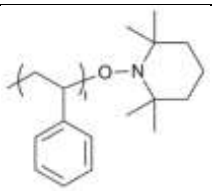
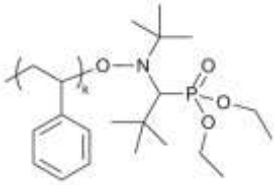
168 **Table 1** Structure and molecular properties of the different macromonomers and macroinitiators.

Entry[a]	M_n[b] (g/mol)	Đ	Structure[c]	End-group fidelity[d] (%)
MI-1a	3,000	1.11		56
MI-1b	18,300	1.26		70
MI-1c	17,300	1.26		56
MM-1a	6,600	1.23		63
MM-1b	18,900	1.27		83

MM-2	13,200	1.06		37.9[e]
MM-3	6,500	1.22		50
MI-2	66,300	1.26		-
MI-3a	50,000	1.18		-
MI-3b	21,500	1.14		-

[a] MI = macroinitiator; MM= macromonomer. [b] Determined by SEC with PS calibration. [c] Only reactive compound is shown but polyether precursors also contained a fraction of unfunctionalised product. [d] Determined by NMR; - = not determined. [e] A small multifunctional fraction is also present.

Block copolymers. The synthesis of block copolymers with varying compositions was performed according to the data presented in Table 2.

Table 2 Synthesis of block copolymers[a].

Entry	MI	[S]/[MI]	*o*-xylene (wt%)	T (°C)	t (h)
1	MI-1a	57/1	20	125	13
2	MI-1b	240/1	20	125	13
3	MI-1c	288/1	30	135	38

[a] S = styrene; MI = macroinitiator.

A typical procedure is given as follows for entry 3 (Table 2): 4.063 g of MI-1c macroinitiator (Table 1) and 7.298 mL of styrene (6.35 x 10^{-2} mol) were dissolved in 5 mL of *o*-xylene and poured into a Schlenk flask. Oxygen was removed by bubbling nitrogen through the mixture for 20 min. The flask was then placed in an oil bath heated at 135 °C for 38 h and consequently quenched in ice. The residual solvent was stripped from the mixture by applying a nitrogen flux under vacuum.

Graft copolymer (4). 5 mL of styrene (4.36 x 10^{-2} mol), 2.841 g of MM-1b macromonomer (Table 1), 8.40 mL of *o*-xylene (50 wt% of the total mixture), 0.00746 g of AIBN (4.54 x 10^{-5} mol) and 0.01065 g of TEMPO (6.82 x 10^{-5} mol) were mixed together and poured into a Schlenk flask. The weight ratio of styrene over macromonomer was chosen to be 2 and the ratio [TEMPO]/[AIBN] was 1.5. Oxygen was removed by three freeze-pump-thaw cycles. The flask was then placed in an oil bath heated at 135 °C for 24 h and subsequently quenched in ice. The copolymer was purified by precipitation in cold methanol and dried under vacuum at 60 °C for 24 h.

Star-grafted copolymer (5). 7.5 mL of styrene (6.55 x 10^{-2} mol), 8.998 g of MM-2 macromonomer (Table 1; weight includes unfunctionalised fraction), 18 mL of *o*-xylene (50 wt% of the total mixture), 0.00560 g of AIBN (3.41 x 10^{-5} mol) and 0.02006 g of SG1 (6.82 x 10^{-5} mol) were mixed together and poured into a Schlenk flask. The weight ratio of styrene over macromonomer was chosen to be 2 and the ratio [SG1]/[AIBN] was 2. Oxygen was removed by three freeze-pump-thaw cycles. The flask was then placed in an oil bath heated at 120 °C for 24 h and subsequently quenched in ice. The residual solvent and monomer were removed under vacuum at 85 °C for 24 h.

Toothbrush copolymer (6). 1 g of PS-TEMPO macroinitiator MI-2 (Table 1), 0.5 g of styrene (4.80 x 10^{-3} mol) and 1.5 g of MM-1a macromonomer (Table 1) were dissolved in 2 mL of *o*-xylene and poured into a Schlenk flask. Oxygen was removed by three freeze-pump-thaw cycles. Subsequently, the flask was placed in an oil bath heated at 135 °C for 4 h. The reaction was then quenched in ice. The residual solvent and monomer were removed under vacuum at 85 °C for 72 h.

Palm tree copolymer. Various palm tree structures were synthesised as described in Table 3.

Table 3 Synthesis of palm tree copolymers with MM-3 macromonomer (Table 1)[a].

Entry	MI	[MM-3]/[MI]	*o*-xylene (wt%)	T (°C)	t[b] (h)

7	MI-2	20/1	50	135	15
8	MI-3a	15/1	50	120	15
9	MI-3b	8/1	30	120	-

[a] MI = macroinitiator; MM = macromonomer. [b] - = not determined.

A standard procedure for the synthesis of palm tree copolymers is given hereafter for entry 7 (Table 3). 1.5 g of MI-2 macroinitiator (Table 1) and 3 g of MM-3 macromonomer (Table 1) were dissolved in 6 mL of *o*-xylene and poured into a Schlenk flask. Oxygen was removed by three freeze-pump-thaw cycles. The flask was then placed in an oil bath heated at 135 °C for 15 h and consequently quenched in ice. The residual solvent was removed under vacuum at 85 °C for 24 h.

Characterisation:

NMR. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz in $CDCl_3$ solution at room temperature on a Bruker Avance 300 spectrometer. A relaxation delay of 30 s between scans was applied to ensure quantitative results.

SEC. Size Exclusion Chromatography (SEC) analyses were performed on an Agilent (Polymer Laboratories) PL-SEC 50 plus instrument, using a refractive index detector, equipped with two PLgel 5 μm MIXED-D columns thermostated at 40°C. PS standards were used for calibration. THF was used as eluent at a flow rate of 1 mL/min. Samples were injected using a PL-AS RT autosampler. Macromonomer conversion was determined, where possible, by comparing, for samples with the same concentration, the peak area corresponding to the macromonomer before and after polymerisation.

LCxSEC. The LCxSEC system consisted of a 1st-dimension (1st-D) LC and a 2nd-dimension (2nd-D) SEC. The 1st-D LC consisted of an Agilent (Waldbronn, Germany) 1100 quaternary pump, an Agilent 1200 autosampler, and a Shimadzu (Tokyo, Japan) SPD-10A VP UV detector, set at 258 nm. The LC column was a Supelco Ascentis Si (5 cm x 2.1 ID mm; 3 μm) column (Sigma-Aldrich) using a mobile phase gradient of A: hexane, B: dichloromethane, C: THF. The gradient LC program used was: 0 min: 100 % A, 1.2 min: 100 % A, 1.3 min: 90 % B and 10 % C, 25 min: 90 % B and 10 % C, 26.6 min: 100 % C, 120 min: 100 % C at a flow rate of 10 μL/min. In order to reduce the total run time, the flow rate was increased in between the peaks of interest to 0.2 mL/min. The 2nd-D SEC system consisted of an Agilent 1200 isocratic pump, a Shimadzu SPD-10A UV detector (258 nm), and an Agilent 1200 RI

detector set at 35 °C. The SEC column was a high speed SDV LIM (50 x 20 ID mm, 5 μm) column from PSS Polymer Standards Service GmbH (Mainz, Germany). THF was used as the solvent. The flow rate was set at 6 mL/min. The 2^{nd}-D sampling frequency used was 2 minutes and the corresponding injection volume was 20 μL. An Agilent 1200 degasser was used for both the 1^{st}-D LC and 2^{nd}-D SEC systems. Both the LC and SEC columns were put in a Shimadzu CTO-10A VP column oven set at 30 °C. The Agilent instrumentation was controlled by Atlas software (version 8.2.; Thermo Fisher Scientific BV, Breda, The Netherlands). The 1^{st}-D LC and 2^{nd}-D SEC were interfaced using a Valco EPC10W 10-port 2-position valve (VICI AG International, Schenkon, Switzerland), with a micro-electric actuator. The valve was equipped with two 50-μL loops. Controlling of the valve was done with WinGPC (version 7.4.0) software from PSS. The WinGPC software was also used for data acquisition and data processing.

The samples were prepared at a concentration of 100 mg/mL in dichloromethane. Narrow PS standards were injected at a concentration of 1.35 mg/mL. Broad PS 1683 was injected at a concentration of 10 mg/mL.

RESULTS & DISCUSSION

The types and composition of the different copolymer architectures, consisting of PS and P(EO-*co*-PO), have been chosen bearing in mind their end-use as polymeric dispersants. The application implied that copolymers composed of relatively high molar mass segments (> 20,000 g/mol for the PS part) and containing 30 to 50 wt% of polyether were aimed for. The targeted structures, in which the polyether segments are usually presented as side-chains, are depicted in Figure 1: block, graft, star-grafted, toothbrush and palm tree copolymers.

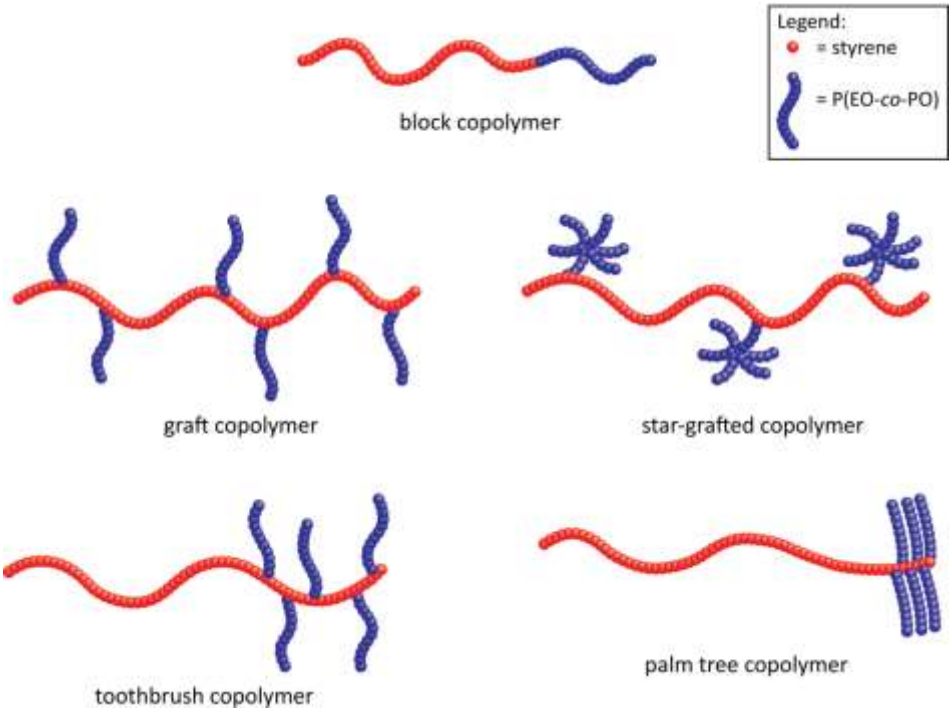


Figure 1 Schematic representation of the investigated range of segmented copolymer architectures

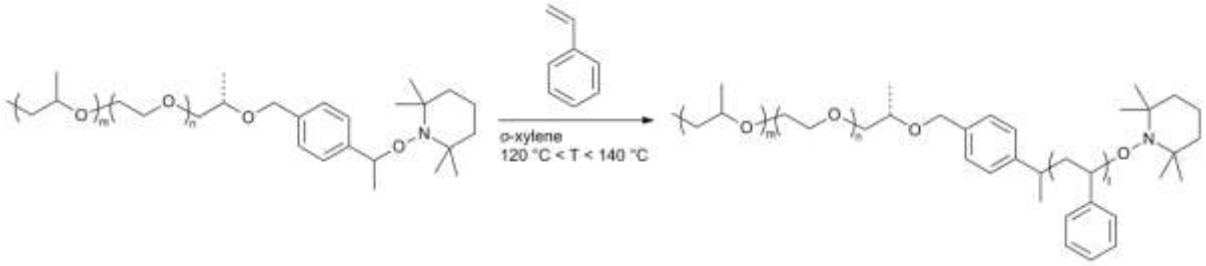
In order to synthesise copolymers amenable to production on an industrial scale, simple reaction pathways with minimal purification procedures have been looked for. In particular, series of macromonomer and macroinitiator prepolymers (Table 1) were obtained through various polymerisation and functionalisation reactions (see ESI). Consequently, the NMP process was chosen to obtain the desired segmented macromolecular architectures with relative high molar mass. As the residual polyether fragments in the final product do not hamper the envisaged application of the copolymer dispersants in a polyether medium, their difficult, time-consuming removal has not been undertaken to guarantee a potential scale-up of the copolymer synthesis. The composition of the end product was in all cases addressed by LCxSEC 2D chromatography.

The synthesis and characterisation of the different PS and P(EO-*co*-PO) copolymers are presented in the following paragraphs.

Block copolymers

P(EO-*co*-PO)-*b*-PS block copolymers were synthesised in a two-step process. First, the polyether macroalkoxyamines MI-1a, MI-1b and MI-1c (Table 1) were prepared by the substitution reaction between a chloride functionalised alkoxyamine and the –OH terminated polyethers (see ESI). Subsequently, NMP of styrene was initiated with the polyether

macroalkoxyamines to form the block copolymers (Scheme 1). The use of *o*-xylene as solvent was necessary to ensure a good homogenisation of the mixture.



Scheme 1 Synthesis of P(EO-*co*-PO)-*b*-PS block copolymer by NMP.

The results presented in Table 4 indicate that the macroinitiators were able to initiate the polymerisation of styrene and impart control over the polymerisation as indicated by the molar mass increase compared to that of the macroalkoxyamines (e.g. from 17,300 to 29,100 g/mol for entry 3 (Table 2 and Table 4)) and the low dispersities (≤ 1.50) of the block copolymers (Table 4). It is noteworthy that the prolonged reaction times – from 13 h for entries 1 and 2 to 38 h for entry 3 in Table 2 – did not appear to favour side reactions that would broaden the molar mass distribution of the copolymers. The conversion difference – 63 and 37 %, respectively – between entries 1 and 2 in Table 4 is explained by the fact that, although polymerisation time and temperature were similar (13 h at 125 °C), the targeted molar masses were different: theoretical DP's of 57 and 240 for the PS blocks corresponding to entries 1 and 2 in Table 2, respectively. Thus, the amount of radicals able to participate in the polymerisation will be higher in the former reaction than in the latter, which will result in distinctive polymerisation kinetics. For entry 3 in Table 2, the temperature was increased to 135 °C in order to obtain faster kinetics in view of the lower amount of initiator used to obtain a higher molar mass.

Table 4 Characteristics of block copolymers.

Entry	M_n [a] (g/mol)	Đ	Styrene Conv.[b] (%)	Estim. homoPS[c] (%)
1	4,950	1.27	63	14
2	19,800	1.38	37	8
3	29,100	1.50	65	15

[a] Molar masses determined by SEC calibrated with PS standards and refractive index (RI) detection. [a] Determined by ^{1}H NMR. [c] Estimation of the volume fraction of the residual homoPS peak determined by LCxSEC.

The characterisation of all entries 1, 2 and 3 in Table 4 revealed a similar composition for the block copolymers (see below and ESI), at the exception of the varying molar masses. Hence, only the analysis of the block copolymer having the highest molar mass (29,100 g/mol; entry 3 in Table 4) is described hereafter. The molar mass distributions before and after chain extension of the polyether macroinitiator with styrene are plotted in Figure 2. A clear shift and decrease in the intensity of the peak corresponding to the macroalkoxyamine was observed after the polymerisation, thereby confirming the formation of the block copolymer. However, since the polyether peak did not disappear entirely after polymerisation, it was concluded that a small amount of unreacted homoP(EO-*co*-PO), which could not be quantified due to the overlapping with the copolymer peak, was still present in the final product. This was expected since an excess of P(EO-*co*-PO), compared to the Cl-BzEt-TEMPO alkoxyamine, was used during the synthesis of the polyether macroalkoxyamine (see ESI) in order to limit the formation of the PS-b-P(EO-*co*-PO)-b-PS triblock copolymer, which could occur due to the presence of a small polyether diol fraction (phenomenon experimentally observed, unpublished results).

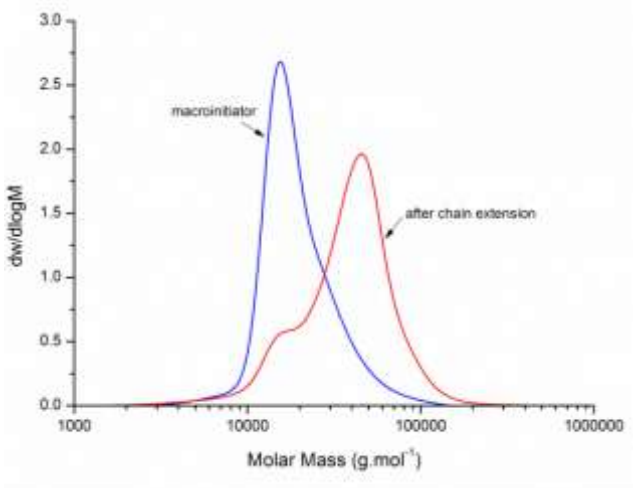


Figure 2 Molar mass distribution before (left) and after (right) NMP of styrene with a P(EO-*co*-PO) macroalkoxyamine (block copolymer, entry 3, Table 4).

In order to gain more insight into the exact composition of the block copolymers, analysis by LCxSEC chromatography was performed as shown in Figure 3 for entry 3 (Table 4). According to the applied LCxSEC method, the more hydrophobic PS elutes first from the 1st-dimension LC – between 15 and 20 min – while the more hydrophilic polyethers elute later – after 50 min. Another feature is that homoP(EO-*co*-PO) and P(EO-*co*-PO)-*b*-PS tend to co-elute in the 1st-dimension LC. This is visible in the RI chromatogram in Figure 3, in which a low molar mass tail can be seen on the upper left side of the peak eluting around 55 –

60 min. This tailing is absent in the UV chromatogram from which it can be deduced that it corresponds to unreacted homoP(EO-*co*-PO), which is transparent to UV radiation at 258 nm, in agreement with the results found by SEC (Figure 2). Nevertheless, a small separation occurs between homoP(EO-*co*-PO) and P(EO-*co*-PO)-*b*-PS since the former is slightly more hydrophilic and the latter has a higher molar mass. In addition, LCxSEC can provide information that is not accessible by standard SEC. Indeed, it is clear from Figure 3 that a small fraction of homoPS, which corresponds to the peak eluting between 15 and 20 min, is also present. This is attributed to the thermal initiation of styrene during NMP with TEMPO[39], which is expected considering the relatively long polymerisation time and high temperature involved (38 h at 135 °C). An estimation of the homoPS content was calculated by integrating the homoPS peak in relation to the copolymer peak and was found to vary between 8 and 15 % for the different block copolymers (Table 4). This is in accordance with a similar system described in the literature where the TEMPO chain-end fidelity was 90 % at most[40]. Taking into account that purification was not applied, it can be concluded that the block copolymers have been synthesised with a relatively high purity.

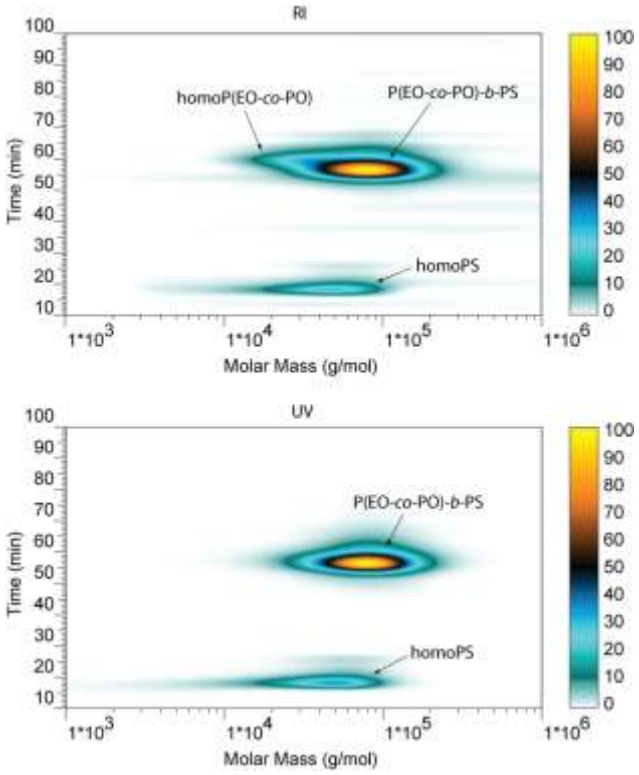
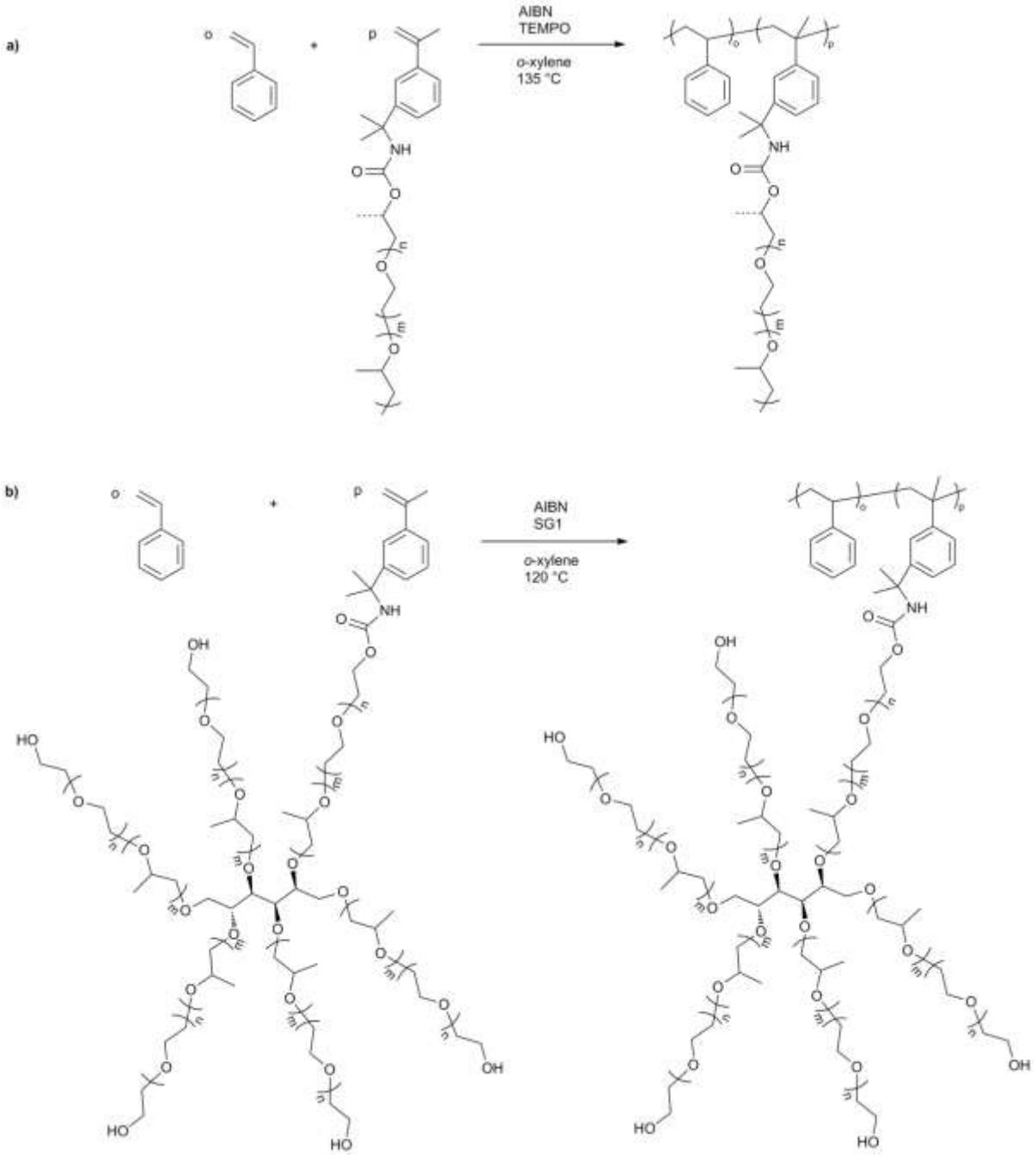


Figure 3 LCxSEC analysis for P(EO-*co*-PO)-*b*-PS block copolymer (entry 3, Table 4). Top chromatogram: RI detection; bottom chromatogram: UV detection. The bars at the right indicate the relative amounts.

Graft and star-grafted copolymers

The graft copolymer was synthesised following a two-step procedure. First, an α-methylstyrene function was introduced onto the polyether chain-end by means of a reaction between the isocyanate of TMI and the –OH group of the polyether (see ESI) in order to obtain a polyether macromonomer (MM-1b in Table 1). Although less reactive, the α-methylstyrene funtionalised macromonomer is able to copolymerise with styrene while retaining a good thermal stability. It was subsequently copolymerised with styrene by NMP in *o*-xylene as solvent to prevent phase separation between a polyether-rich phase and a polystyrene-rich phase during the course of the polymerisation (Scheme 2a).

A linear graft copolymer with a relatively high molar mass (47,600 g/mol) and low dispersity (1.51) – as indicated for entry 4 in Table 5 – was obtained after performing NMP at 135 °C for 24 h. In reality, the dispersity is lower as the copolymer peak partially overlaps with the residual homopolyether peak in the SEC analysis (see ESI). Because of this overlap, it was not possible to determine the macromonomer conversion. However, the styrene conversion (68 % for entry 4, Table 5) was high, even though the theoretical DP of 480 for styrene was elevated, which implied a relatively low concentration of the propagating radicals. The control over the kinetics of the polymerisation was possible owing to the bimolecular initiation system based on AIBN and TEMPO, which allows for a fine tuning of the ratio between stable and initiating radicals ([TEMPO]/[AIBN]). For a high ratio (above 2), the polymerisation rate will be lowered and the control improved as more polymer chains are end-capped with the nitroxide. Oppositely, for a low [TEMPO]/[AIBN] ratio, typically between 1 and 1.5, the polymerisation rate will be significantly higher while the molar mass distribution increase will be moderate[41].



Scheme 2 a) Synthesis of PS-*g*-P(EO-*co*-PO) graft copolymer by NMP. **b)** Synthesis of PS-*g*-(6-*star*-(P(EO-*co*-PO))) star-grafted copolymer by NMP.

Table 5 Characteristics of graft and star-grafted copolymers.

Entry	Structure	M_n (g/mol)	Đ	Styrene Conv.[a] (%)	Estim. homoPS[b] (%)	MM Conv.[c] (%)	N_{MM}[d]	Estim. homoP(EO-*co*-PO)[e] (%)
4	graft copolymer	47,600	1.51	68.2	30	-	-	30
5	star-grafted copolymer	85,100	1.49	60.6	7	90	4	37

[a] Determined by ^{1}H NMR. [b] Estimation of the volume fraction of the residual homoPS peak determined by LCxSEC. [c] Macromonomer conversion determined by SEC; - = not determined. [d] Estimation of the number N of macromonomers incorporated into each copolymer chain; - = not determined. [e] Estimation of the volume fraction of the residual homoP(EO-*co*-PO) peak determined by LCxSEC.

The graft copolymer (entry 4, Table 5) was characterised by LCxSEC chromatography as shown in Figure 4a. A relatively large homoPS fraction, of which the peak volume in the chromatogram represents around 30 % of the total copolymer mixture (Table 5), eluted around 15 – 20 min. One explanation for the presence of homoPS could be again the autopolymerisation of styrene. On the other hand, also the bulkiness of the macromonomer as well as the low reactivity of α-methylstyrene can account for the presence of homoPS. Besides homoPS, a double peak eluting at 55 – 60 min, which is ascribed to unreacted homoP(EO-*co*-PO) (upper left) and PS-*g*-P(EO-*co*-PO) (lower right), is visible in Figure 4a. Interestingly, the residual homoP(EO-*co*-PO) can be seen on both the RI and UV chromatograms, although it is less pronounced on the latter, which means that both TMI-functionalised (end-group fidelity of 80 % for MM-1b (Table 1)) and non-functionalised polyethers are present, since only the polymerisable function of the macromonomer is visible under UV irradiation. Similarly to homoPS, the amount of homoP(EO-*co*-PO) accounts for around 30 % of the total mixture (entry 4, Table 5). A large fraction was indeed expected as the polymerisation did not proceed to full conversion and P(EO-*co*-PO) was reacted in excess with TMI to avoid the formation of a crosslinker from the polyether diol fraction (see ESI). Although homopolymer impurities are present, not disturbing the envisaged application, it is also clear that the PS-*g*-P(EO-*co*-PO) copolymer was formed in the largest amount, thus demonstrating the efficiency of NMP in combination with the ‘grafting through’ strategy as a route towards high molar mass graft copolymers.

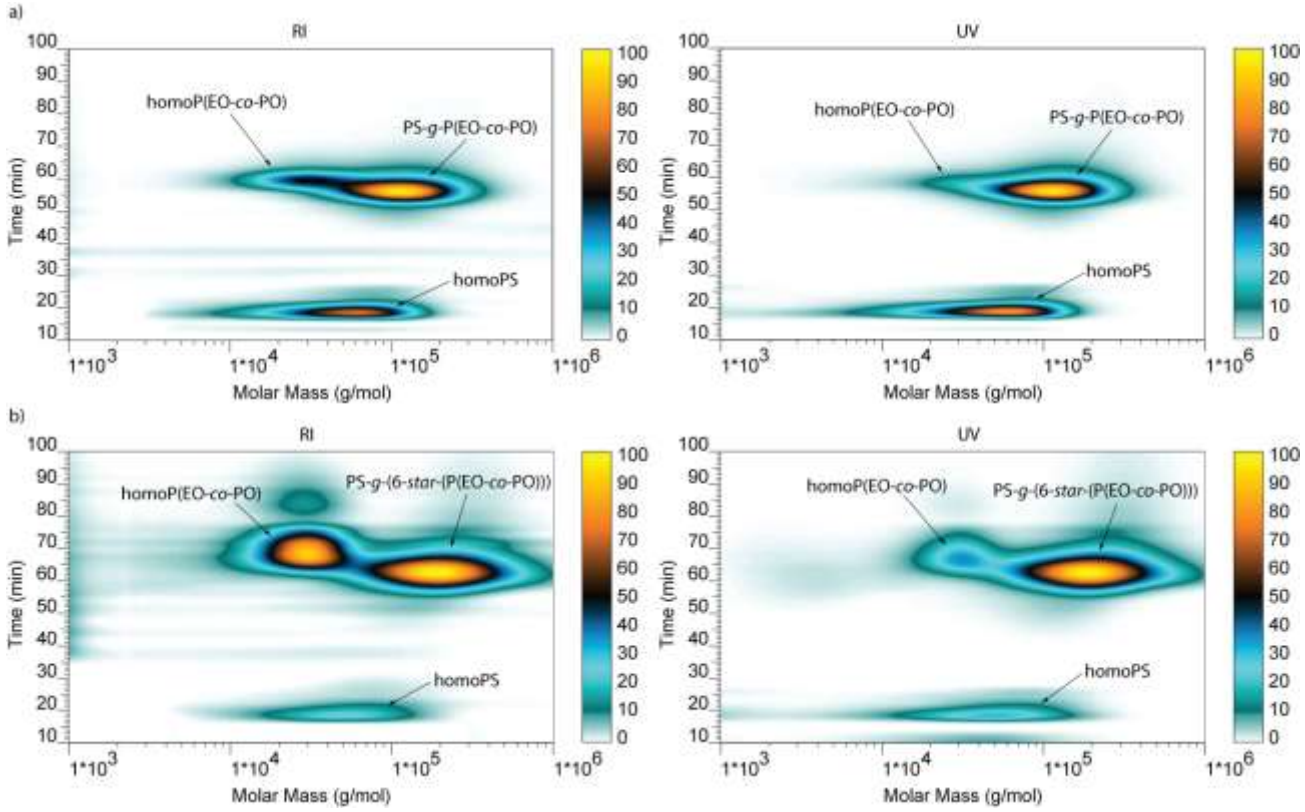


Figure 4 a) LCxSEC chromatogram for PS-*g*-P(EO-*co*-PO) graft copolymer (entry 4, Table 5); left chromatogram: RI detection; right chromatogram: UV detection. **b)** LCxSEC chromatogram for PS-*g*-(6-*star*-(P(EO-*co*-PO))) star-grafted copolymer (entry 5, Table 5); left chromatogram: RI detection; right chromatogram: UV detection.

The star-grafted structure (entry 5, Table 5) was synthesised in a similar way to the graft copolymer (entry 4, Table 5) as shown in Scheme 2b. The only difference was that the macromonomer (MM-2, Table 1) was based on a 6-arms polyether star (6-*star*-(P(EO-*co*-PO))) instead of a linear polyether. The synthesis of uncontrolled star-grafted copolymer architectures by free-radical polymerisation has already been reported in the literature[37, 42]. However, to the best of our knowledge this is the first attempt to produce a well-defined star-grafted structure by a controlled polymerisation method such as NMP.

The results of the copolymerisation between styrene and the 6-*star*-(P(EO-*co*-PO)) macromonomer (MM-2, Table 1) are displayed in Table 5 (entry 5). A copolymer with high molar mass (85,100 g/mol) and relatively low dispersity (1.49) was obtained. In this case SG1 was used instead of TEMPO as mediating agent for NMP as first attempts to synthesise star-grafted copolymers with TEMPO were unsuccessful. This can be explained by the high dilution of the system due to the presence of a large fraction of non-functionalised 6-*star*-(P(EO-*co*-PO)) (end-group fidelity of 37.9 % for MM-2 (Table 1), determined by reacting the –OH groups with isocyanates and subsequently analysis), for which the lower reactivity of

TEMPO compared to SG1[43] does not permit an effective prevention of termination reactions. Also, the optimal value of the ratio [SG1]/[AIBN] was found to be two in order to ensure relatively fast kinetics – styrene conversion of 60.6 % and MM-2 macromonomer conversion of 90 % (entry 5, Table 5) after 24 h – with preservation of a low dispersity. The higher conversion of the macromonomer compared to that of styrene means that a gradient copolymer was obtained, in which the polyether stars are incorporated more favourably at the beginning of the reaction. The macromonomer conversion was determined by SEC (see ESI) and it was estimated that, for each copolymer chain, an average of about 4 polyether stars were incorporated along the PS backbone.

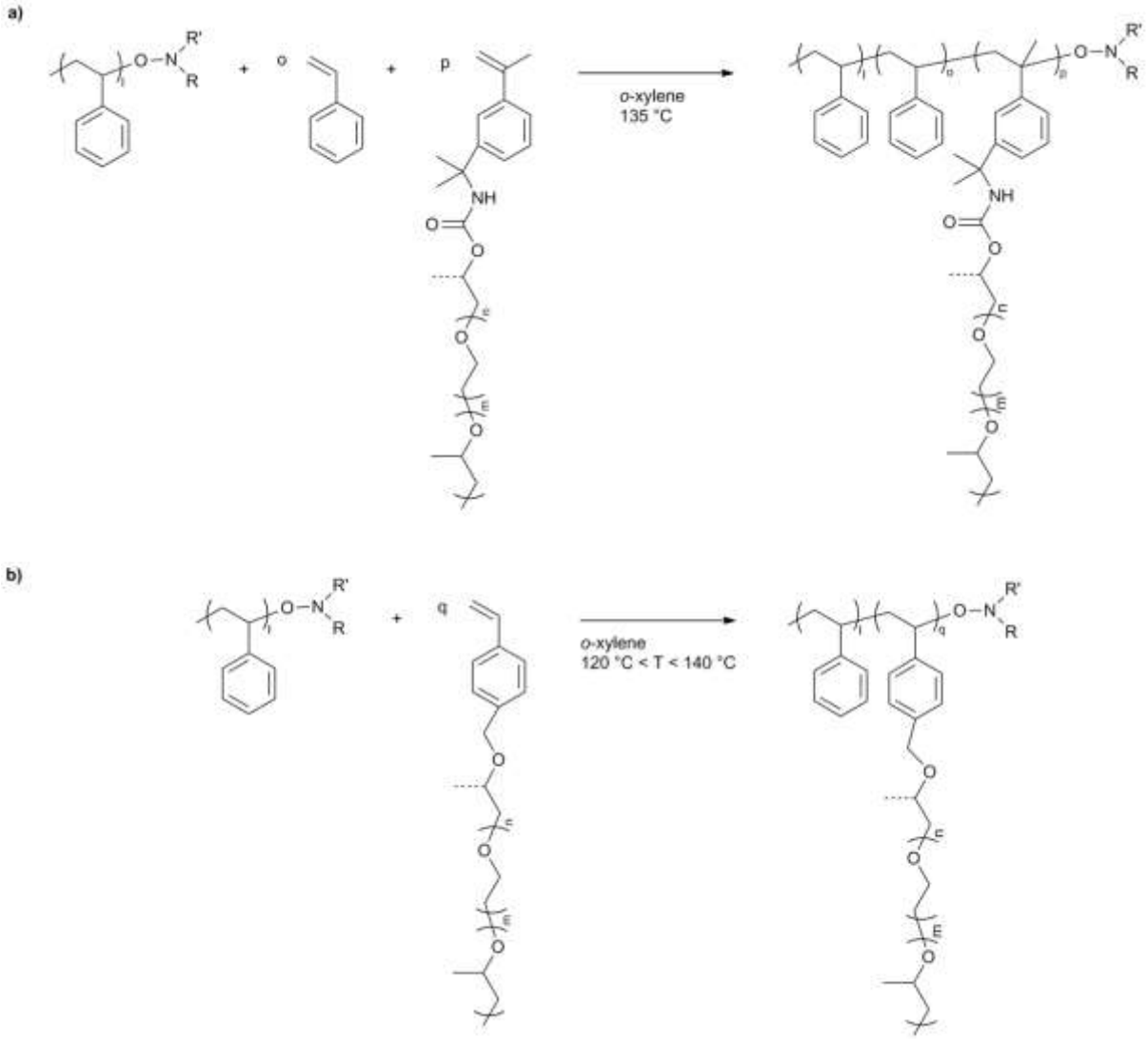
Consequently, the PS-*g*-(6-*star*-(P(EO-*co*-PO))) copolymer was characterised by LCxSEC chromatography (Figure 4b). Similarly to the graft copolymer (Figure 4a), a small fraction of homoPS, which might result from the lower reactivity and accessibility of the TMI function situated on the MM-2 macromonomer, is eluting around 15 – 20 min. However, it was found that the peak corresponding to homoPS represented only 7 % of the total volume of all peaks (entry 5, Table 5). Thus, only a small amount of polymer chains did not contain any polyether stars, which confirms the suitability of NMP to synthesise the star-grafted copolymer. Moreover, an almost complete separation occurs on the molar mass axis between the residual 6-*star*-(P(EO-*co*-PO)) peak and the PS-*g*-(6-*star*-(P(EO-*co*-PO))) peak (Figure 4b), which are both eluting after 55 – 60 min. It can be observed that, as a result of the presence of more hydrophobic PS, the copolymer elutes slightly before homoP(EO-*co*-PO). The amount of residual polyether, around 37 % (Table 5), is relatively high as expected since only 37.9 % of the 6-*star*-(P(EO-*co*-PO) polymer (MM-2, Table 1) could participate in the polymerisation. This is confirmed by the UV chromatogram (Figure 4b) where a much smaller fraction of homoP(EO-*co*-PO), corresponding to unreacted MM-2 macromonomer only, is visible. The presence of another peak eluting after 80 min is believed to arise from impurities present in the MM-2 macromonomer and was not further investigated.

Toothbrush and palm tree copolymers

The toothbrush copolymer was synthesised following a procedure similar to that used for the graft copolymer (entry 4, Table 5) as shown in Scheme 3a. The polyether macromonomer (MM-1a, Table 1) was also prepared by reacting TMI with an –OH terminated polyether and subsequently copolymerised with styrene by NMP in *o*-xylene. However, the main difference can be found in the use of a PS macroalkoxyamine having a

molar mass of 66,300 g/mol (MI-2, Table 1) instead of a low molar mass initiation system. Furthermore, the chain length of the macromonomer was lower than for the graft copolymer (6,600 g/mol instead of 18,900 g/mol).

The toothbrush copolymer was successfully obtained as indicated by the results presented for entry 6 in Table 6. In particular, a noticeable increase of the molar mass was observed (Figure 5a), which confirms the effectiveness of the chain extension. In addition, the relatively low dispersity of 1.46 is in accordance with a controlled process. The styrene conversion of 5 % (entry 6, Table 6) was low after 4 h of reaction, which might be explained by the low amount of styrene used (initial styrene content represented 10.5 wt% of the total reaction mixture) and by the high amount of TEMPO relative to propagating radicals (ratio = 1) due to the use of unimolecular initiation (PS macroalkoxyamine MI-2, Table 1). Nevertheless, the decrease of the molar mass distribution peak corresponding to the P(EO-*co*-PO) macromonomer after the polymerisation (left peak in Figure 5a) is a first strong indication that P(EO-*co*-PO) segments were incorporated into the copolymer to form the toothbrush structure PS-*b*-(PS-*g*-P(EO-*co*-PO)). Moreover, the area of the macromonomer peak before and after reaction was used to determine the conversion. It was found that about 29 % of the MM-1a macromonomer was reacted, from which it was extrapolated that each copolymer chain contained an average of 6 polyether side-chains.



Scheme 3 a) Synthesis of PS-*b*-(PS-*g*-P(EO-*co*-PO)) toothbrush copolymer by NMP. **b)** Synthesis of PS-*b*-(PS-*comb*-P(EO-*co*-PO)) palm tree copolymer by NMP.

Table 6 Characterisitics of toothbrush and palm tree copolymers.

Entry	Structure	M_n (g/mol)	Đ	Styrene Conv.[a] (%)	Estim. homoPS[b] (%)	MM Conv.[c] (%)	N_{MM}[d]	Estim. homoP(EO-*co*-PO)[e] (%)
6	toothbrush	84,600	1.46	5	28	29	6	32
7	palm tree	92,300	1.36	-	16	14	4	35
8	palm tree	84,400	1.39	-	14	24	5	32
9	palm tree	47,400	1.28	-	15	29	3	34

[a] Determined by ^{1}H NMR; - = not applicable for palm tree copolymers. [b] Estimation of the volume fraction of the residual homoPS peak determined by LCxSEC. [c] Macromonomer conversion determined by SEC. [d] Estimation of the number N of macromonomers incorporated into each copolymer chain. [e] Estimation of the volume fraction of the residual homoP(EO-*co*-PO) peak determined by LCxSEC.

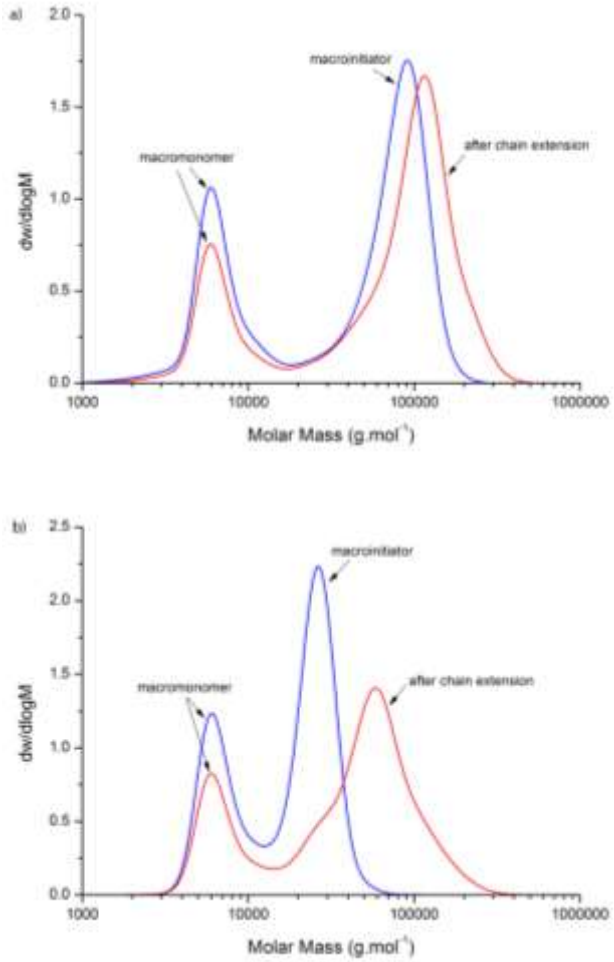


Figure 5 a) Toothbrush copolymer (entry 6, Table 6): molar mass distribution before (left) and after (right) copolymerisation of styrene and a P(EO-*co*-PO) macromonomer (MM-1a, Table 1) by NMP initiated with a PS macroalkoxyamine (MI-2, Table 1). The macromonomer peak is visible on the left. **b)** palm tree copolymer (entry 9, 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-3b, Table 1). The macromonomer peak is visible on the left.

In addition, the toothbrush copolymer (entry 6, Table 6) was characterised by LCxSEC chromatography (Figure 6a). The homoPS peak eluting between 15 – 20 min, which accounts for 28 % of the total peak volume (entry 6, Table 6), is relatively important. This was again expected since the PS-TEMPO macroalkoxyamine possessed a high molar mass of 66,300 g/mol (MI-2, Table 1) and it is known that the end-group fidelity of polymers prepared by NMP with TEMPO decreases significantly with increasing molar mass[40]. Consequently, the PS macroinitiator MI-2 (Table 1) contained a fraction of terminated product, which could not participate in the chain extension process and remained in the mixture as a homoPS impurity. Furthermore, the molar mass difference between the P(EO-*co*-PO) macromonomer (6,600 g/mol) and the PS-*b*-(PS-*g*-P(EO-*co*-PO)) copolymer (84,600 g/mol) is sufficiently important to allow for a clear separation of the two corresponding peaks in the LCxSEC chromatograms (Figure 6a). Similarly to the previous copolymer

architectures, the residual homoP(EO-*co*-PO) is more visible in the RI chromatogram than in the UV chromatogram. The RI homoP(EO-*co*-PO) peak represents about 32 % of the total volume peak. Although the toothbrush copolymer (entry 6, Table 6) contains residual homopolymer impurities, due to the synthetic procedure being devoid of extensive purification, the copolymer was obtained in considerable fraction as indicated by the right peak eluting after 50 min, which was visible both in the UV and RI chromatograms (Figure 6a).

Following the effective synthesis of the toothbrush copolymer (entry 6, Table 6), there was an interest to take the strategy one step further and synthesise palm tree copolymers, which consisted of a linear PS block covalently bonded to a comb-like polyether block instead of a more loosely grafted block (Figure 1). The synthesis of the palm tree copolymers was based on the use of a PS macroalkoxyamine as initiator for the NMP of a polyether macromonomer (Scheme 3b). However, a more reactive styrene-terminated macromonomer had to be synthesised first (MM-3, Table 1, see ESI) as the polyether macromonomers, used previously for the graft and toothbrush copolymers, were endcapped with an α-methylstyrene function that is not susceptible to homopolymerise, thus rendering it inadequate for the synthesis of palm tree architectures.

Palm tree structures with varying compositions were obtained through the use of different PS macroinitiators – MI-2, MI-3a, MI-3b in Table 1 – with molar masses in the range of 21,500 to 66,300 g/mol, while the polyether segments had a molar mass of 6,500 g/mol (MM-3, Table 1).

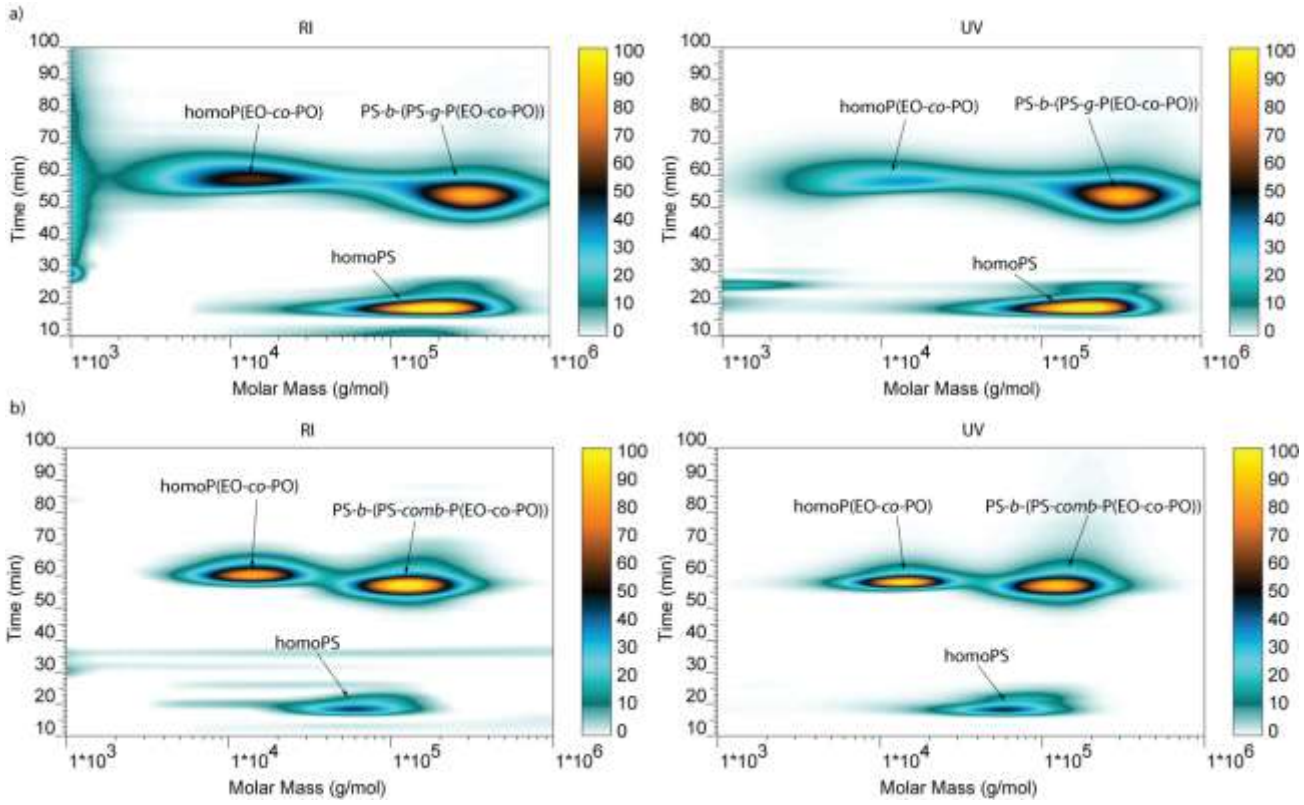


Figure 6 a) LCxSEC chromatogram for PS-*b*-(PS-*g*-P(EO-*co*-PO)) toothbrush copolymer (entry 6, Table 6); left chromatogram: RI detection; right chromatogram: UV detection. **b)** LCxSEC chromatogram for PS-*b*-(PS-*comb*-P(EO-*co*-PO)) palm tree copolymer (entry 9, Table 6); left chromatogram: RI detection; right chromatogram: UV detection.

The results for the synthesis of palm tree copolymers initiated with PS-TEMPO (entry 7) or PS-SG1 (entries 8 and 9) macroinitiators are displayed in Table 6. The success of the procedure was in first instance evidenced by the molar mass increase at the end of the different reactions: from 66,300 to 92,300 g/mol for entry 7; from 50,000 to 84,400 g/mol for entry 8 and from 21,500 to 47,400 g/mol for entry 9. This is further confirmed by the shift of the macroinitiator peak after the polymerisation in the SEC analysis, as shown in Figure 5b for entry 9 (Table 6). In addition, the decreasing intensity of the molar mass distribution peak corresponding to the P(EO-*co*-PO) macromonomer indicates its incorporation in the copolymer. SEC was also used to determine the polyether macromonomer conversion, being 14 %, 24 % and 29 % for entries 7, 8 and 9, respectively (Table 6). As expected, the macromonomer conversion was less important when TEMPO was employed (entry 7, Table 6) compared to the more effective SG1 nitroxide (entries 8,9, Table 6). Nevertheless, both TEMPO and SG1 nitroxides were suitable mediators for the NMP of the P(EO-*co*-PO) macromonomer (MM-3, Table 1). Following the SEC results, it was determined that between 3 and 5 polyether macromonomers were incorporated in average per copolymer chain (Table 6).

The LCxSEC chromatograms obtained for the different samples were similar and only the one of entry 9 in Table 6 is shown in Figure 6b and discussed hereafter (for the others, see ESI). The peak eluting between 15 and 20 min, which corresponds to homoPS, amounts to about 15 % of the total peak volume. The low homoPS content is related to the small number of termination events occurring during the synthesis of the PS macroinitiator (MI-3b, Table 1) by NMP, which consequently remains in the final product as an impurity. Besides homoPS, the homoP(EO-*co*-PO) and PS-*b*-(PS-*comb*-P(EO-*co*-PO)) peaks – eluting around 55 to 60 min – were almost fully separated (Figure 6b), which allows for a more straightforward interpretation of the chromatograms. The homoP(EO-*co*-PO) peak accounts for 34 % of the total peak volume and mostly consists of unreacted polyether macromonomer (MM-3, Table 1) as evidenced by the similar signal intensity in the RI and UV detections. Moreover, the synthesis of the PS-*b*-(PS-*comb*-P(EO-*co*-PO)) copolymer is further demonstrated by the presence of the peak on the upper right of the chromatograms (Figure 6b), which elutes after 55 min and has the highest molar mass.

CONCLUSION

The synthesis of a series of high molar mass copolymer architectures, namely block, graft, star-grafted, toothbrush and palm tree copolymers, which were all composed of PS and P(EO-*co*-PO) segments, was performed in a straightforward two-step procedure. First, the necessary prepolymers – macromonomers or macroinitiators – were designed through diverse functionalisation or polymerisation reactions. Secondly, NMP, in the presence of the necessary precursors, was used as polymerization protocol to obtain the various high molar mass copolymers. Moreover, a detailed analysis of the end-products, performed by SEC and LCxSEC chromatography, verified the suitability of the synthetic procedure to obtain the different structures.

ACKNOWLEDGMENTS

Lionel Petton expresses his gratitude to Dow Chemical for financial support. F.D.P. acknowledges the Belgian Program on Interuniversity Attraction Poles initiated by the

Belgian State, the Prime Minister's office (P7/05) and the European Science Foundation – Precision Polymer Materials (P2M) program.

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