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Full Paper

End-functionalised chains via anionic polymerisation: can the problems with using diphenylethylene derivatives be solved by using Bisphenol F?[a]

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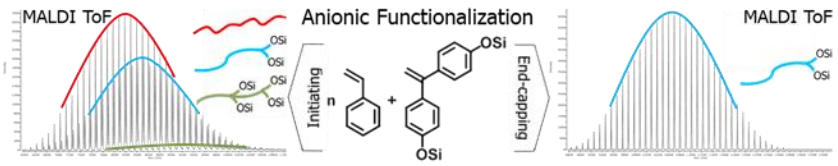
The controlled functionalisation of polymers via anionic polymerisation draws great attention not only because of the importance of introducing functionality into otherwise unfunctionalised polymers, but also because of the possibility to use the resulting macromonomers to make a variety of complex architectures. The versatile family of 1,1-diphenylethylene (DPE) derivatives has been widely-used to produce many different functionalised (co)polymers. DPE can be added either as an end-capping agent or be activated by butyllithium to initiate the polymerisation. However, each approach faces potential problems in gaining precise control over the number of DPE moieties per chain.

In this work, for the first time, the effectiveness of each approach is compared by the characterisation of 1,1-bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) functionalised polystyrene, synthesised via both the procedures. A combination of NMR, SEC, MALDI-ToF Mass Spectrometry and Interaction Chromatography is used.

[a] **Supporting Information** is available online from the Wiley Online Library or from the author.

To overcome the limitations of DPE derivatives, the use of a novel (protected) bisphenol F potassium initiator is proposed.



1. Introduction

Among the different synthetic approaches developed by polymer chemists, living anionic polymerisation of monomers such as styrene, 1,3-butadiene, isoprene, 2-vinylpyridine (2VP), and alkyl methacrylate monomers, is still the gold standard mechanism by which to obtain polymers with predictable, well-defined structures. The absence of termination and chain transfer reactions enables a high degree of control over the major variables affecting polymer properties, such as molecular weight, dispersity, chain-end and in-chain functionality, copolymer composition, molecular architecture and block copolymer morphology. However, the synthesis of such well-defined polymers requires extra care in the procedure and a suitable combination of monomer, solvent and initiator.[1, 2]

The controlled functionalisation of polymers via living anionic polymerisation, whether it be at the chain-end or in-chain, has drawn great attention because it paves the way to various branched architectures, crosslinking reactions, reversible supramolecular non-covalent bonds, coupling with reactive groups of other polymer chains and the initiation of polymers with different monomers.[1] One example of the benefits of chain functionalisation is in the synthesis of macromonomers and indeed, the "macromonomer" approach has become widely adopted as a route to make a variety of complex branched and grafted architectures with a high compositional and molecular homogeneity. Macromonomers are (usually) linear macromolecules, synthesised by a living/controlled polymerisation mechanism, with functional groups at one or both ends, such that they can undergo subsequent coupling reactions, leading to the construction of complex architectures.[2-22] In recent years, we have exploited and developed this concept for the synthesis of a variety of complex dendritically branched polymers including DendriMacs,[23-25] HyperMacs[26-30] and more recently HyperBlocks.[31, 32] One key advantage of this approach is that the coupling reactions need not to be carried out under the rigorously inert conditions required for anionic polymerisation.[33]

There are two main ways to introduce such functionalities at one end of a polymer chain. Traditionally, chain-end functionalisation was achieved through a post-polymerisation reaction of the living anionic chain-end with an electrophilic species carrying the desired functional group. Numerous functionalities may be introduced by the controlled termination of alkyllithium-initiated living polymers with special reagents. For example, a carboxylic acid group can be introduced by the addition of gaseous carbon dioxide to the living solution of the polymeric organolithium compound,[34, 35] hydroxyl-terminated polymers can be obtained by reaction with ethylene oxide,[36, 37] and amino groups can be added through protected α-halo-ω-aminoalkanes.[38-40] Sulfonate end-capped polymers have been synthesised through the reaction of polymeric organolithium compounds directly with sultones.[41] However, many of these reactions are often affected by side reactions, usually leading to a lower degree of functionalisation.[1]

Alternatively, a (protected) functionalised initiator can be used for anionic polymerisation of for example, styrene or dienes. Organolithium initiators with a silyl-protected hydroxy functionality, such as 3-(t-butyldimethylsilyloxy)-1-propyllithium,[24, 26, 42-44] , or with acetal-protected hydroxy functionalities, such as (6-lithiohexyl)acetaldehyde acetal,[45] and (3-lithiopropyl)acetaldehyde acetal,[45, 46] have been used to obtain essentially quantitative hydroxy end-functionalised polymers. Some examples of amino functionalisation can also be found, in which the initiator is p-lithio-N,N-bis(trimethylsilyl)aniline[47] or 3-(N,N-dimethylamino)propyl-lithium.[48] Even though quantitative functionalisation is assured with a (protected) functionalised initiator, limited availability and often limited solubility of the initiators, strongly impact on the practical application of this strategy.[1, 36] In each case, the protection of reactive functional groups is needed, because of the high reactivity of the organolithium reagents.[1]

Of particular interest for the introduction of functionalisation in living anionic polymerisation is the family of monomers based on 1,1-diphenylethylene (DPE). Many examples can be found

in the literature which exploit DPE, mainly via one of two functionalisation methods:[49] the functionalised DPE can be added either as an end-capping agent, before the termination of the polymer,[23, 26, 31] or it can be activated by the alkyl lithium initiator, and the adduct used to initiate the polymerisation.

The end-capping strategy involves the simple addition of the DPE monomer to the polymeric organolithium living chain-end. The addition of DPE to poly(styryl)lithium and poly(dienyl)lithium is a very favourable reaction since the corresponding 1.1-diphenylalkyllithium is approximately 64.5 kJ mol^{-1} more stable than the organolithium species it reacts with.[49] The functionalisation is, thus, practically quantitative.[23, 26, 31, 43, 50] The steric bulk of DPE, however, prevents it from propagating and the DPE monomer is unable to homopolymerise; thus only monoaddition happens, even with an excess of DPE.[43, 49, 51] Moreover, the end-capping procedure is easy to monitor by UV-visible absorbance where the signal of poly(styryl)lithium (λ_{max} = 334 nm, $\varepsilon = 1.30 \cdot 10^4$ l mol^{-1} cm^{-1}) is easily distinguished from the one of polymeric 1,1-diphenylalkyllithium (λ_{max} = 440 nm, $\varepsilon = 1.60 \cdot 10^4$ l mol^{-1} cm^{-1}). By ^{1}H NMR analysis, a peak at δ = 3.5 ppm for the terminal methine hydrogen at the chain end of PS-DPE can be clearly seen.[49] Finally, after the addition of DPE, the product is still a living chain and the obtained polymeric 1,1-diphenylalkyllithium can be used as a macro-initiator to synthesise (block)copolymers, by the sequential addition of monomers.

As an alternative to the end-capping procedure, the reaction of DPE (and derivatives) with a simple alkyllithium compound (e.g. butyllithium) to form the corresponding 1,1-diphenylalkyllithium gives an effective initiator in anionic polymerisation. As previously noted, the diphenylmethyl carbanion is more stable than the carbanions resulting from the subsequent addition of monomers (usually benzyl and allyl carbanion). Thus it would be expected that this initiation reaction would be energetically unfavourable. However, the energy released by the conversion of a π-bond in the monomer to a more stable σ-bond in the adduct is enough to start the polymerisation.[49] Moreover, it is well known that a lower degree of association in

alkyllithium species results in increased reactivity. 1,1-diphenylalkyllithium is associated into dimers in hydrocarbon solutions, while other organolithium species often have a higher degree of association.[1, 49] This contributes to making DPE an effective species to initiate anionic polymerisation. Even if dimerisation of DPE is possible under particular extreme circumstances,[52] the 1,1-diphenylalkyllithium initiator would not be expected to attack another DPE molecule, and homopolymerisation of DPE is avoided, leading to the polymerisation of the desired monomer. The use of 1,1-diphenylalkyllithium (and its derivatives) as an initiator for anionic polymerisation is particularly advantageous for some specific purposes. For example, in the polymerisation of methyl methacrylate (MMA), the use of DPE is essential! Due to the steric hindrance caused by the two bulky phenyl groups adjacent to the carbanion, attack by the initiator on the carbonyl group of MMA is prevented – which would otherwise occur if butyllithium were used.[31, 49] Other authors have also exploited functionalised DPE for living anionic surface initiated polymerisation, to produce surface grafted polymer. Fan *et al.*[53] produced montmorillonite clay nanoparticles, intercalated with a quaternized-amine modified DPE derivative which was immobilised on the clay surface by electrostatic attraction. After being dispersed in benzene, the initiator-clay complex was activated by n-BuLi to initiate polymerisation. Quirk *et al.*[54] used a surface bound 1,1-diphenylethylene monolayer to prepare diblock copolymer brushes onto oxide surfaces by anionic polymerisation.

Whether functionalisation with DPE is performed at the chain-end via the initiating step or in-chain, this particular species is very versatile and allows the introduction of many different functional groups onto the polymer chain. DPE carrying fluorescent moieties, such as naphthyl and pyrenyl groups, have been used to label polymer chains, via the reaction with 1-(2-naphthyl)-1-phenylethylene or 1-phenyl-1-(1'-pyrenyl)ethylene.[55-59] More recently, 1-(2-anthryl)-1-phenylethylene has been used to monitor polymer–polymer coupling by size exclusion chromatography coupled with fluorescence detection.[60, 61] DPE derivatives with amino groups on the aromatic rings, e.g. 1-(4-dimethylaminophenyl)-1-phenylethylene and 1-

(4-(N,N-bis(trimethylsilyl)-amino)phenyl)-1-phenylethylene, have been widely used to obtain amino-functionalised chains of styrene and dienes. The presence even of a small number of these polar groups can dramatically change the solution and aggregation behaviour of non-polar macromolecules. There are examples of such kind of functionalisation at the beginning of the chain,[53] the terminus of the chain,[62-64] in-chain,[65, 66] or to prepare telechelic copolymers.[62, 67] The carboxyl functionality can also be added to a polymer chain through a DPE carboxyl derivative, after protection with an oxazoline group or a diisopropylamide. A post-polymerisation deprotection reaction gives the desired carboxy functionalised product.[1, 68] Similarly, DPE derivatives have been used to introduce a phenol group at the chain terminus.[69] In order to prepare condensation macromonomers with two phenol polymerisable groups at one chain end, 1,1-bis(4-tert-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) has been used as both initiator or end-capping agent in living anionic polymerisation.[28, 43, 49, 70] The resulting macromonomers have been used to synthesise more complex architectures, such as HyperMacs and DendriMacs.[26, 27, 30, 32]. The use of functionalised DPE monomers has also been exploited in studies of monomer sequence control in anionic polymerisation.[51, 71-76]

It is therefore clear that the use of functional derivatives of DPE is a widely-used and valuable strategy to produce functionalised (co)polymers and in particular, end-functionalised polymers. Although the introduction of functionalised DPE derivatives both via the initiation process and via an end-capping reaction has been described as effective, there are potential problems associated with each approach if the objective is to produce chains with 100% end-functionalisation and with accurate control over the number of functional DPE moieties per chain. Moreover, a systematic comparison of the relative effectiveness of the two approaches has never been carried out to the best of our knowledge.

The aim of this work is to evaluate the optimal approach to obtain mono-end-functionalised polymer chains using functionalised DPE derivatives. For this purpose, polystyrene has been synthesised through living anionic polymerisation and functionalised with DPE-OSi via both

the initiating and the end-capping procedure. A combination of NMR, SEC, MALDI ToF mass spectrometry and normal-phase Isothermal Interaction Chromatography (IC) analysis has been used to characterise the resulting polymers with a view to calculating the average degree of functionalisation and to go further and identify the presence of chains with different numbers of DPE units. Recently, Temperature Gradient Interaction Chromatography (TGIC) has emerged as a valuable characterisation technique for polymers, to complement SEC. The latter is intrinsically incapable of separating polymers with identical or nearly identical hydrodynamic volumes, which may differ in other molecular parameters such as molecular weight, chain architecture or chain functionality. However, when using TGIC, an interaction chromatography technique, separation is driven by enthalpic interactions between the solute molecules and the stationary phase. Reversed phase (RP) TGIC resolves polymer samples based on molecular weight, not hydrodynamic volume, and thus is a powerful tool for studying the structural heterogeneity of branched polymers, a field that has been recently reviewed.[77] Normal phase (NP) TGIC has only been applied in a few cases, for the resolution of polymers in terms of functionality and molecular weight, with polymer separation achieved by partition between a polar stationary phase (bare silica or diol bonded silica) and a less polar mobile phase.[78, 79] Most recently[77, 79] it has been shown that end-functionalised polymers can be resolved from unfunctionalised polymers of identical molar mass, for polymers with molecular weights up to 200,000 $gmol^{-1}$ – at such molecular weights any attempt to analyse the extent of end-functionalisation by NMR or MALDI-ToF MS would be an exercise in futility.

Finally, in order to overcome the limitations revealed in the current study, that impact upon both the end-capping and the initiating approaches, a new functionalisation strategy has been developed to introduce two (protected) phenol groups, selectively, at one end of the polymer chain. This was achieved by the use of a functional derivative of related class of initiator: diphenylmethylpotassium (DPMK). Together with cumyl potassium, DPMK is most frequently used for the polymerisation of ethylene oxide (EO). Alkyl lithium initiators are unsuitable for the

polymerisation of EO because the very strong lithium–oxygen bond, produced during its initiation, forms ion pairs that are not able to propagate the polymerisation of EO in weak or medium-polarity solvents. Propagation is able to proceed at a reasonable pace with potassium, though. On the other hand, DPMK is not a commonly used initiator for styrene or diene monomers. DPMK has poor solubility in non-polar solvents resulting in heterogeneous initiation and the polymerisation of chains with a broad dispersity. Moreover, it has been reported that DPMK is not effective as an initiator for styrene and diene monomers due to the delocalisation of the negative charge in the two phenyl rings also leading to high dispersity chains.[80]

However, for the aim of this work, DPMK (and its functional derivative) has been investigated because it is only an initiator and cannot behave as a monomer, as DPE does. Hence, since DPMK is capable of initiation but cannot participate in propagation, it represents an opportunity for the optimisation of end-functionalisation of polystyrene by anionic polymerisation. We therefore report herein, the synthesis and use of a novel functional initiator based on bis-phenol F (BPF), which was designed to overcome the limitations of using DPE-OSi. Finally, we also report the synthesis and characterisation of a series of mikto-arm stars, with arms of polystyrene and polybutadiene, produced via the macromonomer approach, using the prepared end-functionalised polystyrene polymers.

2. Experimental Section

2.1. Materials

Benzene (Aldrich, HPLC grade, ≥99%), cyclohexane (Sigma-Aldrich, ≥99%) and styrene (Sigma-Aldrich, ≥99%) were dried and degassed over calcium hydride (CaH_2) (Acros Organics, 93%) and stored under high vacuum. Tetrahydrofuran (in-house solvent purification) was dried over sodium wire (Aldrich, 99.9%) and benzophenone (Aldrich, 99%) and degassed using freeze-thaw techniques. Sec-butyllithium (1.4 M solution in cyclohexane), N,N,N’N’-tetramethylethylenediamine, cesium carbonate (all Sigma-Aldrich), were used as received.

Methanol (AR grade) and hydrochloric acid (37 wt.%) (both Fischer Scientific) were used as received. Naphthalene and potassium chunks (both Aldrich) were used as received. 4,4'-Dihydroxydiphenylmethane (bisphenol F, BPF) (Tokyo Chemical industry) was used as received. Dimethyl formamide (DMF) (Sigma-Aldrich 99.8%) was stored over molecular sieves (Sigma-Aldrich) under an inert atmosphere. 1,1-Bis(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) was synthesised in two steps from dihydroxybenzophenone (Sigma-Aldrich, 99%) according to the procedure of Quirk and Wang.[70] 1,1-Bis(4-t-butyldimethylsiloxyphenyl)methane was synthesised through the protection of BPF with *t*-butyldimethylsilyl chloride (Sigma-Aldrich, 97%) according to the procedure of Quirk and Wang.[70]

2.2. Characterisation

^{1}H NMR spectra were measured on a Bruker DRX-400 MHz spectrometer using $CDCl_3$ as solvent. Triple detection size exclusion chromatography (SEC) with refractive index, viscosity, and right angle light scattering (RALS) detectors was used for the analysis of molar mass and molar mass distribution of the macromonomers, using a Viscotek TDA 302. Tetrahydrofuran was used as the eluent, at a flow rate of 1.0 mL min^{-1} and at a temperature of 35°C. Separation was achieved using 2 × 300 mm PLgel 5 μm mixed C-columns. A value of 0.185 ml·g^{-1} was used as the dn/dc of functionalised polystyrene, while a value of 0.124 ml·g^{-1} (measured in house) was used as the dn/dc of polybutadiene for the analysis of prepared mikto-star polymers. MALDI ToF MS analysis was carried out on an Autoflex II TOF/TOF mass spectrometer (Bruker Daltonik GmBH) equipped with a 337 nm nitrogen laser. A linear mode of analysis was used typically above *m/z* 5,000. Samples were dissolved in THF or chloroform (~1 mg mL^{-1}) and mixed with a matrix solution (dithranol or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile, ~20 mg mL^{-1}). 1 μL of this mixture was spotted on to a metal target and placed into the MALDI ion source. Ag^+ was used as a dopant.

Isothermal interaction chromatography analysis was performed under normal phase conditions using a diol modified silica column (Nucleosil 100 Å pore, 250 × 4.6 mm I.D., 5 μm). A mixture of THF/isooctane (Fisher, GPC and HPLC grade respectively) was used in a ratio 45/55 (v/v) with a flow rate of 0.5 ml min^{-1}. The temperature was maintained at 15 °C using a ThermoScientific circulating bath and thermostat. Samples were prepared with a concentration of 2.5 mg ml^{-1} in the eluent mixture and the injection volume was 100 μl. The analysis was performed using a modified Viscotek TDA 301, mainly using the RALS detector and a Viscotek UV2600 detector set to a wavelength of 260 nm. For the calculation of the molecular weight by IC chromatography, the dn/dc utilised was 0.1 $ml \cdot g^{-1}$, previously determined. The calibration was achieved using a narrow dispersity PS standard (66 kg mol^{-1}).

2.3. Polymer synthesis

The synthesis of all polymers was carried out through anionic polymerization, using standard high vacuum techniques. Each polymerisation was carried out twice for reproducibility of data, for both the initiated and the end-capped procedure.

2.3.1. Synthesis of functionalised polystyrene via the initiating procedure – iPS-OSi

In a typical reaction and for a target molar mass of 10,000 g mol^{-1}, DPE-OSi (0.26 g, 0.6 mmol) was added to the reaction vessel, sealed and evacuated overnight, then azeotropically dried 3 times through the distillation into and out of ~ 20 ml of dry benzene. Finally ~ 50 ml of fresh benzene were distilled to dissolve the DPE-OSi. Sec-butyllithium was added drop wise, to titrate out any residual impurities, until the red color of living DPE-OSi persisted. The required amount of sec-butyllithium (430 μL, 0.6 mmol) to initiate the polymerisation was then injected, followed by styrene (5.74 g, 55.1 mmol) after 4 hours. The propagation was allowed to proceed for 4 hours at room temperature, then the reaction was terminated with nitrogen-sparged methanol. The polymer was recovered by precipitation into excess methanol, re-dissolved in

THF, precipitated again into methanol, collected by filtration and dried to constant mass under vacuum. Yield 92%. M_n 12,000 g mol^{-1}, M_w 12,500 g mol^{-1}, Đ 1.04. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 6.3 (Ar **H**), 2.3 – 1.2 (aliphatic **H**), 1.1 – 0.9 (18H, (C**H**$_3$)$_3$C-Si), 0.8 – 0.4 (3H, C**H**$_3$CH$_2$), 0.8 – 0.4 (3H, CHC**H**$_3$), 0.3 – 0.1 (12H, (C**H**$_3$)$_2$Si).

Another polymerisation was carried out with the amount of reagents, the yield, the molar mass and the molar mass distribution data reported in **Table 1.**

2.3.2. Synthesis of functionalised polystyrene via the end-capping procedure – ePS-OSi

In a typical reaction and for a target molar mass of 10,000 g mol^{-1}, benzene (~ 50 ml) and styrene (6.44 g, 62 mmol) were distilled under vacuum into the reaction flask, then sec-butyllithium (460 μL, 0.6 mmol) was injected through a septum. The reaction was stirred at room temperature for 3 hours before the addition of a purified solution of DPE-OSi in benzene. The purified solution of DPE-OSi was prepared by azeotropically drying the desired amount of DPE-OSi 3 times with benzene and then dissolving the DPE-OSi into 50 ml of freshly distilled benzene. To this solution, TMEDA was added in a molar ratio of 1: 1 with respect to the initiator. *Sec*-Butyllithium was added drop wise to titrate out any residual impurities until the red colour of living DPE-OSi persisted. The end-capping reaction between the living polymer chain and DPE-OSi was stirred at room temperature for 5 days and then terminated with nitrogen-sparged methanol. The polymer was precipitated into methanol, redissolved in THF, precipitated again into methanol, recovered by filtration and then dried under vacuum. Yield 91%. M_n 11,300 g mol^{-1}, M_w 11,900 g mol^{-1}, Đ 1.05. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 6.3 (Ar **H**), 3.5 – 3.4 (1H, **H**C(Ph)$_2$), 2.3 – 1.2 (aliphatic **H**), 1.1 – 0.9 (18H, (C**H**$_3$)$_3$C-Si), 0.8–0.4 (3H, C**H**$_3$CH$_2$), 0.8–0.4 (3H, CHC**H**$_3$), 0.3–0.1 (12H, (C**H**$_3$)$_2$Si).

Two replicated polymerisations were carried out with the amount of reagents, the yield, the molar mass and the molar mass distribution data are summarised in Table 1.

2.3.3. Deprotection of iPS-OSi to yield iPS-OH

The protected iPS-OSi (4.14 g, 0.52 mmol) was dissolved in THF (10% w/v solution) and the required amount of HCl (1.1 ml, 11 mmol) was added dropwise (mole ratio between acid and protected alcohol groups 10:1). The solution was warmed to 60°C and stirred at reflux overnight. Finally, the solution was cooled and the polymer recovered by precipitation into methanol, re-dissolved in THF, precipitated again into methanol, recovered by filtration and then dried under vacuum. Yield 97% ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 6.3 (Ar **H**), 4.7 – 4.4 (2H, **H**OPh), 2.3 – 1.2 (aliphatic **H**), 0.8–0.4 (3H, C**H**$_3$CH$_2$), 0.8–0.4 (3H, CHC**H**$_3$).

2.3.4. Deprotection of ePS-OSi to yield ePS-OH

ePS-OSi (6.30 g, 0.56 mmol) was deprotected using HCl (1.1 ml, 11 mmol) according to the procedure described above for iPS-OSi. Yield 97% ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 6.3 (Ar **H**), 4.6 – 4.4 (2H, **H**OPh), 3.5 – 3.4 (1H, **H**C(Ph)$_2$), 2.3 – 1.2 (aliphatic **H**), 0.8–0.4 (3H, C**H**$_3$CH$_2$), 0.8–0.4 (3H, CHC**H**$_3$).

2.3.5. Synthesis of mikto-arm stars via Williamson coupling reaction

The synthesis of linear polybutadiene arms, with a molecular weight of about 40,000 g mol^{-1} (PB40-Br), was performed in benzene using sec-BuLi as initiator and the chain-end functionality was introduced via an end-capping reaction of the living polymer with ethylene oxide, as described elsewhere.[79] In a typical reaction, PB40-Br (1.78 g, 0.044 mmol), deprotected end-capped polystyrene ePS-OH (0.20 g, 0.017 mmol) and cesium carbonate (Cs_2CO_3) (0.11 g, 0.35 mmol) were dissolved in 10 ml of dry THF under an inert atmosphere of nitrogen. Dry dimethylacetamide (DMAc) (10 ml) was then added to this solution, the reaction was heated with an oil bath at 60°C and stirred with a mechanical stirrer. The reaction was followed by SEC analysis and when the peak corresponding to the PB40-Br no longer decreased, the reaction was stopped. The polymer was precipitated into methanol, redissolved

in THF, precipitated again into methanol, collected by filtration and dried under vacuum. Yield 67%. M_n 97,900 g mol^{-1}, M_w 104,700 g mol^{-1}, Đ 1.07.

2.3.6. Synthesis of 1,1-*bis*(4-*t*-butyldimethylsiloxyphenyl)methyl potassium (BPFK)

A 50 ml reaction flask was initially put under vacuum to remove air and backfilled with dry nitrogen. Naphthalene (0.41 g, 3.2 mmol) was added to the reaction flask against a continuous flow of nitrogen. After sealing the flask, 9 ml of dry THF were injected via a rubber septum and stirred until complete dissolution of naphthalene. Potassium chunks (0.32 g, 8.1 mmol) were added against a continuous flow of N_2, before the flask was sealed and stirred for 20h at room temperature. 1,1-bis(4-t-butyldimethylsiloxyphenyl)methane (3.04 g, 7.1 mmol) was dissolved in 9 ml of dry cyclohexane and the solution injected into the reaction flask and vigorously stirred for 5 days at room temperature (after the first day the solution turned from a dark green colour to a deep red). Finally the solution was stored in the fridge. An anionic polymerisation of styrene in benzene with the synthesised initiator was performed to determine the concentration of the initiator, giving a value of 0.14 M (see Supporting Information).

2.3.7. Synthesis of polystyrene initiated with BPFK

In a typical reaction and for a target molar mass of 10,000 g mol^{-1}, benzene (~20 ml) and styrene (1.54 g, 14.8 mmol) were distilled under vacuum into the reaction flask, then the BPFK initiator solution (1.1 ml, 1.5 mmol) was injected through a rubber septum. The reaction solution immediately turned red after the injection of the initiator, thus revealing the formation of the living polystyrene species. The reaction was stirred at room temperature for 3 hours, then terminated with nitrogen-sparged methanol. The polymer was precipitated into methanol, redissolved in toluene, precipitated again into methanol, recovered by filtration and then dried under vacuum. Yield 77%. M_n 15,800 g mol^{-1}, M_w 17,700 g mol^{-1}, Đ 1.12. ^{1}H NMR (400 MHz,

$CDCl_3$, δ): 7.4 – 6.2 (Ar **H**), 2.4 – 1.2 (aliphatic **H**), 1.1 – 0.9 (18H, $(C\mathbf{H}_3)_3C$-Si), 0.3–0.1 (12H, $(C\mathbf{H}_3)_2Si$).

2.3.8. Deprotection of BPFK initiated polystyrene (BPFPS-OSi) to yield BPFPS-OH

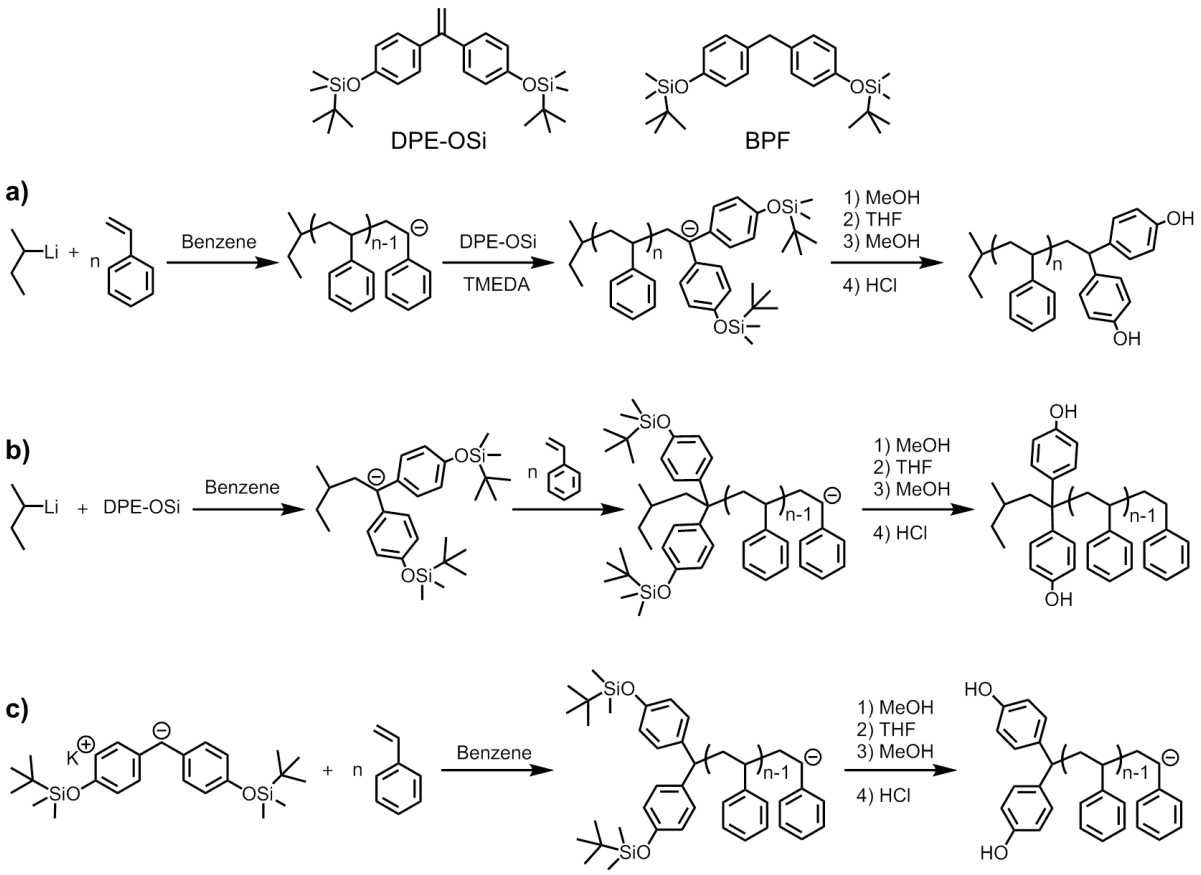
BPFPS-OSi (1.01 g, 0.06 mmol) was deprotected using HCl (130 μl, 1.3 mmol) according to the procedure described above for iPS-OSi. Yield 62% ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 6.3 (Ar **H**), 4.6 – 4.4 (2H, O**H**Ph), 2.4 – 1.2 (aliphatic **H**).

3. Results and Discussion

DPE-OSi mono end-functionalised polystyrene has been synthesised through both an end-capping and an initiation procedure, as described above, with a view to comparing the two strategies in terms of quantitative functionalization, i.e. which way provides the optimal approach for introducing a single (and no more than one) DPE-OSi end group per chain. Although both approaches have been widely used, by us and others, with apparent success, it is clear that both approaches have potential advantages and disadvantages. For a comprehensive comparison of the two approaches, and in an attempt to highlight the potential disadvantages/limitations of each approach, a combination of NMR, SEC, MALDI ToF mass spectrometry and Isothermal Interaction Chromatography (IC) characterisation is required, in order to determine the average degree of functionalisation and to identify the presence of chains with different numbers of DPE-OSi units.

3.1. Synthesis of end-functionalised polystyrene using DPE-OSi

With the explicit aim of introducing a single DPE-OSi group to the chain-end of polystyrene, prepared by living anionic polymerisation, two different functionalisation procedures were



Scheme 1. Synthesis of functionalized polystyrene through: a) end-capping procedure with DPE-OSi; b) initiating procedure with DPE-OSi; c) 1,1-bis(4-t-butyldimethylsiloxyphenyl)methyl potassium (BPFK) as initiator.

followed; the end-capping and the initiating procedure (**Scheme 1** a and b). Both procedures require high vacuum techniques and each has its pros and cons. The initiation approach, i.e. initiating polymerisation with the adduct of butyllithium and DPE-OSi, relies on very careful control of the stoichiometry of the reaction between BuLi and DPE-OSi, which in turns also requires careful management of impurities. Should there be an excess of BuLi with respect to DPE-OSi, then some chains will be initiated by BuLi and remain unfunctionalised. However, if there is an excess of DPE-OSi with respect to BuLi, then some propagating chains may react with the excess DPE-OSi and end up with more than one DPE-OSi per chain. Achieving perfect stoichiometry is practically impossible, although in an attempt to minimise any imbalance, butyllithium may be added dropwise to the DPE-OSi in the reaction vessel, prior to the addition of monomer, to "titrate" out any residual impurities. The presence of the characteristic deep red colour of diphenylhexyllithium, indicates the end-point of the titration. Even so, any slight

variation in the concentration of active BuLi in the stock initiator solution may still result in a stoichiometric imbalance. However, the significant advantages of this approach are i) that at the end of the reaction the propagating chain-end is still available for further functionalisation and ii) that the reaction is complete in less than one day.

Table 1. Quantity of reagents, yield, molar mass and dispersity values of the initiated and end-capped polystyrene samples. Two replicated polymerisations were performed for each procedure.

Data	**iPS OSi 1**	**iPS OSi 2**	**ePS OSi 1**	**ePS OSi 2**
DPE-OSi	0.242 g 0.55 mmol	0.263 g 0.60 mmol	0.49 g 1.1 mmol	0.46 g 1.0 mmol
Styrene	4.94 g 47.4 mmol	5.74 g 55.1 mmol	4.95 g 47.5 mmol	6.44 g 61.8 mmol
Sec-BuLi	400 µl 0.56 mmol	430 µl 0.60 mmol	360 µl 0.5 mmol	460 µl 0.6 mmol
TMEDA	-	-	90 µl 0.6 mmol	90 µL 0.6 mmol
Yield	4.18 g, 81%	5.51 g, 92%	4.98 g, 91%	6.31 g, 91%
M_n [g mol^{-1}]	8,000	12,000	12,500	11,300
M_w [g mol^{-1}]	8,300	12,500	13,000	11,900
Đ	1.05	1.04	1.04	1.05
Avg. DPE-OSi monomer per chain [a)]	0.68	0.99	0.95	0.91

[a)](Calculated via ^{1}H NMR)

In contrast, the end-capping approach does not rely on careful control of stoichiometry and an excess of DPE-OSi can be added on complete consumption of monomer, since the DPE moiety is incapable of homopolymerisation. Of course, one still must ensure that the DPE-OSi is scrupulously free of impurities to ensure a clean end-capping reaction and since the end-capping reaction itself requires up to 5 days to reach completion, the reaction mixture must be kept free of impurities for the duration of the end-capping reaction. Should any impurities be introduced with the DPE-OSi, less than quantitative end-capping will result. In the present work, SEC analysis of the polymers made by each approach reveals, that in each case, good control over the molecular weight and the dispersity of the products was achieved (Table 1) although SEC

can tell us nothing about the extent of end-capping. ^{1}H NMR spectroscopy however, enables a calculation of the average ratio of styrene units in the polymer backbone to DPE-OSi units per chain, as described in detail in Electronic Supporting Information (ESI). The data are summarised in Table 1 and one might conclude that the immediately obvious difference between the two functionalisation approaches, in terms of average number of DPE-OSi units per chain, is that the "initiation" approach resulted in worse reproducibility and in the case of **iPS OSi 1**, the first sample of initiated polystyrene, a low degree of functionalisation with only 0.68 DPE-OSi units per chain. This discordant value is consistent with the poor control over the reaction stoichiometry achievable by the initiating procedure and would appear to suggest that in this case, an excess of BuLi was present. In contrast, the NMR data would suggest that the "end-capping" approach delivers a consistently higher degree of end-capping. Although NMR can tell us the average number of DPE-OSi units per chain, NMR cannot give any information about the distribution of DPE-OSi units per chain. In order to identify the (potential) presence of chains with different numbers of DPE-OSi units (0, 1, 2…..), a combination of NMR and SEC with MALDI ToF mass spectrometry and IC analysis is essential.

3.2. MALDI characterisation

MALDI ToF MS analysis was performed on the 4 samples of functionalised polystyrene obtained via the two functionalisation procedures. Using this technique, the molar mass corresponding to each individual polymer chain could be found, and it was possible to identify different series of peaks ascribable to different degree of DPE-OSi incorporation. The MALDI ToF mass spectra (**Figure 1)** provide an excellent indication of the samples' composition and suggest that the effectiveness, in terms of introducing a single DPE-OSi moiety per chain, is not the same for each approach.

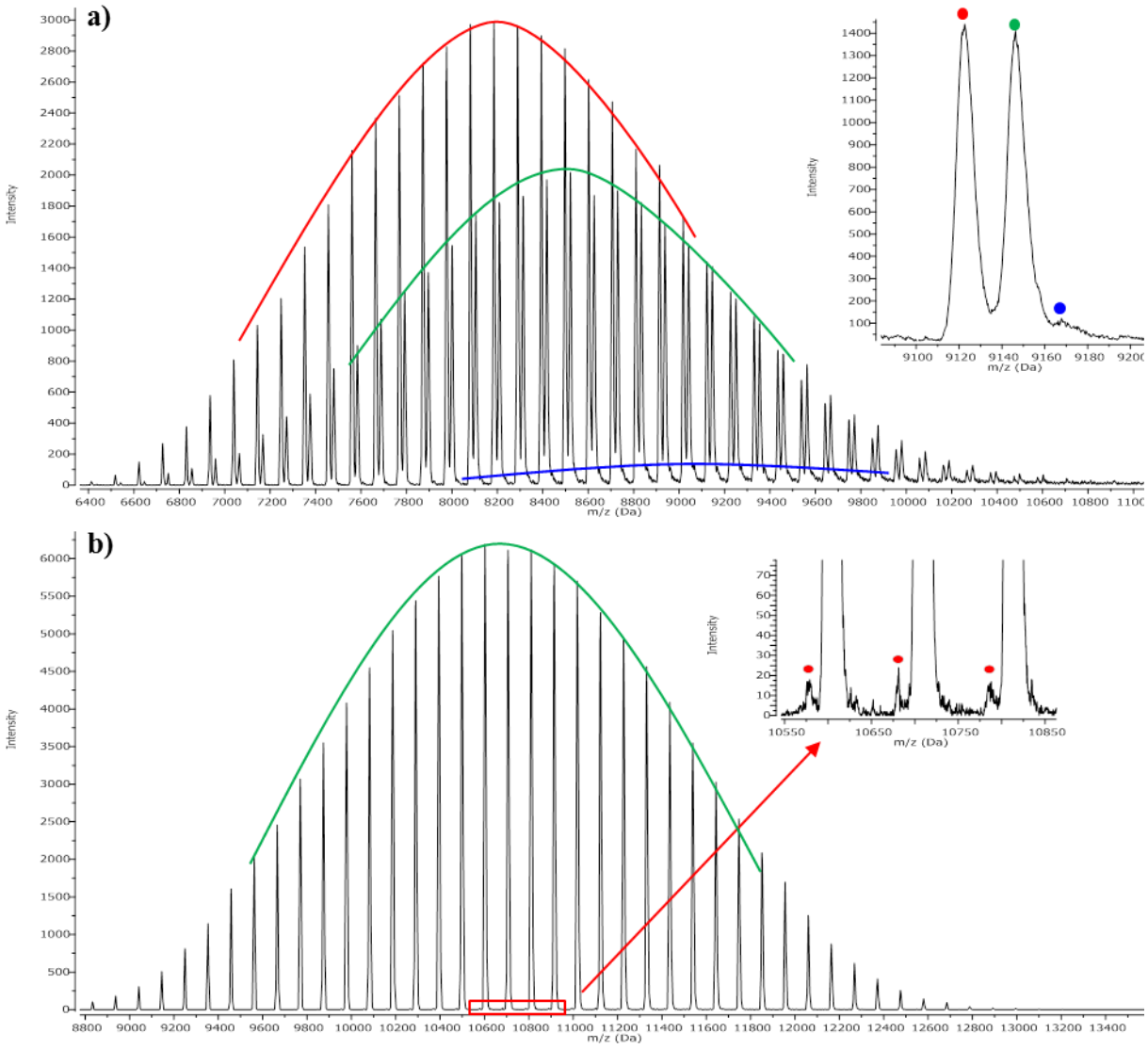


Figure 1. MALDI ToF mass spectra for a) **iPS-OSi 1**; b) **ePS-OSi 2**. The different series of peaks are highlighted respectively in red for un-functionalised chains, in green for the mono-functionalised chains, and in blue for the di-functionalised chains.

The MALDI spectra for the functionalised polymer samples produced via the "initiating procedure" – **iPS-OSi** – clearly show three series of peaks (see Figure 1a), which correspond to mono-, di and un-functionalised chains. For example (see the insert in Figure 1a), the peak of mono-functionalised chains in **iPS-OSi 1** sample, with an *m/z* of 9,147 u corresponds to 82 units of styrene (82 × 104.15 u) + 1 units of DPE-OSi (440.77 u) + the counterion, Ag (107.87 u) + the *sec*-butyl end-group (57.12 u) + the hydrogen end-group (1.01 u). The peak of un-functionalised chains in the same sample, with an *m/z* of 9,123 u corresponds to 86 units of

styrene (86 × 104.15 u) + the counterion, Ag (107.87 u) + the sec-butyl end-group (57.12 u) + the hydrogen end-group (1.01 u). Finally, the peak of di-functionalised chains, with an *m/z* of 9171 u corresponds to 78 units of styrene (78 × 104.15 u) + 2 units of DPE-OSi (2 × 440.77 u) + the counterion, Ag (107.87 u) + the sec-butyl end-group (57.12 u) + the hydrogen end-group (1.01 u).

On the other hand, the MALDI spectra for the functionalised polymer samples produced via the "end-capping procedure" – **ePS-OSi** – reveal one dominant series of peaks (example in **Figure 1b**) corresponding to mono-end functionalised polymer chains. For example, the most intense peak of mono-functionalised chains in the **ePS-OSi 2** sample, with an *m/z* of 10603 u corresponds to 96 units of styrene (96 × 104.15 u) + 1 unit of DPE-OSi (440.77 u) + the counterion, Ag (107.87 u) + the sec-butyl end-group (57.12 u) + the hydrogen end-group (1.01 u). However, close inspection does indicate a trace amount of un-functionalised chains (see the insert of **Figure 1b**). The presence of small amounts of unfunctionalised chains is consistent with the NMR analysis of the same samples which revealed that the average number of DPE-OSi units was less than 1.0 in all cases.

It should be noted that the relative intensity of individual peaks is not a reliable quantitative measure of abundance, since some chains may be more or less prone to ionisation than others.[81] Nevertheless, the MALDI analysis clearly and unambiguously indicates that initiating procedure is less effective that the end-capping procedure, for control over the degree of end-functionalisation of polystyrene with DPE-OSi.

3.3. Interaction Chromatography (IC) characterisation

The MALDI analysis described above gives initial proof that the samples obtained through the two procedures are different in terms of the degree of functionalisation, even if MALDI data does not allow us to quantify, neither relatively or absolutely, the abundance of chains with different degrees of functionalisation in each sample. Recently, normal phase (NP) IC has

emerged as a useful technique for the resolution of polymers in terms of functionality and molecular weight. Thus (NP) IC was exploited in this study to complete the analysis and to provide quantitative data to augment the MALDI and NMR data. The relative amount of each species revealed in the NP IC study was estimated by deconvolution of the peaks from the UV detector (proportional to concentration), using a standard Gaussian distribution, and calculating the area under each curve. It should be remembered that it is a normal phase chromatography, with a polar column, thus the more polar species, the functionalised polystyrene in this case, elutes at longer retention times than apolar un-functionalised polystyrene. Moreover, where polymers have the same polarity (functionalised or unfunctionalised), lower molecular weight polymers elute at shorter times.

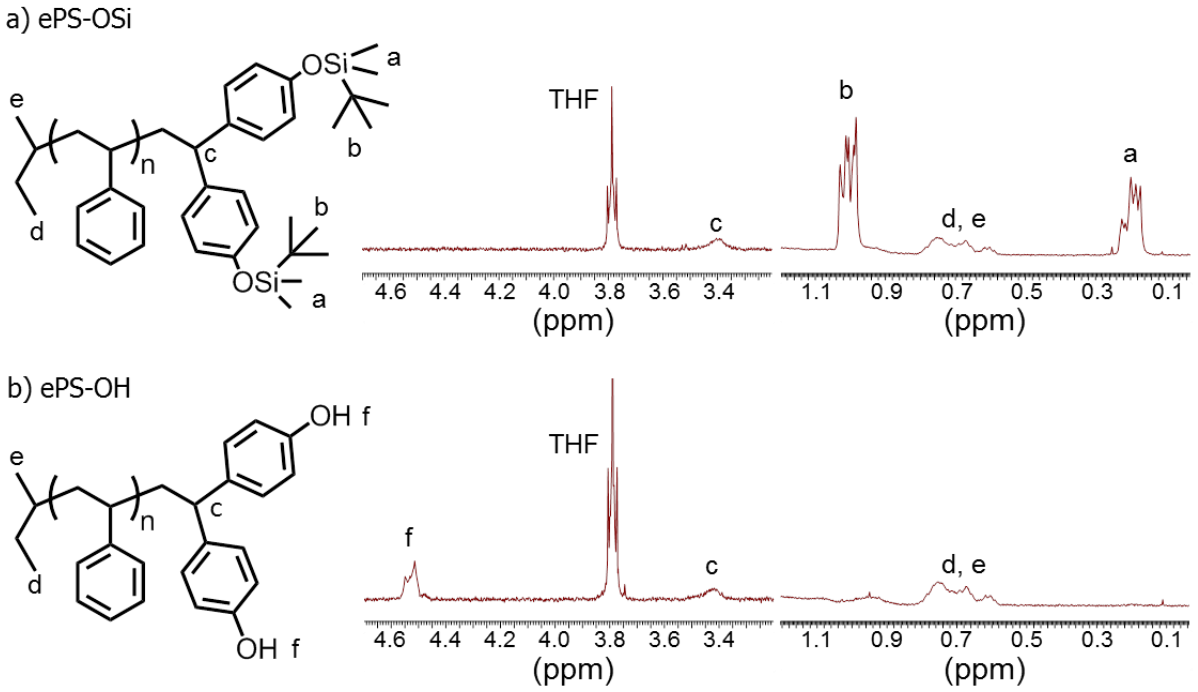


Figure 2. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra fragments of a) protected and b) deprotected end-capped polystyrene.

IC analysis was performed on the deprotected samples (iPS-OH and ePS-OH). The deprotection was achieved by acid hydrolysis, as described above. The reaction was followed by ^{1}H NMR, until the complete disappearance of the signals corresponding to the *tert*-butyldimethylsilyl protection groups at δ 0.3–0.1 ppm ($(C\underline{\mathbf{H}}_3)_2Si$) and δ 1.1 – 0.9 ppm ($(C\underline{\mathbf{H}}_3)_3C$-Si). The

appearance of a new peak at δ 4.6 – 4.4 ppm, corresponding to the phenol groups (**H**OPh), was also detected - for typical NMR data see **Figure 2**).

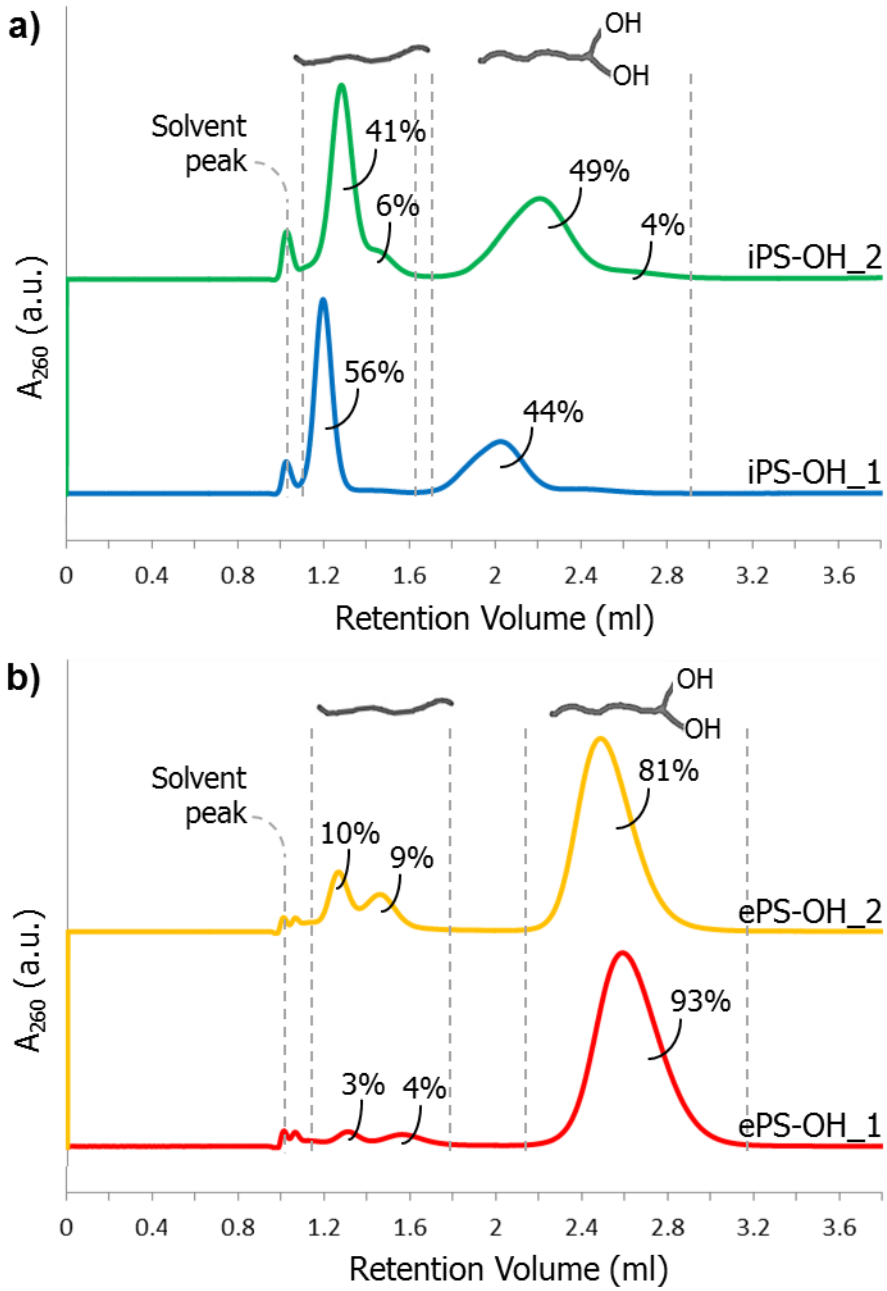


Figure 3. Isothermal IC chromatograms of a) iPS-OH 1 and iPS-OH 2; b) ePS-OH 1 and ePS-OH 2 recorded by UV detector. The relative amount (weight fraction) of each species was estimated by deconvolution of the chromatograms using a Gaussian distribution.

The NP-IC chromatograms of the deprotected samples recorded by UV detector are shown in **Figure 3**. These data are in good agreement with the MALDI spectra. Indeed, it is possible to identify two main groups of peaks in each sample, one corresponding to the un-functionalised chains, the peaks at c. 1.2 ml retention volume and the other corresponding to the mono-

functionalised chains, the broad peaks between 1.8 and 2.5 ml. The two resolved peaks that are visible at low retention volume (c. 1.3 and 1.6 ml) in both the end-capped samples (Figure 3b), and to a lesser extent in the initiated samples (Figure 3a), are due to chains which are unfunctionalised but with different molecular weights. Specifically the later eluting peak of this pair corresponds to chains with approximately double molecular weight of the earlier eluting peak. This higher molar mass peak is due to the post-polymerisation chain-coupling, arising from reaction with environmental impurities, such as oxygen or carbon dioxide, introduced at the termination stage. The same phenomenon is also evident for the peaks corresponding to mono-functionalised chains in the samples produced via the "initiation procedure" (Figure 3a), where it is possible to see a little shoulder between 2.6 and 2.8 ml, with double the molecular weight. Although MALDI data (Figure 1a) indicated that a small fraction of polymer chains produced via the "initiation procedure" were di-functionalised, i.e. possessed two DPE-OSi groups per chain, the presence of such species could not be confirmed by NP-IC. It would be expected that such chains would elute at greater retention volumes, however, even with the application of a temperature gradient with a maximum of 40 °C, nor with a more polar solvent (Isooctane: THF 50: 50), were further peaks evident. NP-IC also allows the abundance of unfunctionalised and monofunctionalised chains in each sample to be quantified, which indicates that the "end-capping procedure" produces chains with 81% (ePS-OH 1) and 93% (ePS-OH 2) functionalisation, whereas the "initiating procedure" is less effective, indicating about almost equal amounts of mono-functionalisation and unfunctionalised chains and an undetected quantity of di-functionalised chains.

When considering all of the analytical data combined, a reasonably clear picture emerges about the relative effectiveness of the two different functionalisation approaches. The NMR analysis only gives information about the average number of DPE-OSi units per chain but still indicated that the "end-capping" approach produced a consistently higher degree of functionalisation. On the other hand, MALDI demonstrated the existence of different species of functionalised

polystyrene in the samples i.e. polystyrene chains with different numbers of DPE-OSi units. For polymer chains produced via the "initiating procedure", MALDI revealed the desired mono-functionalised polymer, together with un-functionalised chains, and small peaks corresponding to di-functionalised chains. However, for chains produced via the "end-capping procedure" MALDI indicated predominantly peaks corresponding to the desired mono-functionalised chains with very small peaks corresponding to unfunctionalised chains. The relative abundance of each species cannot be accurately quantified by MALDI. Finally, the IC analysis was qualitatively in agreement with the MALDI data but also allowed us to quantify the relative abundance of each species identified. Thus the IC analysis indicated that "initiating procedure" resulted in almost equal quantities of mono- and unfunctionalised chains.

There are some discrepancies in the data – which are most evident for the sample produced via the "initiating procedure". For example the NMR analysis of **iPS-OSi 1** indicates that the resulting chains possess an average of 0.68 DPE units whereas the IC analysis of the same polymer suggests that less than 50% of the chains are functionalised. However, MALDI clearly indicates the presence of a third distribution of chains with two DPE-OSi units. The abundance of these difunctionalised chains cannot be quantified by MALDI although their prevalence looks to be low compared to the other species. Their presence was not detected at all by NP-IC, probably due to a much stronger retention which resulted in much longer retention times and possibly very shallow/broad (undetectable) peaks. If one was to assume as little as 5% of chains were difunctionalised then the discrepancies between NMR and NP IC are significantly diminished.

However, despite the discrepancies the overall picture is clear. The effectiveness of the "initiation procedure" is compromised by the dependence upon controlling the stoichiometry of the reaction between BuLi and the DPE-OSi and the fate of the DPE-OSi which can act as a comonomer. The result is a varying extent of functionalisation and a degree of functionalisation which varies from chain to chain. On the other hand, the "end-capping procedure" is far more

effective, in so much that difuntionalisation with DPE-OSi is not possible but careful control of impurities is required to ensure a high degree of end-capping and up to 93% end-capping was achieved in this work. In conclusion, it is clear that although both approaches can be used effectively, there is certainly scope for improvement.

3.4. Mikto-arm stars

Since, according to the data discussed above, the "end-capped" polymers showed the highest level of mono-functionalisation and no evidence of chains containing more than a single DPE-OH, **ePS-OH 1**, with 93% end-functionalisation according to NP-IC, was used as macromonomer for the synthesis of asymmetric three-arm mikto stars, in which the "short" arm is DPE-OH mono-functionalised polystyrene, while the "long" arms are brominated polybutadiene of 40,000 g mol^{-1} (PB40-Br). This experiment was carried out for two reasons, firstly to demonstrate one of the potential applications of well-defined end-functionalised polymers – macromonomers – but also to supplement the characterisation data above. Thus assuming that the NP-IC data is correct, we would expect to see all of the DPE-OH end-functionalised polymer react and this should be evident using by SEC analysis. The arms were coupled together by a Williamson coupling reaction, after the deprotection of the OH groups of the polystyrene macromonomer by acid hydrolysis, as described above. Following the deprotection reaction, the Williamson coupling was carried out with the "long" arms (PB40-Br) in the presence of Cs_2CO_3. A slight excess (mole ratio long arm: short arm of 2.5: 1) of the long arm was used in an attempt to drive the reaction to high degrees of coupling, as previously demonstrated.[23, 24, 43] The extent of coupling was followed by periodic SEC analysis of small samples. **Figure 4** compares the chromatograms of the polymer mixture at the beginning of the reaction and at the end.

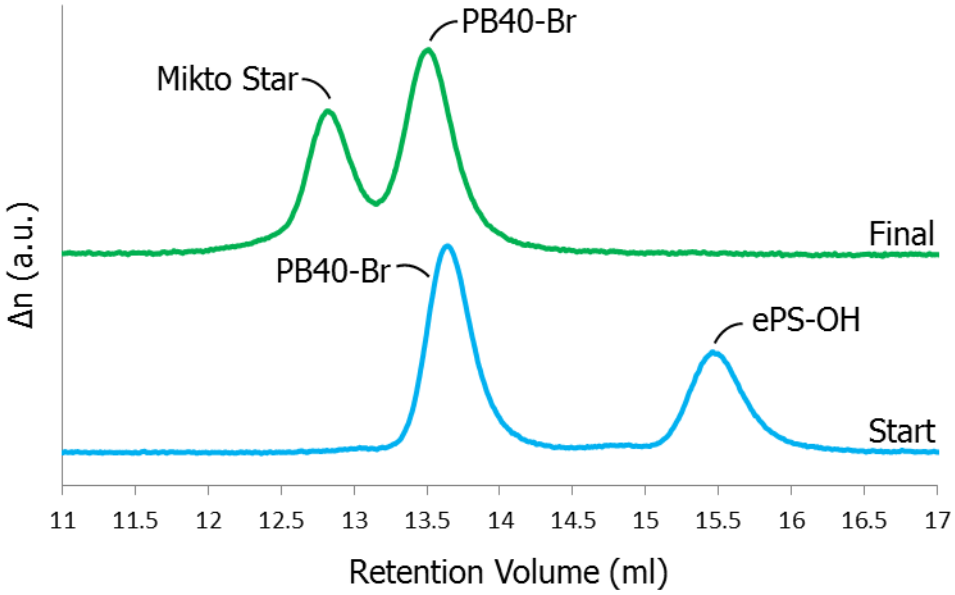


Figure 4. SEC (RI detector) chromatograms of mikto-arm stars polymer synthesised by Williamson coupling reaction between 'short' arm ePS-OH_1 and 'long' arm PB40-Br. Samples were collected for analysis at the beginning and after 27 h.

Table 2. Molar mass and dispersity data for starting materials and mikto-arm star produced via Williamson coupling of PB40-Br and ePS-OH 1.

Data	**ePS-OH 1**	**PB40-Br**	**Target**	**Mikto Star**	**Residual PB40-Br**
M_n [g mol^{-1}]	12,500	40,300	93,100	97,900	42,100
M_w [g mol^{-1}]	13,000	41,600	-	104,700	44,400
Đ	1.04	1.03	-	1.07	1.05

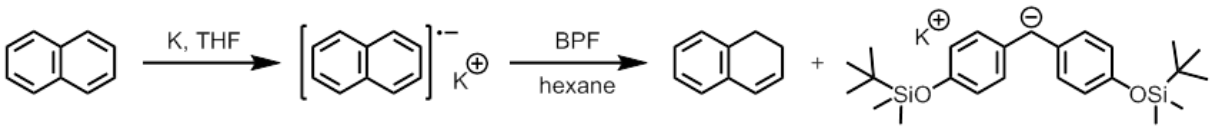
It is clear from the SEC chromatograms in **Figure 4** and molar mass data presented in **Table 2** that in most respects this demonstration coupling reaction was a success. The reaction mixture at the start of the reaction had two peaks at 13.7 ml and 15.5 ml for the PB40-Br and ePS-OH respectively. The final product had a bimodal distribution comprising a new peak at c. 12.8 ml (M_n 97,900 gmol^{-1}) which can be attributed to the desired mikto-arm star and a second peak at 13.5 ml (M_n 42,100 gmol^{-1}, M_w 44,400 gmol^{-1}). This second peak is shifted to slightly lower retention volume and has a slightly higher molecular weight than PB40-Br suggesting that it represents predominantly unreacted PB40-Br and a small quantity of partial coupled product – i.e. a single chain of PB40-Br coupled to ePS-OH. However, of prime significance to the current

study is the complete absence of any unreacted 'short' arm (ePS-OH) at 15.5 ml, evidence that the polystyrene macromonomers were almost quantitatively end-capped with DPE-OSi.

3.5. Polystyrene initiated by BPFK

Although the end-capping approach to end-functionalisation of polystyrene with DPE-OSi proved to be the better of the two options, it is not perfect. Even if levels of end-capping can exceed 90%, 100% functionalisation is practically impossible due to the inevitable introduction of traces of impurities. Moreover, the end-capping reaction takes up to five days to complete. With this in mind, a new approach to introduce the same bis-phenol functionality to the chain-end of polymers produced by anionic polymerisation has been conceived and is reported here. This new approach uses a functionalised initiator which overcomes the limitations of using the adduct of BuLi and DPE as an initiator – namely the need to use an exact stoichiometric equivalence of BuLi and DPE. As reported above, an excess of BuLi results in the production of unfunctionalised chains and an excess of DPE results in chains with more than one functional DPE moiety per chain, since DPE can copolymerise. The proposed solution is to use a functional initiator based on BPF – or a functional derivative of diphenylmethyl potassium, which has been widely used for the anionic ring opening polymerisation of ethylene oxide.[1, 80] The advantage of this approach is that the BPF is cheap and readily available, the resulting initiator carries the two required protected phenol groups but is an initiator in its own right, so does not need to be produced in-situ, avoiding the issues of stoichiometry (Scheme 1c). Moreover, whilst DPE-OSi is also a monomer, the protected BPFK cannot copolymerise so it should be impossible to produce polymer chains with more than one functionalised diphenyl moiety. This approach should allow the production of polymers in which each and every chain has one and only one bisphenol functionality.

Thus the polymerisation of styrene with 1,1-bis(4-t-butyldimethylsiloxyphenyl)methyl potassium (BPFK) as initiator, was performed in benzene under high vacuum conditions,



Scheme 2. Synthesis of BPFK

according to the standard procedure for anionic polymerisation. However, this diphenyl methane derivative required a previous protection of the phenol groups, followed by the synthesis of the potassium salt, as described above (**Scheme 2**).

To determine the concentration of active initiator, a polymerisation of styrene in benzene was carried out using BPFK, and from the resulting molecular weight, a value of 0.14 M was calculated (see Supporting Information). Using this concentration, the synthesis of polystyrene,

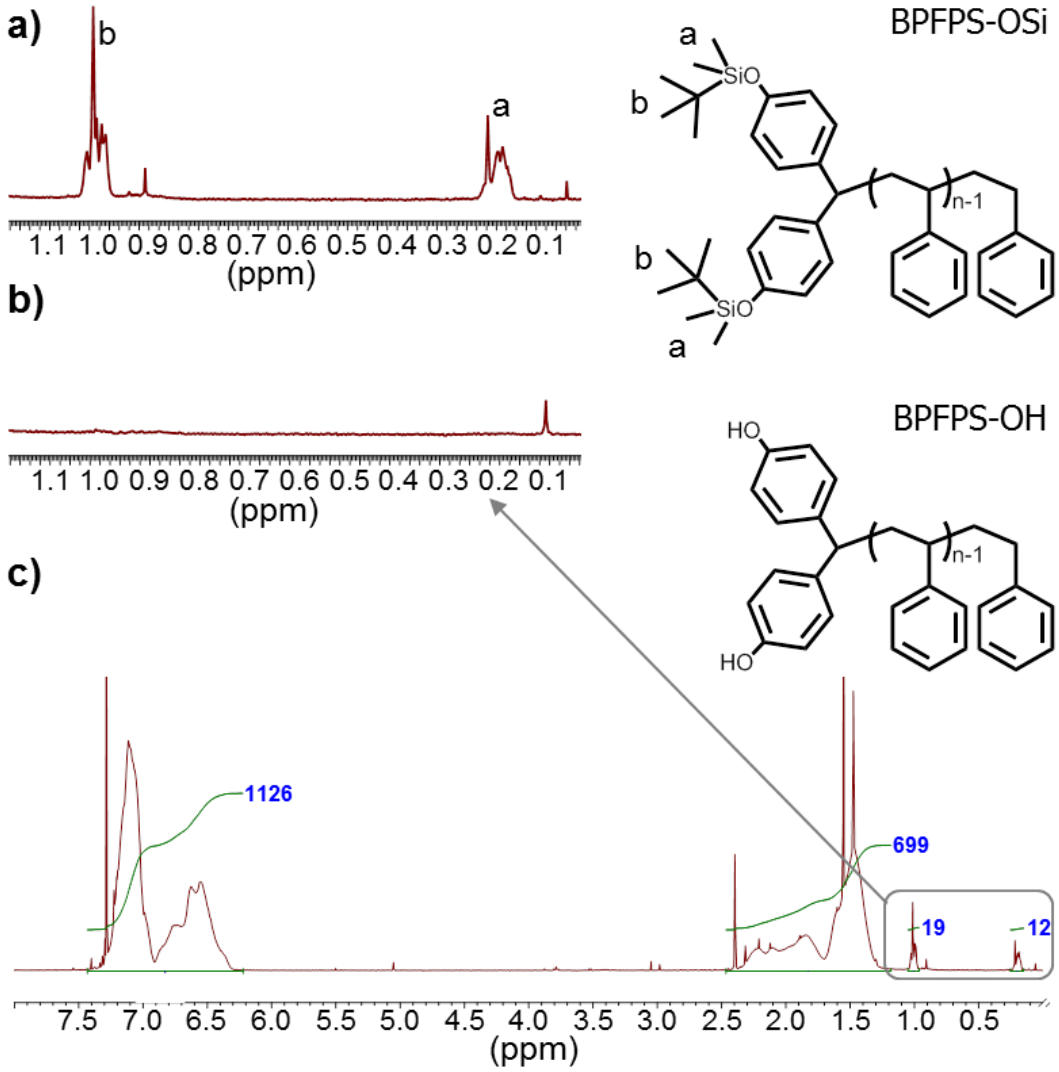


Figure 5. a) TBDMS peaks in the spectra of BPFK initiated polystyrene before the deprotection (BPFPS-OSi); b) TBDMS peak region in the spectra of BPFK initiated polystyrene after the deprotection (BPFPS-OH) c) ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of BPFK initiated polystyrene before the deprotection.

with a target molar mass of 10,000 g mol^{-1} was carried out, followed by characterisation of the resulting polymer. The SEC analysis gave M_n 15,800 g mol^{-1} and Đ 1.12. In the ^{1}H NMR spectrum (**Figure 5**), the peaks of the *tert*-butyldimethylsilyl protection groups at δ 0.3–0.1 ppm ((C**H**$_3$)$_2$Si) and δ 1.1 – 0.9 ppm ((C**H**$_3$)$_3$C-Si) are well visible, proving the functionalisation of the chains. After deprotection, the signals corresponding to the *tert*-butyldimethylsilyl protective groups at δ 0.3–0.1 ppm ((C**H**$_3$)$_2$Si) and δ 1.1 – 0.9 ppm ((C**H**$_3$)$_3$C-Si) disappear.

Despite a reasonable control over the molecular weight, the dispersity was a little broader than analogous polymers prepared using alkyl lithium initiators (usually Đ < 1.1), in line with what has been previously discussed and reported in literature as regards the DPMK initiator.[80] However, these results, in terms of dispersity, are much better than the results obtained when using (unfunctionalised) DPMK initiator for the polymerisation of styrene in benzene (in-house attempt gave a Đ > 1.3). For further dispersity data obtained using BPFK, see the polymerisation carried out to calculate the concentration of BPFK in Supporting Information). The lower dispersity of polystyrene initiated with BPFK in benzene compared to initiation with DPMK arises for two reasons. Firstly DPMK is not very soluble in benzene and the DPMK initially precipitates upon addition to benzene, then following initiation the precipitate re-dissolves at the onset of chain growth. Secondly, the electron-donating effect of the (protected) OH groups on the phenyls makes the BPF anion more nucleophilic.

NP IC analysis of the BPFK initiated polystyrene, before and after the deprotection, was carried out using a RALS detector. The use of RALS coupled with a refractive index detector enables the calculation of both molar mass and abundance of each species and the results are shown in **Figure 6**. In the chromatogram of the sample before the deprotection (blue curve), two peaks are clearly visible: the first, eluting at ~2 ml, with a molar mass of 16,900 gmol^{-1} and comprising the majority of the total peak area (94%), is ascribable to the desired BPF-initiated polystyrene, while the second, at ~2.6 ml, with a molar mass of 28,600 gmol^{-1} comprises of only 7% of the total polymer. It is believed that the higher molar mass and later retention volume of the smaller

peak, indicates that it represents un-functionalised chains that may have been initiated by residual potassium naphthalenide radical anion (species I in Scheme 2) which may still be present in the initiator solution. The higher molecular weight is in accordance with initiation by the naphthalenide radical anion which reacts with monomers such as styrene by reversible electron transfer followed by radical coupling, leading to a dianionic initiator that grows in two directions, giving longer chains.[1]

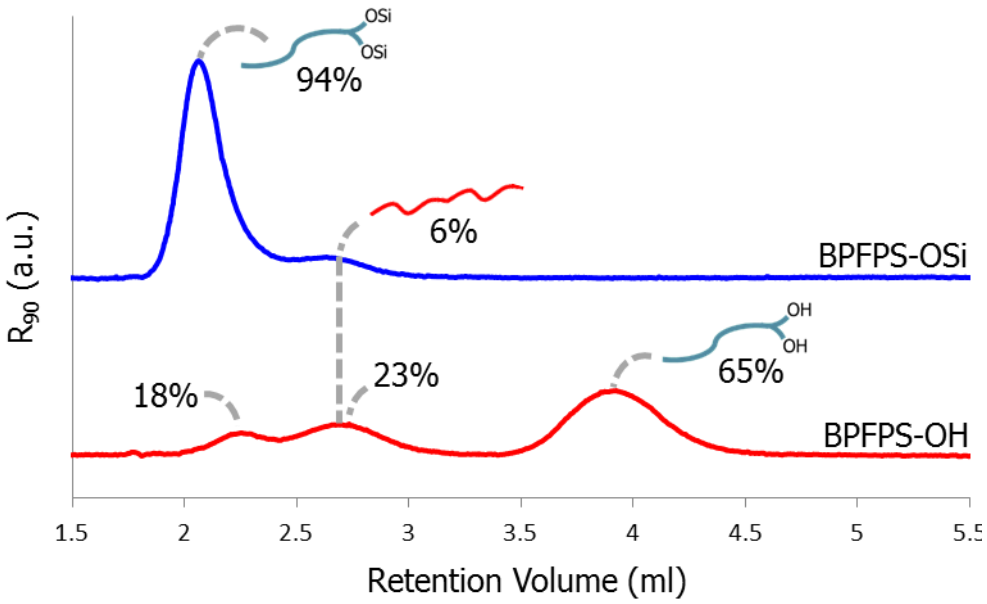


Figure 6. Isocratic IC chromatograms of BPFK initiated polystyrene, recorded by RALS detector. The blue curve is the sample before the deprotection of the phenol group, while the red curve is the sample after the deprotection of the phenol groups.

Further proof that the peak at ~2.6 ml is ascribable to un-functionalised chains is that the same peak appears to still be present after the deprotection (red curve). Following deprotection, a significant decrease in the intensity of the peak at ~2 ml can be seen, accompanied by a new peak at 3.9 ml, which can be ascribed to the deprotected polymer. This is consistent with the stronger interaction between the OH groups and the polar column, compared to the interaction between the protected OH groups and the same polar column – moreover, this has been previously reported.[79] Analysis of the area under the peak indicates that the deprotected,

functionalised polymer represents about 65% of the total mass of sample. This value is in good agreement with NMR analysis of the protected sample which indicated 68% of chains were end-functionalised. This analysis was carried out using the molar mass obtained by SEC and a comparison of the integrals of peaks representing the aromatic protons of the polystyrene backbone (7.3 – 6.3 ppm) and the peaks representing the TBDMS protecting group at 0.2 and 1.0 ppm (Figure 5c).

It is clear that the polymer sample (nominally) initiated with BPFK is not fully functionalised as intended and the IC chromatogram of the polymer, post-deprotection, contains unresolved peaks between 2 and 3 ml which are probably due to un-functionalised polymer. The estimated molar masses of these peaks are 15,800 g mol^{-1} (2.25 ml) and 18,900 g mol^{-1} (2.65 ml) respectively, which is not dissimilar to the target, end-functionalised polymer (15,800 g mol^{-1}). However, the deprotection reaction appeared to be complete according to NMR (Figure 5) so we don't believe that these peaks represent end functionalised chains which are still protected. At the present time we are still investigating the origin of these peaks and the cause of the less than quantitative end-capping when using BPFK.

Accepting that this new strategy is not yet perfected the characterisation data of the polystyrene initiated with BPFK demonstrates that this strategy presents an excellent and novel alternative to achieve selectively mono-functionalisation of polymers, albeit further optimisation is needed to overcome some issues encountered during the synthesis of the initiator and during the polymerisation step. It is a promising procedure, though, because BPFK acts exclusively as an initiator and cannot behave like a monomer, as DPE and its derivatives do. Thus, each chain initiated by BPFK carries the functional groups of the functionalised diphenyl methane moiety, thereby removing the issue of incomplete activation of DPE by sec-BuLi or incomplete end-capping, which leads to un-functionalised chains. Moreover, the possibility that a second monomer could be included into the chain during the propagating phase, resulting in a di-functionalisation, is avoided. Finally, it is a straightforward polymerisation procedure that does

not require long reaction times to reach completion, as in the case of the end-capping procedure with DPE-OSi. We believe with further (ongoing) studies this new initiator will allow the synthesis of mono-functionalised macromonomers, with (only) 2 phenol groups at one end, whilst allowing further functionalisation to be carried out at the still-living chain end on completion of propagation.

4. Conclusions

The main aim of the current work was to optimise the synthesis of polystyrene macromonomers with absolute control of the degree of functionalisation such that a single functional group could be introduced, selectively at one end of the chain, and heterogeneity of product avoided. To this end we investigated the effectiveness of the use of the monomer 1,1-bis(4-tert-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) to functionalise polystyrene via two strategies: the end-capping procedure and the initiating procedure. The combined characterisation through NMR, SEC, MALDI ToF and IC has allowed us to compare the two procedures and to better understand the outcome in terms of number of functional DPE-OSi units per chain. MALDI and IC data proved particularly useful in showing that the initiating procedure gave (only) approximatively 50% of a mono-functionalised product, along with both un-functionalised and di-functionalised product. In contrast, the end-capping procedure proved much more successful with up to 93% end-capping and no difunctionalised product.

Even if the end-capping procedure proved to give better results both procedures showed intrinsic limitations: 100% functionalisation is practically impossible due to the inevitable introduction of traces of impurities and in the case of the initiating procedure, the need to precisely control the stoichiometry of the butyllithium and DPE-OSi resulted in a mixture of products. As a final consideration, the end-capping reaction takes up to five days to complete.

With this in mind, we developed a new approach to introduce the same bis-phenol functionality to the chain-end of polymers obtained by anionic polymerisation. By using a functional initiator

based on bisphenol F, the initiation process is simplified, avoiding the issues of stoichiometry and, in contrast to DPE-OSi, the protected BPF is not a monomer and cannot copolymerise, thus avoiding also the possibility to add more than one functionalised diphenyl moiety. However, despite the encouraging early results and potential for the use of the BPF initiator, the question in the title remains: can the problems with using diphenylethylene derivatives be solved by using Bisphenol F? At the moment it is probably too early to answer with a definitive "yes". A more suitable answer to this question is probably "not yet" and more work is ongoing to perfect this new strategy. Finally, embarking on a comprehensive characterization strategy, such as that described herein, for other common functionalisation reactions which also claim a high degree of functionalization – for example the use of ethylene oxide and chlorosilanes – might prove interesting, in order to reveal the actual degrees of functionalisation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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References

[1] H. L. Hsieh, R. P. Quirk, *Anionic polymerization: principles and practical applications*, Marcel Dekker, New York, **1996**.

[2] A. Hirao, R. Goseki, T. Ishizone, *Macromolecules* **2014**, *47*, 1883.

[3] F. Wurm, F. J. López-Villanueva, H. Frey, *Macromol. Chem. Phys.* **2008**, *209*, 675.

[4] S. Hilf, F. Wurm, A. F. M. Kilbinger, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6932.

[5] L. Z. Kong, M. Sun, H. M. Qiao, C. Y. Pan, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 454.

[6] C. He, L. W. Li, W. D. He, W. X. Jiang, C. Wu, *Macromolecules* **2011**, *44*, 6233.

[7] D. Konkolewicz, M. J. Monteiro, S. Perrier, *Macromolecules* **2011**, *44*, 7067.

[8] L. Li, C. He, W. He, C. Wu, *Macromolecules* **2011**, *44*, 8195.

[9] M. Jikei, M. Suzuki, K. Itoh, K. Matsumoto, Y. Saito, S. Kawaguchi, *Macromolecules* **2012**, *45*, 8237.

[10] L. Li, J. Zhou, C. Wu, *Macromolecules* **2012**, *45*, 9391.

[11] S. Ito, R. Goseki, T. Ishizone, A. Hirao, *Polym. Chem.* **2014**, *5*, 5523.

[12] L. Hong, S. Yang, J. He, *Eur. Polym. J.* **2015**, *65*, 171.

[13] T. Higashihara, M. Hayashi, A. Hirao, *Prog. Polym. Sci.* **2011**, *36*, 323.

[14] A. Gregory, M. H. Stenzel, *Prog. Polym. Sci.* **2012**, *37*, 38.

[15] W. Zhang, A. H. E. Müller, *Prog. Polym. Sci.* **2013**, *38*, 1121.

[16] B. V. K. J. Schmidt, M. Hetzer, H. Ritter, C. Barner-Kowollik, *Prog. Polym. Sci.* **2014**, *39*, 235.

[17] K. Matyjaszewski, N. V. Tsarevsky, *J. Am. Chem. Soc.* **2014**, *136*, 6513.

[18] Y. Zheng, S. Li, Z. Weng, C. Gao, *Chem. Soc. Rev.* **2015**, *44*, 4091.

[19] J. M. Ren, T. G. McKenzie, Q. Fu, E. H. H. Wong, J. Xu, Z. An, S. Shanmugam, T. P. Davis, C. Boyer, G. G. Qiao, *Chem. Rev.* **2016**, *116*, 6743.

[20] A. Thomas, K. Niederer, F. Wurm, H. Frey, *Polym. Chem.* **2014**, *5*, 899.

[21] X. Cao, C. Zhang, S. Wu, Z. An, *Polym. Chem.* **2014**, *5*, 4277.

[22] Y. C. Teo, Y. Xia, *Macromolecules* **2015**, *48*, 5656.

[23] L. R. Hutchings, S. J. Roberts-Bleming, *Macromolecules* **2006**, *39*, 2144.

[24] S. M. Kimani, L. R. Hutchings, *Macromol. Rapid Commun.* **2008**, *29*, 633.

[25] H. Ma, Q. Wang, W. Sang, L. Han, P. Liu, H. Sheng, Y. Wang, Y. Li, *Macromol. Rapid Commun.* **2016**, *37*, 168.

[26] L. R. Hutchings, J. M. Dodds, S. J. Roberts-Bleming, *Macromolecules* **2005**, *38*, 5970.

[27] J. M. Dodds, E. De Luca, L. R. Hutchings, N. Clarke, *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 2762.

[28] N. Clarke, E. D. Luca, J. M. Dodds, S. M. Kimani, L. R. Hutchings, *Eur. Polym. J.* **2008**, *44*, 665.

[29] J. M. Dodds, L. R. Hutchings, *Macromol. Symp.* **2010**, *291-292*, 26.

[30] L. R. Hutchings, J. M. Dodds, S. J. Roberts-Bleming, *Macromol. Symp.* **2006**, *240*, 56.

[31] L. R. Hutchings, J. M. Dodds, D. Rees, S. M. Kimani, J. J. Wu, E. Smith, *Macromolecules* **2009**, *42*, 8675.

[32] L. R. Hutchings, S. Agostini, I. W. Hamley, D. Hermida-Merino, *Macromolecules* **2015**, *48*, 8806.

[33] F. J. López-Villanueva, F. Wurm, A. F. M. Kilbinger, H. Frey, *Macromol. Rapid Commun.* **2007**, *28*, 704.

[34] R. P. Quirk, J. Yin, *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2349.

[35] R. P. Quirk, J. Yin, L. J. Fetters, *Macromolecules* **1989**, *22*, 85.

[36] C. Tonhauser, H. Frey, *Macromol. Rapid Commun.* **2010**, *31*, 1938.

[37] R. P. Quirk, J. J. Ma, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031.

[38] K. Ueda, A. Hirao, S. Nakahama, *Macromolecules* **1990**, *23*, 939.

[39] R. P. Quirk, Y. Lee, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 145.

[40] M. Ganß, B. K. Satapathy, M. Thunga, U. Staudinger, R. Weidisch, D. Jehnichen, J. Hempel, M. Rettenmayr, A. Garcia-Marcos, H. H. Goertz, *Eur. Polym. J.* **2009**, *45*, 2549.

[41] R. P. Quirk, J. Kim, *Macromolecules* **1991**, *24*, 4515.

[42] C. L. Elkins, K. Viswanathan, T. E. Long, *Macromolecules* **2006**, *39*, 3132.

[43] S. Agostini, L. R. Hutchings, *Eur. Polym. J.* **2013**, *49*, 2769.

[44] J. Hwang, M. D. Foster, R. P. Quirk, *Polymer* **2004**, *45*, 873.

[45] M. Gauthier, L. Tichagwa, J. S. Downey, S. Gao, *Macromolecules* **1996**, *29*, 519.

[46] A. Búcsi, J. Forcada, S. Gibanel, V. Héroguez, M. Fontanille, Y. Gnanou, *Macromolecules* **1998**, *31*, 2087.

[47] D. N. Schulz, A. F. Halasa, *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2401.

[48] S. Pispas, N. Hadjichristidis, *Macromolecules* **1994**, *27*, 1891.

[49] R. P. Quirk, T. Yoo, Y. Lee, J. Kim, B. Lee, *Biopolymers - PVA Hydrogels, Anionic Polymerisation Nanocomposites*, Springer Berlin Heidelberg, Berlin, Heidelberg **2000**, p. 67.

[50] Zhang, H.; He, J.; Zhang, C.; Ju, Z.; Li, J.; Yang, Y., *Macromolecules* **2012,** *45* (2), 828-841.

[51] L. R. Hutchings, P. P. Brooks, D. Parker, J. A. Mosely, S. Sevinc, *Macromolecules* **2015**, *48*, 610.

[52] R. P. Quirk, C. Garcés, S. Collins, D. Dabney, C. Wesdemiotis, V. Dudipala, *Polymer* **2012**, *53*, 2162.

[53] X. Fan, Q. Zhou, C. Xia, W. Cristofoli, J. Mays, R. Advincula, *Langmuir* **2002**, *18*, 4511.

[54] R. P. Quirk, R. T. Mathers, T. Cregger, M. D. Foster, *Macromolecules* **2002**, *35*, 9964.

[55] L. Chen, M. A. Winnik, E. T. B. Al-Takrity, A. D. Jenkins, D. R. M. Walton, *Die Makromolekulare Chemie* **1987**, *188*, 2621.

[56] R. P. Quirk, S. Perry, F. Mendicuti, W. L. Mattice, *Macromolecules* **1988**, *21*, 2294.

[57] R. P. Quirk, L. E. Schock, *Macromolecules* **1991**, *24*, 1237.

[58] Z. Hruska, B. Vuillemin, G. Riess, A. Katz, M. A. Winnik, *Die Makromolekulare Chemie* **1992**, *193*, 1987.

[59] F. Caldérara, Z. Hruska, G. Hurtrez, T. Nugay, G. Riess, M. A. Winnik, *Die Makromolekulare Chemie* **1993**, *194*, 1411.

[60] B. Moon, T. R. Hoye, C. W. Macosko, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2177.

[61] H. K. Jeon, C. W. Macosko, B. Moon, T. R. Hoye, Z. Yin, *Macromolecules* **2004**, *37*, 2563.

[62] R. P. Quirk, L. F. Zhu, *Br. Polym. J.* **1990**, *23*, 47.

[63] R. P. Quirk, T. Lynch, *Macromolecules* **1993**, *26*, 1206.

[64] S. Pispas, N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3791.

[65] L. Wu, Y. Wang, Y. Wang, K. Shen, Y. Li, *Polymer* **2013**, *54*, 2958.

[66] A. Hirao, Y. Karasawa, T. Higashihara, Y. Zhao, K. Sugiyama, *Des. Monomers Polym.* **2004**, *7*, 647.

[67] M. Hayashi, *Macromol. Symp.* **2004**, *215*, 29.

[68] G. J. Summers, R. P. Quirk, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1233.

[69] R. P. Quirk, L.F. Zhu, *Die Makromolekulare Chemie* **1989**, *190*, 487.

[70] R. P. Quirk, Y. Wang, *Polym. Int.* **1993**, *31*, 51.

[71] P. P. Brooks, A. Natalello, J. N. Hall, E. A. L. Eccles, S. M. Kimani, K. Bley, L. R. Hutchings, *Macromol. Symp.* **2013**, *323*, 42.

[72] A. Natalello, J. N. Hall, E. A. L. Eccles, S. M. Kimani, L. R. Hutchings, *Macromol. Rapid Commun.* **2011**, *32*, 233.

[73] P. Liu, H. Ma, W. Huang, H. Shen, L. Wu, Y. Li, Y. Wang, *Polymer* **2016**, *97*, 167.

[74] P. Liu, H. Ma, W. Huang, L. Han, X. Hao, H. Shen, Y. Bai, Y. Li, *Polym. Chem.* **2017**, *8*, 1778.

[75] A. Natalello, M. Werre, A. Alkan, H. Frey, *Macromolecules* **2013**, *46*, 8467.

[76] Ma, H.; Han, L.; Li, Y., *Macromol. Chem. Phys.* **2017,** *218* (12).

[77] L. R. Hutchings, *Macromolecules* **2012**, *45*, 5621.

[78] W. Lee, D. Cho, B. O. Chun, T. Chang, M. Ree, *J. Chromatogr. A* **2001**, *910*, 51.

[79] L. R. Hutchings, S. Agostini, M. E. Oti, J. Keth, *Eur. Polym. J.* **2015**, *73*, 105.

[80] N. Ekizoglou, N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1198.

[81] L. Li, *MALDI Mass Spectrometry for Synthetic Polymer Analysis*, John Wiley & Sons, New York **2009**.

Anionic polymerisation is still the gold standard for the synthesis of well-defined polymers but the controlled functionalisation of such polymers remains a challenge. The use of diphenylethylene derivatives is a well-used approach but this paper reveals limitations in the control achievable using this strategy and reports a novel approach using a new initiator based on bisphenol F.

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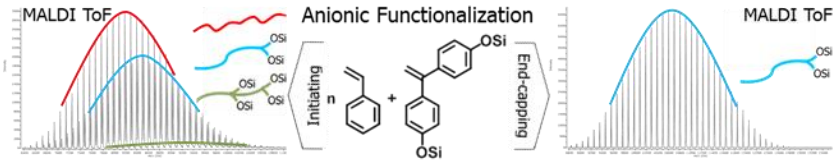
End-functionalised chains via anionic polymerisation: can the problems with using diphenylethylene derivatives be solved by using Bisphenol F?



Supporting Information

Average number of DPE-OSi monomers per chain calculation

The average number of DPE-OSi monomer per chain was calculated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum for one such polymer (iPS-OSi 1) is shown in **Figure S1**. The average number was determined from the ^{1}H NMR spectrum by comparing the integrals of the aromatic protons to the methyl protons of the silyl groups. The broad signals between 6.2 and 7.4 ppm represents 8 aromatic protons per DPE-OSi monomer and 5 aromatic protons per styrene monomer, while the signal between 0.1 and 0.3 ppm can be ascribed to 12 equivalent Si-(C**H**$_3$)$_2$ protons per DPE-OSi unit.

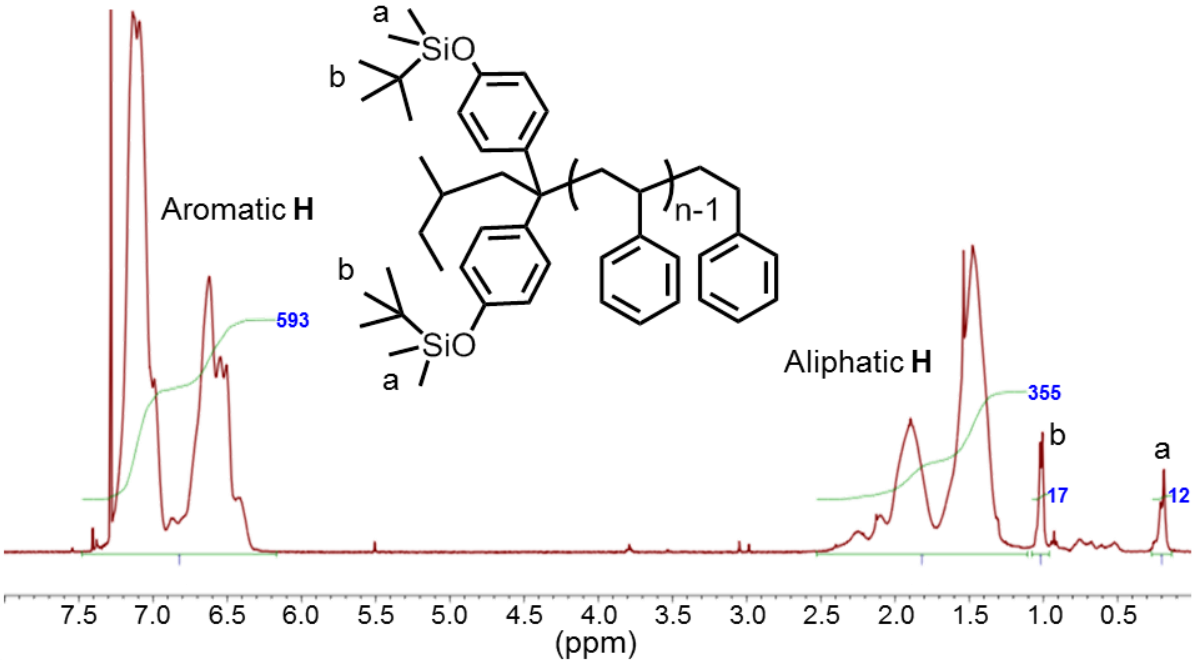


Figure S1. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of iPS-OSi_1 synthesised by the initiating procedure.

Setting a value of 12 for the integral of the silyl group protons, the following equations can be solved to give the chain composition:

$$(8 + 5x = 593) \qquad (1)$$

where x is the relative number of styrene unit. The Equation gives as a result a DPE-OSi: styrene ratio of 117:1. According to the M_n value calculated through SEC analysis, there should be an

average of 77 styrene monomers in each chain (M_n/ styrene molecular weight). Thus this means an average of 0.68 DPE-OSi monomers per chain (number of styrene monomers in each chain/ number of styrene monomers per each DPE-OSi monomer).

BPFK initiator concentration determination through anionic polymerisation of polystyrene

A polymerisation of styrene in benzene was performed, in order to determine the concentration of the initiator BPFK. Benzene (~ 50 ml) and styrene (2.22 g, 21 mmol) were distilled under vacuum into the reaction flask, and then BPFK (500 μl) was injected through a septum. The reaction was stirred at room temperature for 3 hours before being terminated with nitrogen-sparged methanol. The polymer was precipitated into methanol, redissolved in THF, precipitated again into methanol, recovered by filtration and then dried under vacuum. Yield 97%. M_n 32,800 g mol^{-1}, M_w 36,600 g mol^{-1}, Đ 1.12. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.4 – 6.2 (Ar **H**), 2.4 – 1.2 (aliphatic **H**), 1.1 – 0.9 (18H, (C**H**$_3$)$_3$C-Si), 0.3 – 0.1 (12H, (C**H**$_3$)$_2$Si).
Knowing the volume of initiator injected, it was possible to calculate the concentration of the initiator by the following Equation:

$$M_n = \frac{M_m}{I} \qquad (2)$$

where M_m is the mass of monomer in grams used and I is the number of moles of initiator.
These data give a value of 0.14 M.

Supporting Information

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