Synthesis and Temperature Gradient Interaction Chromatography of Model Asymmetric Star Polymers by the "Macromonomer" Approach

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Abstract. We describe herein the synthesis and characterisation of a series of asymmetric three arm polystyrene stars via the "macromonomer" approach. The stars have been designed as model polymers to probe branched polymer dynamics and in particular to establish the chain-length of side-arm which precipitates a change in the rheological properties of the resulting polymers from "linear-like" to "star-like". Thus, a homologous series of three arm stars have been prepared in which the molar mass of two (long) arms are fixed at 90 000 $gmol^{-1}$ and the molar mass of the remaining (short) arm is varied from below the entanglement molecular weight (M_e) to above M_e. The arms were prepared by living anionic polymerisation, resulting in well-defined chain lengths with narrow molecular weight distribution. In contrast to the usual chlorosilane coupling approach, the macromonomer approach involves the introduction of reactive chain-end functionalities on each of the arms, either through the use of a functionalised (protected) initiator or a functional end-capping agent, which allows the stars to be constructed by a simple condensation coupling reaction. In this study we will compare the relative efficiency of a Williamson and 'click' coupling reaction in producing the stars. Most significantly, although this approach maybe a little more time-consuming than the more common silane coupling reaction, in the present study the "long" arm may be produced in sufficient quantity such that all of the asymmetric stars are produced with long arms of identical molecular weight – the only remaining variable being the molecular weight of the short arm. This will allow for a far more robust interpretation of the resulting characterisation of the dynamic properties. Temperature gradient interaction chromatography was used alongside size exclusion chromatography to characterise the structural dispersity of the resulting stars and establish the degree of structural homogeneity.

Key Words: branched polymer; temperature gradient interaction chromatography (TGIC); anionic polymerization; macromonomer.

Introduction.

For many decades the synthesis and characterisation of model branched polymers has contributed hugely to the understanding of the relationship between polymer architecture and the physical properties of branched polymers. Star polymers with varying numbers of arms have been widely produced and studied [1-8] and branched polymers of increasing complexity and diverse structures have evolved. These include H-shaped polymers [9-15], comb-shaped polymers [16-28] and more recently dendritically branched polymers [29-48]. Fundamental to all these studies is the ability of the synthetic polymer chemist to control structural homogeneity and produce branched polymers with narrow dispersity both in terms of molecular weight and architecture. Central to achieving that aim has been the use of living anionic polymerisation, a technique first establish by Szwarc in the 1950's [49]. The term "living" was coined to describe a mechanism which proceeds in the absence of inherent

termination reactions and, provided initiation is rapid with respect to propagation and the presence of impurities is avoided, anionic polymerisation is capable of producing polymers with predictable molecular weights and very narrow dispersity – molecular weight distributions with a dispersity index of 1.05 or less are easily achievable. Although many strategies have been developed to couple the ends of living polymer chains to produce branched polymers, the combination of living anionic polymerisation and multifunctional chlorosilane coupling agents has proved the most successful in producing star branched polymers with a high degree of structural homogeneity and stars with 3 to 128 arms produced by this method have been reported [1, 2, 50-52]. The three arm star polymers required for the current study are effectively a series of identical linear polymers with a single branch emanating from the centre of the linear chain. The 'perfect' series of stars would be identical with the exception of the molecular weight of the single branch i.e. the molar mass of the linear backbone and the position of the branch would be identical in each case. One might describe these asymmetric star polymers as 'mikto' star polymers, in so much that the nature of the arms varies in respect of molecular weight. Whilst it would have been possible to prepare such a series of stars by the more traditional approach for the synthesis of mikto stars first reported by Hadjichristidis [53], namely by the arm-first methodology and a chlorosilane coupling agent such a methyltrichlorosilane - a method exploited previously by us for the synthesis of isotopic mikto arms stars [2] and DendriMacs [38] - it would not be possible to produce a series of stars in which the effective chain length of the linear backbone polymer was *identical* in every case. Even the most careful use of anionic polymerisation results in some batch to batch variation in molecular weight. The 'macromonomer' approach, first reported by our group for the synthesis of complex dendritically branched polymers such as DendriMacs [33,38], HyperMacs [54-56] and more recently HyperBlocks [57], has become widely adopted as a useful route to make a variety of complex dendritic branched architectures with polymer segments between branch points [58-67]. In essence the 'macromonomer' approach involves the synthesis of the linear segments of a branched polymer by a living/controlled polymerisation mechanism such that the linear segments contain chain-end functionalities which allow the subsequent construction of branched polymers via coupling reactions between macromonomers. In our previous work we have produced AB_2 macromonomers in which the A functionality (introduced via a protected, functionalised initiator is able to react with the two B functionalities (introduced by a difunctional end-capping agent) to form dendritically branched architectures. One key advantage of this approach is that the coupling reactions need not be carried out under the rigorously inert conditions required for anionic polymerisation. We believe the 'macromonomer' approach described herein is the only method capable of producing such a set of stars with the desired consistent degree of control over the molecular structure. The arms were synthesised by living anionic polymerisation and the star polymers were prepared in a separate coupling reaction, either by a Williamson or 'click' coupling reaction and the resulting stars purified by fractionation to obtain well-defined, structurally homogeneous star branched polymers. The efficiency of the two coupling methods are compared and the 'purified' star polymers characterised by both SEC and Temperature Gradient Interaction Chromatography (TGIC). Whilst SEC has been the characterisation method of choice for many decades, for the analysis of molecular weight and molecular weight distribution of polymers, in recent years TGIC has emerged as a technique capable of significantly enhanced resolution compared to SEC, especially in the characterisation of branched polymers [12,14, 68-71] – a subject recently reviewed in detail [72]. In the current work TGIC revealed low levels of heterogeneity in the purified (fractionated) stars - heterogeneity which could not be detected by SEC.

Experimental

Materials

Benzene (Aldrich, HPLC grade, ≥ 99%), styrene (Sigma-Aldrich, ≥ 99%) and dichloromethane (in-house solvent purification) were dried and degassed over calcium hydride (CaH_2) (Acros Organics, 93%) and stored under high vacuum. 3-tert-butyldimethylsiloxy-1-propyllithium in cyclohexane (InitiaLi 103, FMC Corporation), triphenylphosphine, carbon tetrabromide (99%), cesium carbonate, sodium azide (≥ 99.5%) copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), (+)-sodium L-ascorbate, 1,1,1,-tris(4-hydroxyphenyl)ethane (98+%) and N,N,N'N'-tetramethylethylenediamine (all Sigma-Aldrich) were used as received. Dimethyl formamide (DMF) (Sigma-Aldrich 99.8%) was stored over molecular sieves (Sigma-Aldrich) under inert atmosphere. Sec-Butyllithium (Sigma-Aldrich) 1.4M solution in cyclohexane, was used as received. Propargyl bromide (Sigma-Aldrich) 80 wt. % solution in toluene was used as received. Tetrahydrofuran, methanol (AR grade) and hydrochloric acid (~36 wt. %) (all Fischer Scientific) were used as received. 1,1-Bis(4-tert-butyldimethylsiloxyphenyl)ethylene (DPE) was synthesised in two steps from dihydroxybenzophenone according to the procedure of Quirk and Wang [73].

Characterisation

^{1}H-NMR spectra were measured on Varian VNMRS 700 MHz or Bruker DRX-400 MHz spectrometer using either C_6D_6, DMSO or $CDCl_3$ as solvents. Triple detection size exclusion chromatography (SEC) was used for the analysis of molar mass and molar mass distribution of the macromonomers and star–branched polymers, using a Viscotek TDA 302 with refractive index, right angle light scattering and viscosity detectors and two PLgel 5 µm mixed C columns (300 x 75 mm). Tetrahydrofuran was used as the eluent at a flow rate of 1.0 ml/min and at a temperature of 35 °C. The calibration was carried out with a single narrow distribution polystyrene standard purchased from Polymer Laboratories. A value of 0.185 mL/g (obtained from Viscotek) was used as the dn/dc of polystyrene both for the calibration and the analysis of prepared polymers. Reverse phase temperature gradient interaction chromatography (RP-TGIC) analysis was carried out using a single C18 bonded silica column (Nucleosil C18, 100Å pore 250×4.6 mm I.D., 5 µm) and a mixed solvent of CH_2Cl_2/CH_3CN (55/45 v/v) as the mobile phase. The flow rate was set to 0.25 ml/min. Polymer solution concentrations of approximately 2 mg/ml dissolved in the eluent mixture were used and the injection volume was 100 µl. The TGIC system used was a modified Viscotek TDA 302 with refractive index, viscosity, right angle and low angle light scattering detectors (Viscotek) and an external UV detector (Knauer). The temperature of the column was controlled by a Thermo Scientific thermostatically controlled circulating bath. A dn/dc of 0.213 mL/g was used for polystyrene in the mixed solvent eluent [74]. In the majority of cases where multiple SEC or TGIC datasets are presented in a single figure, the data has been imported into excel and normalised.

Polymer Synthesis

Synthesis of PS90-A Macromonomer (long arm)

PS90-OH (protected)

The polystyrene macromonomer carrying a single 'A' functionality at the chain-end was synthesised by living anionic polymerisation using standard high vacuum techniques. Benzene (500ml) and styrene (104.0g, 1.0 mol) were distilled under vacuum into a 1L

reaction flask. To the monomer solution was injected through a septum, TMEDA (0.309ml, 2.1 mmol) in a molar ratio of 2:1 with respect to the initiator before the injection of the initiator 3-*tert*-butyldimethylsiloxy-1-propyllithium (2.25 ml of a 0.47M solution in cyclohexane, 1.06 mmol). The reaction was stirred at room temperature overnight and then terminated with nitrogen-sparged methanol. The polymer was recovered by filtration following precipitation into methanol (8:1 with respect to benzene) and then dried under vacuum. Yield 95%. M_n 89 900 g mol^{-1}, M_w 92400 g mol^{-1}, PDI= 1.03. ^{1}H-NMR (C_6D_6, δ in ppm): 3.3-3.5 [C**H**$_2$OSi], 0.9-1.0 [(C**H**$_3$)$_3$C-Si], 0.0 [(C**H**$_3$)$_2$SiO].

PS90-OH In a 2L flask, the protected 'long' arm (99.0g, 1.1 mmol) was dissolved in THF (1.0L, 10% w/v solution). To the solution was added concentrated HCl (1.0 ml, 10.0 mmol) in a 10:1 molar ratio with respect to the 'long' arm. The solution was stirred under reflux at 80 °C overnight and the complete deprotection of the alcohol established by ^{1}H-NMR analysis. The deprotected polymer was precipitated into methanol, redissolved in THF, precipitated again into methanol, collected by filtration and dried under vacuum. Yield 94%. ^{1}H-NMR (C_6D_6, δ in ppm): 3.0-3.3 [C**H**$_2$OH].

PS90-Br In a 500ml flask, a sample of the PS90-OH (15.65g, 0.17 mmol) and triphenyl phosphine (PPh_3) (0.14g, 0.53mol) were azeotropically dried three times with benzene under vacuum and the dry polymer dissolved in dichloromethane (DCM) (150ml) to form a 10% w/v solution. Meanwhile, carbon tetrabromide (CBr_4) (0.22g, 0.66mol) was collected in another flask, DCM (5ml) was added and the solution was brought to atmospheric pressure with nitrogen. The CBr_4 solution was injected into the polymer solution through a septum at a temperature of 0°C maintained with a water/ice bath. The reaction was allowed to rise to room temperature and left to stir at room temperature for 24 hours. A sample was removed to confirm completion of the reaction by ^{1}H-NMR analysis before stopping the reaction. The polymer was precipitated into methanol, redissolved in THF, precipitated again into methanol, collected by filtration and dried under vacuum. Yield >98%. ^{1}H-NMR (C_6D_6, δ in ppm): 2.7-2.85[C**H**$_2$Br].

PS90-Azide. In a 250ml flask, PS90-Br (10.05g, 0.11mmol) was dissolved in 100ml of dimethylformamide (DMF) to form a 10% w/v solution and the solution heated at 50°C. To the solution was added sodium azide (0.036g, 0.55mmol) in a 1:5 molar ratio with respect to PS90-Br and the reaction mixture stirred overnight. The reaction was followed by ^{1}H-NMR and was considered complete when the signal at 2.7-2.85 corresponding to C**H**$_2$Br had completely disappeared. The azide functionalised polymer was precipitated into methanol and redissolved in THF, precipitated again, recovered by filtration and dried under vacuum. Yield 94%. ^{1}H-NMR (C_6D_6, δ in ppm): disappearance of the peak at 2.7-2.85[C**H**$_2$Br].

Synthesis of series of PSXB$_2$ Macromonomers (short arms)

Synthesis of PS10-OH$_2$ protected

Benzene (50ml) and styrene (4.98 g, 47.82 mmol) were distilled under vacuum into a 250 ml reaction flask. To the monomer solution was injected *sec*-butyllithium (1.4M in cyclohexane, 0.45 ml, 0.63 mmol) through a septum. The reaction was stirred at room temperature overnight before the addition of 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (DPE-OSi) (0.56 g, 1.27 mmol) as a solution in benzene in a molar ratio of 2:1 with respect to the initiator. A solution of purified DPE-OSi was prepared by adding the desired amount of DPE-OSi into a flask which was then sealed and evacuated. Benzene was distilled in under vacuum and removed by distillation to azeotropically dry the DPE-OSi before the DPE-OSi was redissolved in benzene. To this solution was added TMEDA in an equimolar ratio with

respect to the initiator (0.093 ml, 0.63 mmol). To the mixture was added sec-butyllilthium drop wise until a faint but persistent deep red colour was seen, thereby indicating the removal of all impurities. 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 in methanol, recovered by filtration and then dried under vacuum. Yield 98%. M_n 10 000 g mol^{-1}, M_w 10 500 g mol^{-1}, PDI 1.05. ^{1}H-NMR (C_6D_6, δ in ppm): 3.5-3.7 [**H**C(Ph)$_2$], 0.0-0.2 [(C**H**$_3$)$_2$Si], 0.6-0.8 [C**H**$_3$CH$_2$], 0.6-0.8 [CHC**H**$_3$], 0.9-1.1 [(C**H**$_3$)$_3$C-Si].

Synthesis of PS16-OH$_2$ protected was prepared according to the procedure described above Thus to a solution of benzene (50ml) and styrene (5.24g, 50.31mmol) was added *sec*-butyllithium (1.1M in cyclohexane, 0.30ml, 0.33mmol). The reaction was stirred at room temperature overnight before the addition of DPE-OSi (0.29g, 0.66mmol). Yield 98%. M_n 16 200 g mol^{-1}, M_w 16 800 g mol^{-1}, PDI 1.04. ^{1}H-NMR (C_6D_6, δ in ppm): 3.5-3.7 [**H**C(Ph)$_2$], 0.0-0.2 [(C**H**$_3$)$_2$Si], 0.6-0.8 [C**H**$_3$CH$_2$], 0.6-0.8 [CHC**H**$_3$], 0.9-1.1 [(C**H**$_3$)$_3$C-Si].

Synthesis of PS20-OH$_2$ protected was prepared according to the procedure described above Thus to a solution of benzene (50ml) and styrene (5.08g, 48.78 mmol) was added *sec*-butyllithium (1.1M in cyclohexane, 0.19 ml, 0.21 mmol). The reaction was stirred at room temperature overnight before the addition of DPE-OSi (0.19g, 0.43 mmol). Yield 98%. M_n 19 600 g mol^{-1}, M_w 20 500 g mol^{-1}, PDI 1.05. ^{1}H-NMR (C_6D_6, δ in ppm): 3.5-3.7 [**H**C(Ph)$_2$], 0.0-0.2 [(C**H**$_3$)$_2$Si], 0.6-0.8 [C**H**$_3$CH$_2$], 0.6-0.8 [CHC**H**$_3$], 0.9-1.1 [(C**H**$_3$)$_3$C-Si].

Synthesis of PS32-OH$_2$ protected was prepared according to the procedure described above Thus to a solution of benzene (50ml) and styrene (5.00 g, 48.0 mmol) was added *sec*-butyllithium (1.4M in cyclohexane, 0.11 ml, 0.15 mmol). The reaction was stirred at room temperature overnight before the addition of DPE-OSi (0.13 g, 0.30 mmol). Yield 94%. M_n 32 100 g mol^{-1}, M_w 33 700 g mol^{-1}, PDI 1.05. ^{1}H-NMR (C_6D_6, δ in ppm): 3.5-3.7 [**H**C(Ph)$_2$], 0.0-0.2 [(C**H**$_3$)$_2$Si], 0.6-0.8 [C**H**$_3$CH$_2$], 0.6-0.8 [CHC**H**$_3$], 0.9-1.1 [(C**H**$_3$)$_3$C-Si].

Synthesis of PS10-OH$_2$

Deprotection of PS10-OH$_2$ (protected) was achieved in the same way as described above for the deprotection of PS90-OH. Thus PS10-OH$_2$ (protected) (5.1g, 0.51mmol) was dissolved in THF (50 mL, 10% w/v solution). Concentrated HCl (1.02ml, 10.2mmol) was added and the reaction was stirred overnight under reflux and the complete deprotection of the alcohol established by ^{1}H-NMR analysis. The deprotected polymer was precipitated into methanol, redissolved in THF, precipitated again into methanol, collected by filtration and dried under vacuum. Yield>95%. ^{1}H-NMR (C_6D_6, δ in ppm): 0.6-0.8 [C**H**$_3$CH$_2$], 0.6-0.8 [CHC**H**$_3$], 3.5-3.9 [**H**OPh], 3.5-3.7 [**H**C(Ph)$_2$].

PS16-OH$_2$, PS20-OH$_2$ and PS32-OH$_2$ were deprotected following the same procedure described above for PS10-OH$_2$ and the products characterized by ^{1}H-NMR.

Synthesis of PS16-Alkyne$_2$

The phenolic alcohol groups were converted to alkyne functionalities to facilitate a subsequent 'click' coupling reaction. The conversion was carried out as follows. In a 50ml flask under an inert atmosphere of nitrogen, deprotected PS16-OH$_2$ (1.01g, 0.062mmol) and cesium carbonate (0.051g, 0.157mmol) were dissolved in 5ml of DMF (20% w/v solution) which had been previously dried over molecular sieves. To the solution was added propargyl bromide (0.018g, 0.15mmol). The reaction was heated with an oil bath at 60°C and stirred

overnight. The complete conversion was verified with ^{1}H-NMR analysis. The alkyne functionalized polymer was precipitated into methanol and redissolved in THF, precipitated again and dried under vacuum. Yield 94%. ^{1}H-NMR (C_6D_6, δ in ppm): 0.6-0.8 [C**H**$_3$CH$_2$], 0.6-0.8 [CHC**H**$_3$], 3.5-3.7 [C**H(**Ph)$_2$], 4.1-4.3 [C**H**$_2$C≡CH].

PS32-OH$_2$ was converted to PS32-Alkyne$_2$ according to the same procedure described above and the product characterized by ^{1}H-NMR.

Synthesis of asymmetric three-arm stars via Williamson coupling reaction

Synthesis of Star10

In a 250ml flask, under an inert atmosphere of nitrogen, PS90-Br 'long' arm (2.25g, 0.025mmol), PS10-OH$_2$ 'short arm' (0.1g, 0.01mmol) and cesium carbonate (Cs_2CO_3) (0.033g, 0.101mmol) were dissolved in 23ml of dry DMF. The reaction was heated with an oil bath at 150°C and it was stirred with a mechanical stirrer. The progress of the reaction was followed by SEC analysis and when the peak corresponding to the PS90-Br no longer decreased the reaction was stopped. The polymer was precipitated into methanol and redissolved in THF, precipitated again and dried under vacuum. Yield 98%. Star10: M_n 143300 g mol^{-1}, M_w 168300 g mol^{-1}, PDI 1.18. The crude polymer was purified by fractionation using toluene/methanol to yield pure Star10: M_n 193300 g mol^{-1}, M_w 197700 g mol^{-1}, PDI 1.02.

Synthesis of Star16

Star16 was prepared and purified according to the procedure described above for the synthesis of Star10. M_n 198800 g mol^{-1}, M_w 205100 g mol^{-1}, PDI 1.03.

Synthesis of Star20

Star20 was prepared and purified according to the procedure described above for the synthesis of Star10. M_n 202000 g mol^{-1}, M_w 208300 g mol^{-1}, PDI 1.03.

Synthesis of Star32 Star32 was prepared and purified according to the procedure described above for the synthesis of Star10. Star32: M_n 211000 g mol^{-1}, M_w 218300 g mol^{-1}, PDI 1.03.

Synthesis of asymmetric stars via azide-alkyne 'click' coupling reaction.

Synthesis of Star16 Click

In a 250ml flask under an inert atmosphere of nitrogen PS90-Azide (2.04g, 0.023mmol) and PS16-Alkyne$_2$ (0.15g, 0.009mmol) were dissolved in 20ml of DMF which was previously dried over molecular sieves to form a 10% w/v solution. The reaction was heated with an oil bath at 50°C and stirred with a mechanical stirrer. To the solution was added first sodium ascorbate (0.008g, 0.04mmol) and then the catalyst $CuSO_4 \cdot 5H_2O$ (0.005g, 0.020mmol) in few drops of water. The progress of the reaction was followed by SEC analysis and when the peak corresponding to PS90-Azide no longer decreased, the reaction was stopped. The polymer was precipitated into methanol and redissolved in THF, precipitated again and dried under vacuum. Yield 96%. Star16 Click: M_n 195800 g mol^{-1}, M_w 204300 g mol^{-1}, PDI 1.04.

Synthesis of Star32 Click

Star32 Click was prepared according to the procedure described above for the synthesis of Star16 Click. Star32 Click: M_n 153400 g mol^{-1}, M_w 17300 g mol^{-1}, PDI 1.13.

In both the case of Star16 Click and Star32 Click, the crude star polymers prepared via click coupling were combined with the crude star polymers prepared via Williamson coupling reaction for purification by fractionation.

Synthesis of symmetric three-arm star – Star90 via 'click' coupling reaction

In a 250ml flask under an inert atmosphere of nitrogen, PS90-Azide (7.05g, 0.078mmol) and propargylated B3 core (0.0098g, 0.023mmol) were dissolved in 36ml of DMF which was previously dried over molecular sieves to form a 20% w/v solution. The reaction was heated with an oil bath at 60°C and stirred with a mechanical stirrer. To the heated solution was added first sodium ascorbate (0.037g, 0.19mmol) and then the catalyst $CuSO_4 \cdot 5H_2O$ (0.022g, 0.088mmol) both in few drops of water. The progress of the reaction was followed by SEC analysis. After 19h a second aliquot of sodium ascorbate (0.022g, 0.11mmol) and then catalyst $CuSO_4 \cdot 5H_2O$ (0.015g, 0.060mmol) were added to the reaction. When the peak corresponding to the PS90 arm no longer decreased the reaction was stopped. The polymer was precipitated into methanol and redissolved in THF, precipitated again and dried under vacuum. Yield 99%. Star90: M_n 170300 g mol^{-1}, M_w 214300 g mol^{-1}, PDI 1.29. The crude polymer was purified by fractionation using toluene/methanol to yield pure Star90: M_n 279700 g mol^{-1}, M_w 289100 g mol^{-1}, PDI 1.03.

Results and Discussion

A cartoon schematic illustrating the general concept for the macromonomer approach for the synthesis of three-arm stars is illustrated in Figure 1. It can be seen that the stars are prepared by the coupling of two 'long' arms – each with a reactive functionality at one chain-end – to a 'short' arm carrying a difunctional end-group. Two different coupling strategies are described and compared, each requiring different reactive functional groups. The synthesis of the arms, the introduction of the appropriate functional groups and the coupling strategies are described below.

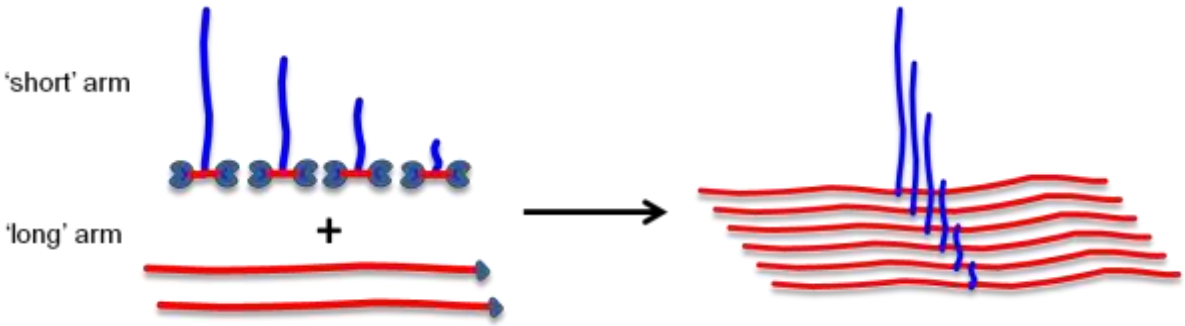


Figure 1 General schematic for the synthesis of asymmetric three-arm stars via macromonomer approach

Synthesis of arms (macromonomers)

The synthesis of the arms was carried out by living anionic polymerization but in order to allow the successful subsequent coupling of the arms to create stars, two different procedures were required for the 'long' and the 'short' arms respectively. Each type of arm used a different initiator and the synthesis of the 'short' arm required the use of a particular end-capping agent to introduce the desired chain-end functionalities. In order to produce stars in which the molar mass of the 'long' arm was identical in each case, the synthesis of the 'long' arm was carried out on a large scale (c. 100 g) to ensure the same 'long' arm could be used for all the stars created. The two coupling reactions chosen for the assembly of the stars were

the Williamson coupling reaction [54] and the copper (I)-catalyzed azide-alkyne 'click' reactions [75-77]. These coupling methods, combined with the use of living anionic polymerization (for the arms synthesis) enables the production of well-defined star polymers with an exact number of arms, narrow molar mass distributions and crucially, a series of stars in which the 'long' arm is identical in all cases. The Williamson coupling reaction has been extensively by our group for the synthesis of architecturally complex branched polymers [37,57]. The ether linkage formed in this reaction is stable and its formation requires functionalities that can be easily introduced on the polymer chain-ends during living anionic polymerization and by deprotection and conversion reactions. The 'click' coupling reaction has been used widely in polymer synthesis and has proved an efficient reaction for the synthesis of a variety of polymeric architectures and the synthesis of block copolymers, cyclic polymers, star-shaped polymers, hyperbranched and dendritic polymers has been recently reviewed [78].

Synthesis of the polystyrene 'long' arm macromonomer– PS90

As mentioned above two coupling strategies have been used for the synthesis of three-arm stars in the current work – Williamson and 'click' coupling. Each of these coupling reactions requires different chain-end functionality on the 'long' arm. In the case of a Williamson coupling reaction an alkyl halide is required and previous work [56] has shown that a bromide group is particularly effective. The experimental detail for the synthesis of PS90-Br is described above and follows a previous reported methodology [33,56]. In brief the polymerization of styrene is initiated by 3-*tert*-butyldimethylsiloxy-1-propyllithium (in the presence of TMEDA) which carries a protected primary alcohol functionality. Upon termination with methanol the primary alcohol group at the α end of the chain is deprotected by mild acid hydrolysis and the alcohol group converted into a bromide using CBr_4/PPh_3 via the Appel reaction to yield PS90-Br. Each step of this process can be verified by ^{1}H-NMR, see figure 2.

In order to carry out the coupling reaction by a 'click' mechanism it is necessary to convert the bromide functionality at the chain end of the 'long' arm into an azide functionality. This functional group modification was carried out in DMF in the presence of sodium azide (NaN_3) according to an analogous procedure carried out in our group and reported elsewhere [79]. The successful conversion of alkyl bromide to alkyl azide was confirmed by ^{1}H-NMR (figure 2) in which the complete disappearance of the peak at δ 2.7-2.85 ppm [C**H**$_2$-Br] was observed. It is not possible to observe the appearance of any new peaks representing the protons next to the azide group [C**H**$_2$-N_3] since the substitution of the bromide group with an azide group shifts the peak of the relevant protons to higher field with a chemical shift which coincides with intense peaks due to the aliphatic protons of the polystyrene backbone.

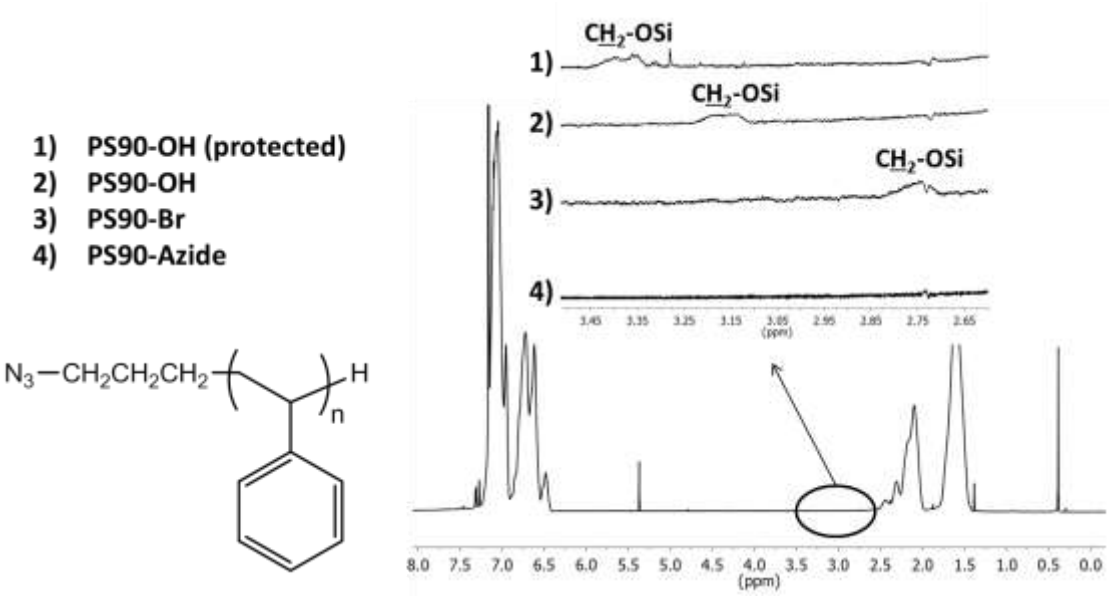


Figure 2. ^{1}H-NMR spectrum in C_6D_6 (700 MHz) of PS 'long' arm (PS90) comparing spectra collected during the conversion of the end group from PS90-OH (protected) [C**H**$_2$OSi], to PS90-OH [C**H**$_2$OH], to PS90-Br [C**H**$_2$Br] and to the final PS90-Azide [C**H**$_2$N$_3$].

Synthesis of the polystyrene 'short' arm macromonomers

The procedure for the synthesis of the 'short' arm macromonomers again exploits living anionic polymerisation of styrene. Briefly s*ec*-butyllithium was used to initiate the polymerisation which was allowed to proceed overnight to ensure the complete consumption of the monomer. To the living solution was then added the end-capping agent 1,1-*bis*(4-*tert*-butyldimethylsiloxyphenyl)ethylene (**DPE-OSi**) as reported previously [54]. This diphenylethylene derivative results in the introduction of two silyl-protected phenol functionalities which (following deprotection) are used in the subsequent coupling reactions for the synthesis of the star polymers. It was possible to add an excess of DPE-OSi with respect to the concentration of propagating chain ends because although DPE-OSi will react with the living polystyrene chain end, it is too sterically bulky to propagate and a nearly quantitative reaction with the living polymer chains end results. The use of an excess of the DPE-OSi results in practically quantitative end-capping (greater than 95%) in all cases as previously reported [33,54,57]. The resulting polymers were analysed by ^{1}H-NMR – for typical data (PS16-OH$_2$) see figure 3. The characteristic peaks corresponding to the protected phenol groups at the polymer chain ends can be observed at δ 0.0-0.2 ppm [(C**H**$_3$)$_2$Si] and at δ 0.9-1.1 ppm [(C**H**$_3$)$_3$C-Si]. In addition it is possible to observe the peak at δ 3.5-3.7 representing the proton [C**H**(Ph)$_2$] of the DPE-OSi end-capping group following termination with methanol. The silyl-protected phenol groups on the resulting polymers were subsequently deprotected by mild acid hydrolysis as described above. In the ^{1}H-NMR spectrum (figure 3) of the resulting deprotected 'short' arm macromonomer PS16-OH$_2$ it is possible to observe the disappearance of the signals corresponding to the *tert*-butyldimethylsilyl protection groups at δ 0.0-0.2 ppm [(C**H**$_3$)$_2$Si] and δ 0.9-1.1 ppm [(C**H**$_3$)$_3$C-Si]. It is also possible to observe the appearance of new peaks in the spectrum at δ 3.7-3.9 corresponding to the phenol groups [**H**OPh]. It should be noted that the signal observed at 0.4 ppm is the characteristic peak for water in deuterated benzene. Following deprotection the phenol groups can be used directly in a subsequent Williamson coupling reaction. A series of polystyrene 'short' arm macromonomers was prepared with molecular weights varying from below the entanglement molar mass (M_e), equal to M_e and above M_e –

where M_e is approximately 16,000 $gmol^{-1}$ [6]. The molar masses obtained by SEC are shown in Table1.

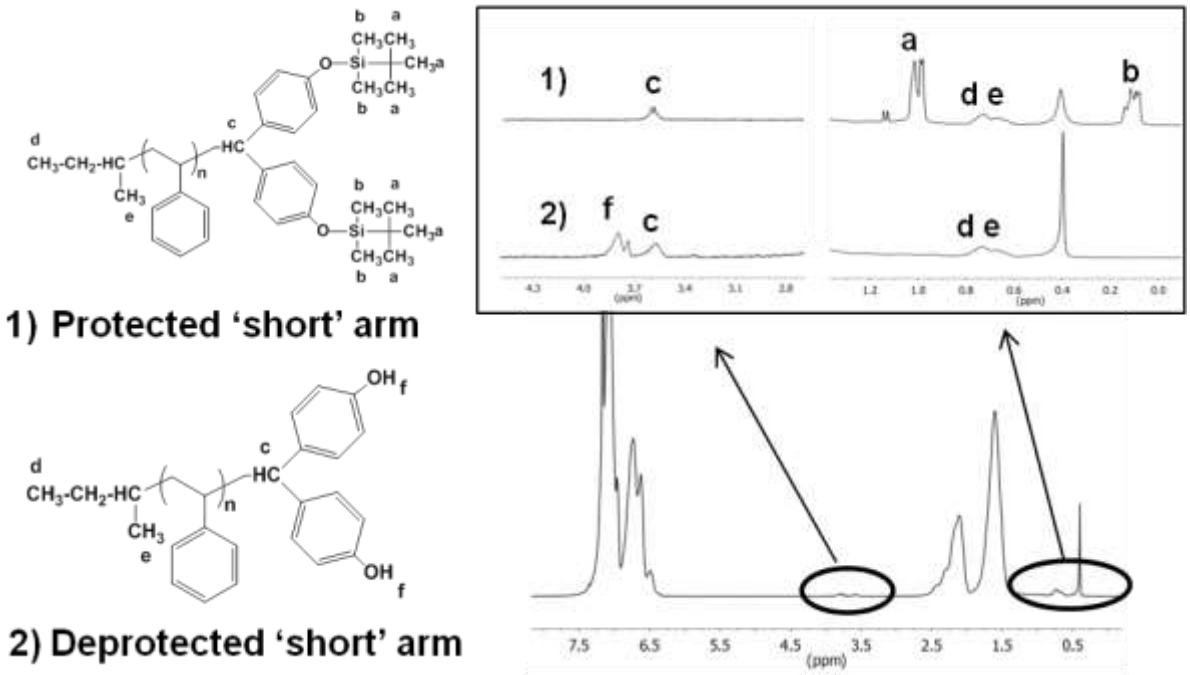


Figure 3. ^{1}H-NMR spectra (C_6D_6, 400 MHz) of protected and deprotected 'short' arm macromonomer PS16-OH_2 - a comparison of the main spectra fragments before and after deprotection. (Peak at 0.4 ppm corresponding to H_2O protons)

Table 1. Molar mass and polydispersity values of the polystyrene short arm macromonomers.

Short arm	M_n ($g{\cdot}mol^{-1}$)	M_w ($g{\cdot}mol^{-1}$)	PDI
PS10-OH₂	10000	10500	1.05
PS16-OH₂	16200	16800	1.04
PS20-OH₂	19600	20500	1.05
PS32-OH₂	32100	33700	1.05

Just as the chain-end functionality on the 'long' arm macromonomer needs to be suitably modified to enable a 'click' coupling reaction, so do the functionalities on the short arm macromonomers need to be converted - in this case the two phenol functionalities are converted into alkynes. This conversion was carried out via a Williamson coupling reaction between the phenol groups and propargyl bromide in the presence of Cs_2CO_3 in DMF. The conversion was monitored by ^{1}H-NMR (figure 4) which showed the appearance of the peaks at δ 4.1-4.3 ppm due to the presence of the new alkyne functionality [C**H**$_2$C≡CH]. This has been verified by the value of the integrals of peak *a* and *b* in figure 4 having a ratio of 4:1. The peak corresponding to the alkyne protons is not visible because they are in the region of the polystyrene backbone aliphatic protons.

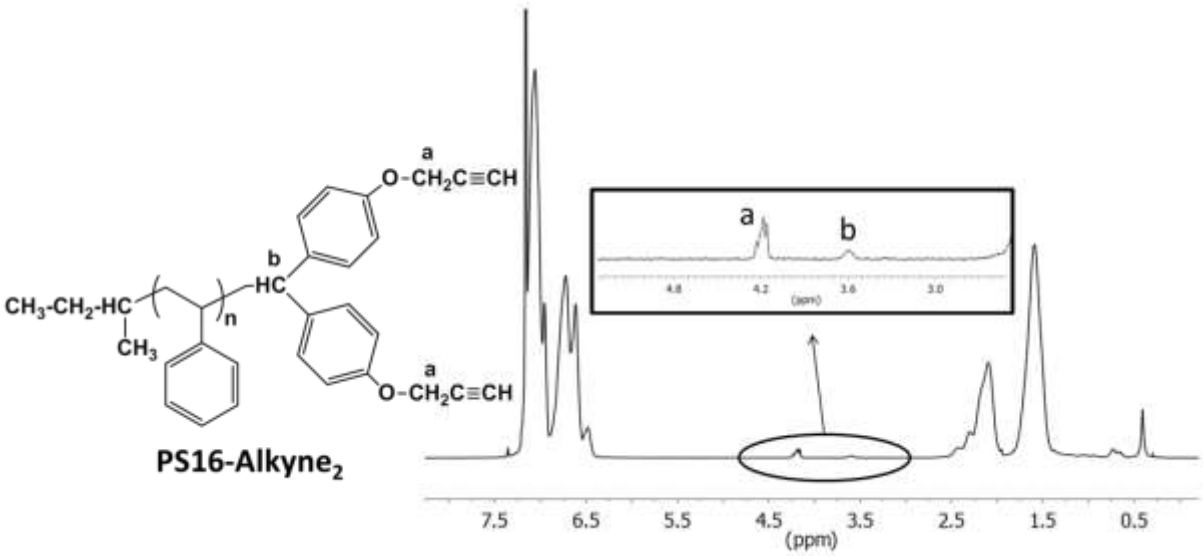


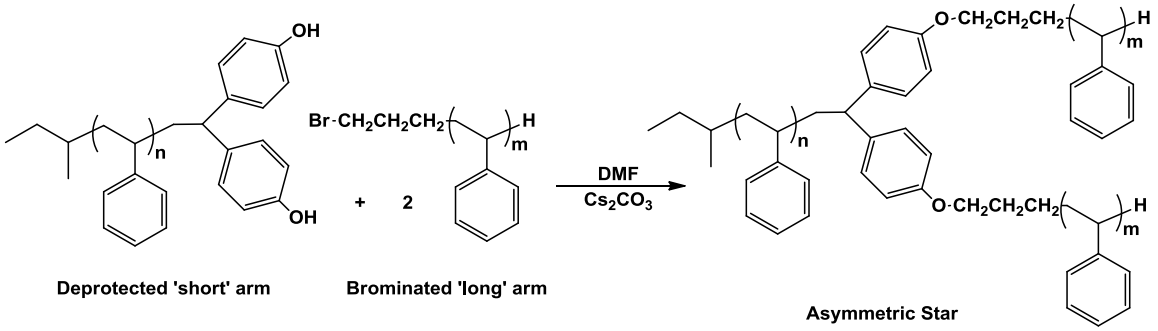
Figure 4 ^{1}H-NMR spectra (C_6D_6, 400 MHz) illustrating the conversion of phenol (PS16-OH_2) to alkyne (PS16-Alkyne$_2$) functionality on the 'short' arm macromonomer.

Synthesis of Stars

The assembly of the stars was conducted using two different approaches. The arms were coupled either by a Williamson coupling reaction or by a copper (I)-catalysed azide-alkyne 'click' reaction. The two coupling strategies were carried out as described below for a synthesis of four asymmetric three-arm stars and one symmetric three-arm star. In each case the molar mass of the two 'long' arms was c. 90 Kgmol^{-1} and the molar mass of the 'short' arm varied - the stars are named "StarX" where X denotes the molar mass of the 'short' arm. The symmetric star (Star90) is produced from 3 'long' arms. In the case of both the Williamson and Click coupling reactions, a slight excess of the long arm was used with respect to the short arm in an attempt to drive the reaction to high degrees of coupling. A mole ratio of 2.5 : 1 (long arm : short arm) was used in all cases. This mole ratio has been shown to be optimal for analogous reactions described elsewhere [33,38]. As well as describing the two synthetic strategies we will compare the efficiency of the two approaches.

Synthesis of Stars via Williamson Coupling Reaction

The synthesis of stars by Williamson coupling reaction consists of a nucleophilic substitution reaction between an alkyl bromide (the bromide being the leaving group) and a phenol (the nucleophile) that results in an ether linkage – scheme 1



Scheme 1 Williamson coupling reaction for the synthesis of asymmetric star polymers.

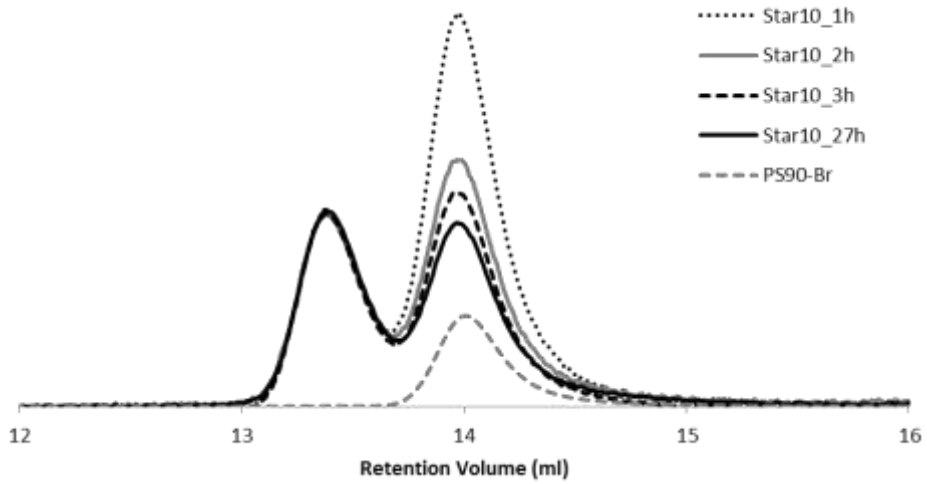


Figure 5. SEC (RI detector) chromatograms of Star10 synthesised by Williamson coupling reaction between 'short' arm PS10-OH_2 and PS90-Br at a temperature of 60°C. Samples were collected for analysis after 1, 2, 3 and 27 hours.

The substitution reaction is carried out in DMF in the presence of cesium carbonate (Cs_2CO_3) [56] with an excess of the long arm. The molar ratios of the reagents are 1 : 2.5 : 10 respectively for 'short' arm, 'long' arm and Cs_2CO_3 - a slight molar excess of the 'long' arm being used to drive the reaction towards completion. The extent of coupling was followed by extracting small samples periodically and subjecting them to SEC analysis as shown in figure 5 which shows data for the formation of Star10. As the reaction proceeds the intensity of the peak at 14 ml corresponding to the 'long' arm (PS90) decreased accompanied by the appearance of a peak at 13.3 ml corresponding to the resulting star. It is also worth noting the complete absence of any unreacted 'short' arm – evidence of the quantitative end-capping with DPE-OSi. It is also possible/likely that a third (unresolved) peak exists corresponding to a linear polymer chain arising from the coupling of the 'short' arm to only one 'long' arm, thereby representing an incomplete coupling reaction. Given the relatively small difference in molar mass between the 'long' arm (c. 90 $Kgmol^{-1}$) and a linear polymer arising from incomplete coupling (c. 100 $Kgmol^{-1}$), it is extremely unlikely that the presence of such a peak could be observed by SEC. However, experience tells us that it is likely that such an intermediate product may be present – see later discussion on TGIC analysis of stars. The reaction conditions chosen for the initial attempt at star synthesis by Williamson coupling reaction (fig 5) were based on a previously reported procedure for the synthesis of polystyrene HyperMacs [56]. Although it is clear from the SEC data in figure 5 that the reaction proceeds with reasonable efficiency, appearing to be almost complete after 3 hours, the overall extent of coupling was a little disappointing and attempts were made to improve the ultimate extent of reaction. With this aim in mind different reaction conditions were investigated. A series of coupling reactions were carried out in which the reaction temperature and the solution concentration were varied – the SEC chromatograms of the final products are shown in figure 6. It is clear from figure 6a that increasing the temperature (at constant solution concentration) from 60°C to 150°C resulted in an increase in the extent (as well as the rate) of arm coupling to yield stars. The effect of the solution concentration was less conclusive. At a constant temperature of 150°C the polymer solution concentration increased from 5 wt. % to 20 wt. % (figure 6b). One might have expected that increasing the concentration would result in an increase in the rate of conversion. Moreover past experience has told us that under these conditions (150°C in DMF) the desired nucleophilic substitution reaction is in competition with side reactions involving the solvent [56]. In light of these

competing side reactions we might have expected that a higher concentration and concomitant higher rate of coupling would have favoured the desired formation of star polymers and therefore a higher extent of reaction. However the results did not bear this out. In light of these results all subsequent Williamson coupling reactions were carried out at 150°C at a solution concentration of 10 wt. % and the result of the synthesis Star16, Star20 and Star32 under these conditions are shown in figure S1 (ESI). As mentioned above and observed previously, the Williamson coupling reactions do not always yield consistent results. For this reason we decided to investigate the use of azide-alkyne 'click' coupling reactions for the star synthesis.

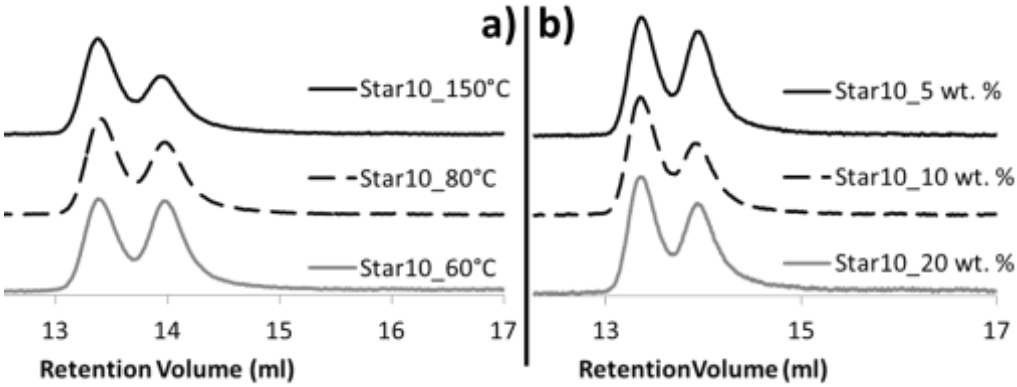
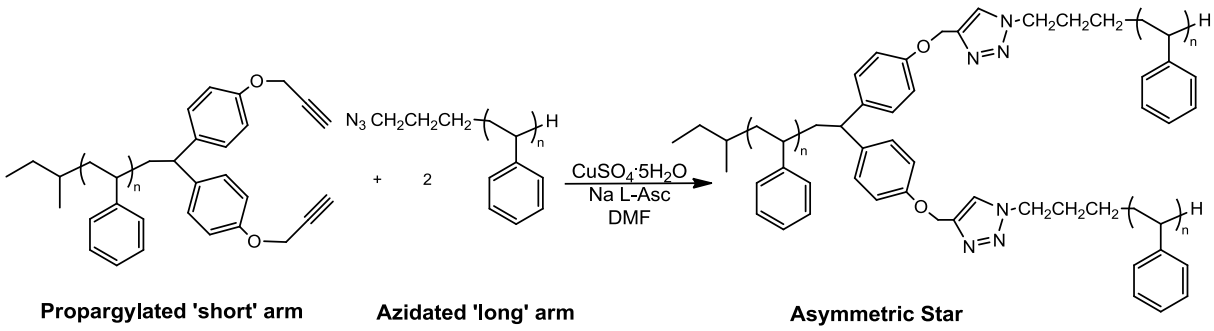


Figure 6. SEC (RI detector) chromatograms of Star10 synthesised via Williamson coupling reaction representing **a)** the effect of temperature at constant solution concentration (10 wt. %) and **b)** the effect of solution concentration at constant temperature (150°C)

Synthesis of Stars via azide-alkyne 'click' Reaction

The synthesis of stars by azide-alkyne 'click' reaction (scheme 2) proceeds by the addition reaction between the azide functionality carried by the 'long' arm and the alkyne functionality carried by the 'short' arm resulting in the formation of a 1,2,3-triazole linkage. The reaction was carried out in DMF in the presence of catalyst $CuSO_4 \cdot 5H_2O$ and reducing agent sodium ascorbate (Na L-Asc). The 'short' arm is reacted with the same stoichiometric excess of 'long' arm used in Williamson coupling reaction (1:2.5) and the extent of coupling was followed by extracting samples and characterising them by SEC.



Scheme 2. Azide-alkyne 'click' reaction for the synthesis of star polymers.

Synthesis of asymmetric three-arm stars

The azide-alkyne click reaction was exploited for the synthesis of the asymmetric three-arm stars, Star16 and Star32. After the introduction of azide and alkyne functionalities at the chain end of the 'long' arm and 'short' arm respectively, the arms were coupled in DMF under a variety of conditions in and attempt to optimise the conversion into stars. In the preparation of Star16, the azide functionalised 'long' arm (PS90-Azide) was used in molar excess (2.5:1) with respect to the alkyne functionalised short arm (PS16-Alkyne$_2$) as indicated in table 2. Three different reactions were carried out, all at 50°C and a solvent concentration of 10 wt. %. The amount of catalyst in each experiment was varied and in the first instance (experiment 1) the molar ratio of copper sulphate and ascorbate reducing agent was 1.25 and 2.5 respectively with respect to the moles of short arm. The reaction proceeded successfully as it can be observed in the first SEC chromatogram shown in figure 7.

Table 2. Reaction conditions for azide-alkye 'click' coupling reactions for the synthesis of Star16 carried out at 50°C with solution concentration of 10% w/v.

Expt	**$CuSO_4 \cdot 5H_2O$**	**Na L-Ascorbate**	**Time (h)**
1	1.25	2.5	-
2	1.25$^{(a)}$	2.5$^{(a)}$	48
3	2	4	35

(a) More catalyst in the same ratio of 1.25 : 2.5 : 1 with respect to PS16 was added to the reaction during the reaction.

When this experiment was repeated (experiment 2 – table 2) using the same amount of the two component catalytic system, initial SEC results after 24 hours (red line in expt 2, figure 7) did not show the same good conversion as seen in expt. 1. In an attempt to improve this initial conversion a second (identical) quantity of catalyst was added to the reaction mixture which resulted in some additional conversion (blue line in expt 2, figure 7).

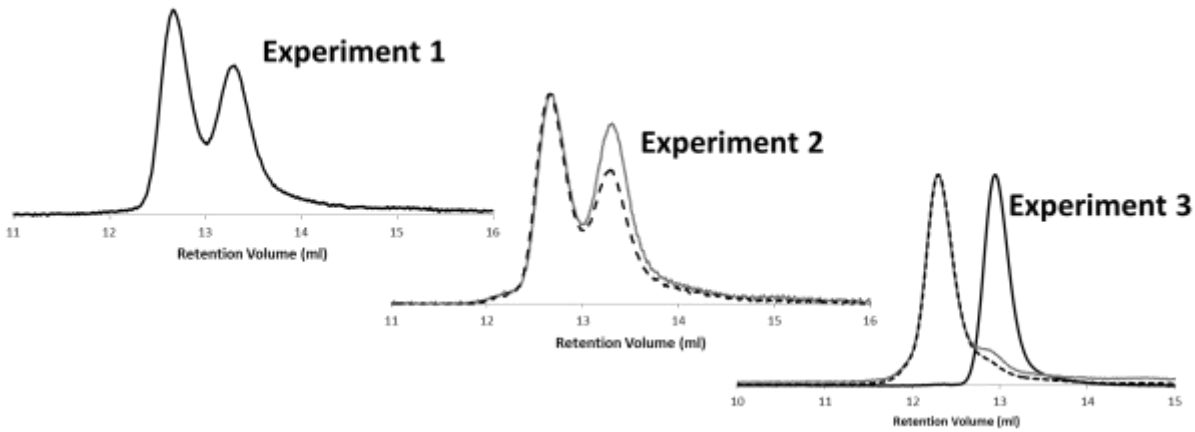


Figure 7. SEC data (RI detector) showing the extent of click coupling reaction in the synthesis of Star16 Click with varying amounts of catalyst – see table 2.

It should be noted that the amount of catalyst being used in these experiments is extremely small – just a few milligrams and it is possible that errors in weighing out and delivering the exact amount required to the reaction could account for the inconsistent results. Moreover, although the reactions were significantly more efficient than the comparable Williamson coupling reactions in terms of reaction time/temperature (50° C for click versus 150° C for

Williamson) the overall extent of reaction was not much improved. Considering the possible problems associated with using such small amounts of reagent, a third experiment was carried out in which the molar ratio of the catalytic system was further increased (see table 2) with dramatic effect. The reaction underwent a significant improvement with a very high, almost quantitative degree of conversion after only 2.5 hours. The data for experiment 3 in figure 7 shows the SEC chromatogram for the PS90-Azide starting material (green line) with a retention volume of 13 ml and the resulting star after 2.5 hours (blue line) and 30 hours (red line). After 30 hours the reaction showed only a modest increase in the extent of reaction suggesting the reaction was almost complete after 2.5 hours.

After the successful synthesis of Star16 via a 'click' coupling reaction, a series of reactions were carried out to ascertain whether the 'click' coupling approach would also be more successful than the Williamson coupling for the synthesis of Star32 and a series of reactions were carried out in which the mole ratio of catalyst was varied in a similar fashion to the synthesis of Star16 see table 3. Since the extent of reaction was initially less spectacular than for Star16, the reaction temperature and solvent concentration were also varied.

Table 3. Reaction conditions for the several experimented azide-alkye click reactions conducted for the synthesis of Star32.

Expt	**T(°C)**	**Polymer Conc. (% wt/v)**	**[$CuSO_4 \cdot 5H_2O$]**	**[Na L-Ascorbate]**
1	50	10	1.25[(a)]	2.5[(a)]
2	60	10	2[(b)]	4[(b)]
3	60	20	2	4
4	60	20	3	6

a) More catalyst was added during the reaction in a molar ratio of (1 : 7.5 : 15) with respect to PS32-Alkyne$_2$
b) More catalyst was added during the reaction in a molar ratio of (1 : 1.16 : 2.32) with respect to PS32-Alkyne$_2$.

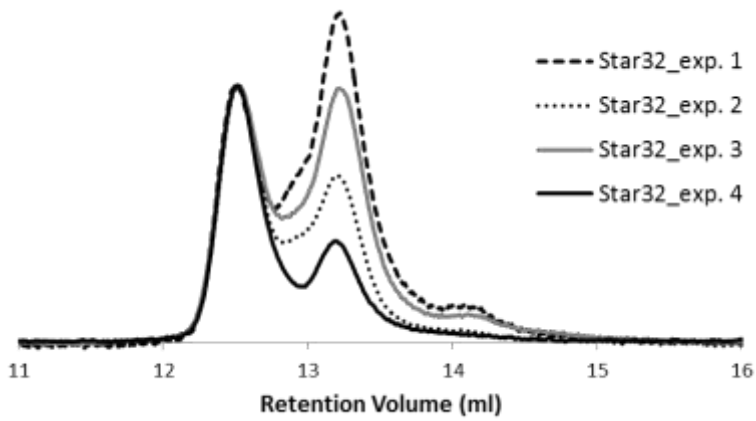


Figure 8. SEC chromatogram (RI detector) of Star32. On the left: comparison of the final polymer mixture resulting from exp. 1 and 2. On the right: comparison of the final polymers mixtures obtained from experiment 2, 3 and 4.

Experiment 1 (table 3) for the synthesis of Star32 was initially carried out under the same conditions as experiments 1 and 2 for Star16 (table 2). The addition of extra catalyst in a molar ratio of 1 : 7.5 : 15 with respect to PS32-Alkyne$_2$, a much larger quantity than used at

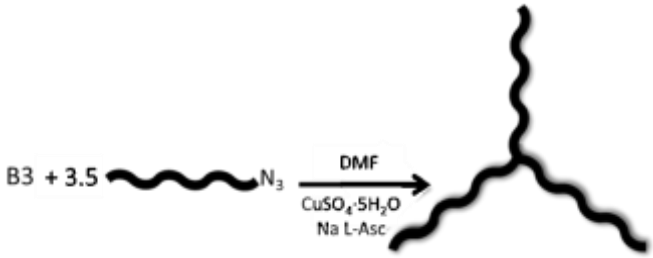


Figure 9. General schematic for the synthesis of symmetric three-arm stars via Azide-alkyne 'click' coupling reaction.

the beginning of the reaction, did not generate any improvements and the reaction was stopped at a very low conversion to star (figure 8). It is not immediately obvious what the cause of this disappointing result was. It is clear however that the reaction is most sensitive to the amount of catalyst and this was borne out in subsequent experiments in which both the temperature and polymer solution concentration were varied, (table 3 and figure 8) neither of which made a substantive difference to the overall extent of reaction. The best results were obtained when a higher mole ratio of catalyst was used from the start of the reaction (experiment 4, table 3). The SEC chromatograms shown in figure 8 clearly suggest the presence of a peak/shoulder in between the two major peaks with a retention volume of approximately 12.9 ml – this is particularly evident in experiment 1. As mentioned above this additional peak is an indication of incomplete coupling in the synthesis of the star, i.e. in this case a linear polymer formed by the coupling of PS32-Alkyne$_2$ and only 'long' arm PS90-Azide.

Synthesis of symmetric three-arm star

In addition to the synthesis of the asymmetric three-arms stars described above, the synthesis of one example of a symmetric three-arm star was carried out by coupling the 'long' arm (PS90-Azide) to a trifunctional core carrying 3-alkyne groups via an azide-alkyne click reaction (figure 9) – for the synthesis of trifunctional core see electronic supplementary information. The coupling reaction for the synthesis of the symmetric star was conducted at a temperature of 60°C and a solution concentration of 20 wt. %. At the beginning of the reaction the catalytic system had a molar ratio of (1:4:8) with respect to the B3 core utilised. The synthesis was carried out twice under the same conditions. An initial small scale (1 g) reaction was carried out and it was noticed that the reaction was slower in comparison to the stars synthesised before. This slower rate is likely be due to the longer polymer chains involved creating additional steric congestion at the core which will in particular slow down the coupling of the final arm. It can be seen in the SEC chromatogram below (figure 10), that the reaction had low conversion after 1 hour and 50 minutes but after 18 hours the conversion improved. After a further 25 hours the conversion was slightly better but further prolonged reaction times did not yield an improved conversion.

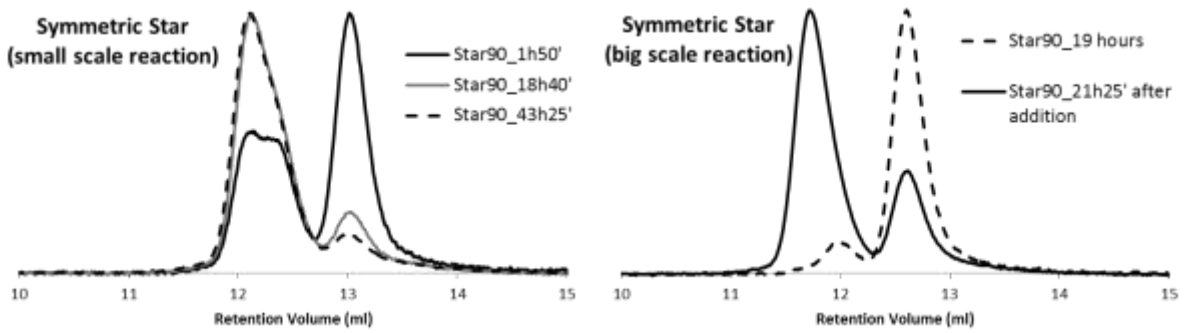


Figure 10. SEC chromatograms (RI detector) of the synthesis of the symmetric star on a small scale (left hand side) and on a larger scale (right hand side).

A second reaction was carried out on a larger scale (about 7g) to allow for the synthesis of enough material for the subsequent characterisation studies. Initially the coupling reaction proceeded very slowly and the conversion was still very low after 19 hours. It was decided to add a second amount of the catalytic system in a molar ratio of (1 : 2.7 : 5) with respect to the B3 core and 21 hours and 25 minutes after the addition of this second batch of catalyst, the reaction had proceeded to a good conversion (figure 10). Further prolonged reaction times did not result in enhanced conversion of arms into star.

Williamson versus 'click' coupling reaction

It is clear from the data above that both Williamson and 'click' coupling reactions can be used for the synthesis of stars via the macromonomer approach and it is possible to compare the effectiveness of the two coupling reactions by considering the synthesis of Star16 and 32 which were synthesised by both types of reactions. Moreover in both cases the mole ratio of short arm to long arm was identical. The Williamson coupling reaction offers an advantage over 'click' coupling in so much that the required functional groups can be introduced in fewer reaction steps. However, when it comes to the coupling reaction itself, we would have to argue that the 'click' reaction produces the more satisfactory approach. We have previously encountered problematical side reactions involving the solvent (DMF) accompanying a Williamson coupling reaction [56] and it is likely that the same side reactions inhibit the coupling reactions in this work. Moreover, high temperatures (150 ^{o}C) were required to drive the reactions towards a reasonable conversion. In contrast the 'click' reactions were carried out at much lower temperatures (50-60 ^{o}C) and in both Star16 and 32, the degree of coupling achieved via click coupling was much superior to that obtained by Williamson coupling – see figures S3 and S4 (electronic supporting information) and in the case of Star16, the coupling was almost quantitative. The only drawback in using the 'click' coupling reactions was that they appeared to be very sensitive to the amount of catalyst and incomplete coupling in the synthesis of stars via click coupling reactions have been observed before [80] and is possibly a consequence of the very small quantities of catalyst required to carry out rections between high molecular weight polymer chains. Pragmatically, in this study it was found that if relatively high levels of catalyst were used, efficient coupling could be achieved and the extent of coupling is at least as efficient as the more established chlorosilane coupling approach.

Fractionation and Temperature Gradient Interaction Chromatography (TGIC) Characterisation

Although a comparison of the Williamson and 'click' coupling mechanisms is interesting, the primary advantage of the macromonomer approach in the current work is that it enables the synthesis of a "perfect" series of asymmetric stars in which the only variable is the molecular weight of the "short" arm. As mentioned from the outset, this series of stars were designed and synthesized to probe branched polymer dynamics and in particular to establish the chain length of side arm which precipitates a change in the rheological properties of the resulting polymers from "linear-like" to "star-like" – results that will be published elsewhere. However before these studies could proceed it was necessary to purify the crude stars to remove unreacted arms or part-coupled products and this was achieved by fractionation using toluene/methanol as the solvent/non-solvent.

Since structural homogeneity is of fundamental importance in the study of branched polymer rheology, temperature gradient interaction chromatography (TGIC) was used alongside size exclusion chromatography (SEC) to establish complete purification of the stars by fractionation and to confirm structural purity. It has often been assumed (until relatively recently) that purification by fractionation of structurally polydisperse branched polymers is sufficient to remove by-products such as partially coupled polymer from the desired product; a false assumption often reinforced by a monomodal, narrow molecular weight distribution obtained by SEC which has long been the primary method for the characterization of polymer molecular weight and molecular weight distribution. However, due to its mode of separation (by molecular size rather than molar mass) SEC has an intrinsic limitation – namely that it is unable to separate polymers with identical or nearly identical hydrodynamic volumes, which may differ in other molecular parameters such as molar mass or chain architecture. Such a limitation is a particular concern for the characterization of model branched polymers for structure-property correlation studies – a topic recently reviewed [72].

TGIC, is a technique that was first described more than 15 years ago [81] in which separation is driven by enthalpic interactions between the solute molecules and the stationary phase and these interactions, which can be controlled by temperature variation during the elution, are to a first approximation, proportional to the molecular weight NOT the hydrodynamic volume. The additional variable (temperature) also allows control over the retention time and as a consequence, superior resolution over SEC even in the case of linear polymers [81]. As such TGIC is the optimum technique to characterise the purity of the stars produced in this study. It was mentioned above that the product of many, if not all, of the coupling reactions may be contaminated with small quantities of part-coupled star, i.e. linear polymer comprising of one 'long' arm coupled to the 'short' arm or two 'long' arms (in the case of the symmetric star) and unreacted arms. We have also seen that SEC analysis is not capable of identifying the presence (or otherwise) of this intermediate product due to the small differences in hydrodynamic volume. TGIC (and SEC for comparison) was carried out on each star before and after purification by fractionation and SEC data for each star polymer (before and after fractionation) can be seen in figure 11. In each case the fractionated product has a monomodal SEC chromatogram suggesting a high degree of structural homogeneity. It should also be noted that in each case the crude star (prior to fractionation) shows (only) two main peaks, in each case the peak at retention volume of approximately 13.4 ml arises as a result of uncoupled "long" arm – PS90. SEC is incapable of resolving any additional peaks between the two main peaks.

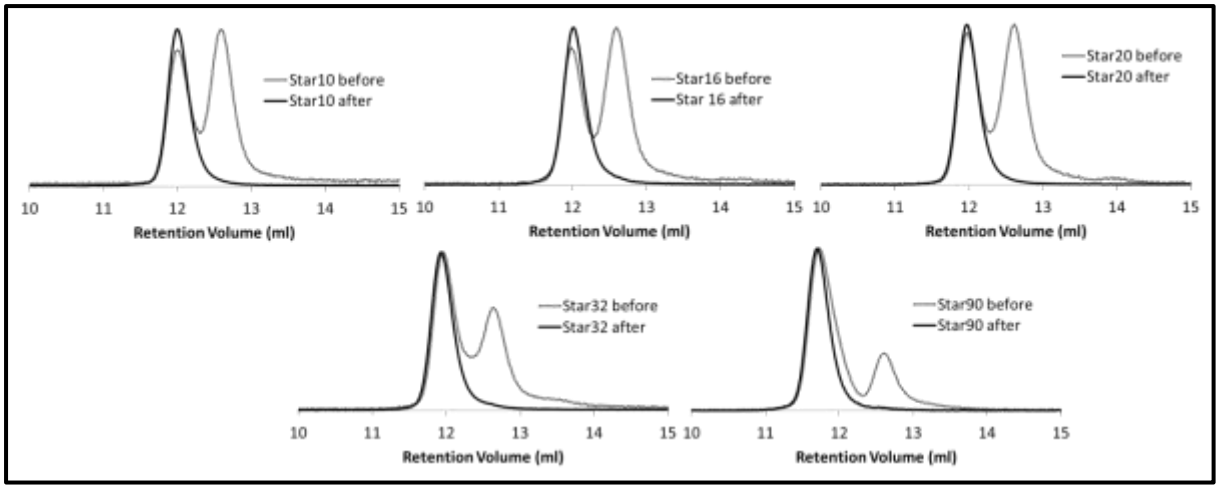


Figure 11. SEC chromatograms (RI detector) for each star before and after purification by fractionation.

In contrast TGIC analysis of the crude stars (before fractionation) is more than capable of detecting three peaks corresponding to the uncoupled "long" arm, part-coupled material (one long arm and the short arm) and the fully coupled star. TGIC data for Star16 and Star20 are shown below (figure 12) and the data for all stars included as electronic supporting information (figure S5). When considering the TGIC data it should be remembered that the order of elution is reversed compared to SEC, so in figure 12, the peak corresponding to the star – the highest molecular weight component elutes at the longest time. In figure 13 we report the TGIC data for Star16 and Star20 following fractionation and the analogous TGIC data for all the stars is included as electronic supporting information (figure S6). Whilst the SEC analysis (fig 11) would seem to suggest that the fractionation had been a complete success and the "purified" stars were free of by-products, the superior resolution of TGIC reveals otherwise. We can see in figure 13, small peaks at shorter elution times (lower molecular weight) which correspond to unreacted "long" arm and/or part-coupled material consisting of a linear polymer arising from the coupling of one "long" arm to the "short" arm.

Table 4. Molar mass data obtained by SEC for the polystyrene arms and the purified asymmetric and symmetric three-arm stars.

	Molar mass of arms/ gmol^{-1}						**Molar mass of stars/gmol^{-1}**		
StarX	Long arm			Short arm PSX					
	M_n	M_w	PDI	M_n	M_w	PDI	M_n	M_w	PDI
10	89900	92400	1.03	10000	10500	1.05	193300	197700	1.02
16	89900	92400	1.03	16200	16800	1.04	198800	205100	1.03
20	89900	92400	1.03	19600	20500	1.05	202000	208300	1.03
32	89900	92400	1.03	32100	33700	1.05	211000	218300	1.03
Symmetric star									
90	89000	92400	1.03	-	-	-	279700	289100	1.03

The relative amount of each component in the mixture was estimated by deconvoluting the peaks from the UV (concentration) detector using a standard Gaussian distribution and calculating the area under each curve. Although the amount of "impurity" in the fractionated stars is small (less than 5% in most cases) the TGIC analysis demonstrates that the

fractionation process has not completely removed all traces of low molecular weight by-products and unreacted starting materials. More significantly the TGIC data once again clearly demonstrates that SEC does not give sufficient resolution to adequately interrogate the structural homogeneity of model polymers which have been produced for structure-property correlation studies. Although the amounts of impurity are small they have the potential to impact upon physical properties and in such studies it is clearly important that the presence of such "impurities" is both detected and quantified. The molar mass details of the arms and the purified stars are shown in table 4.

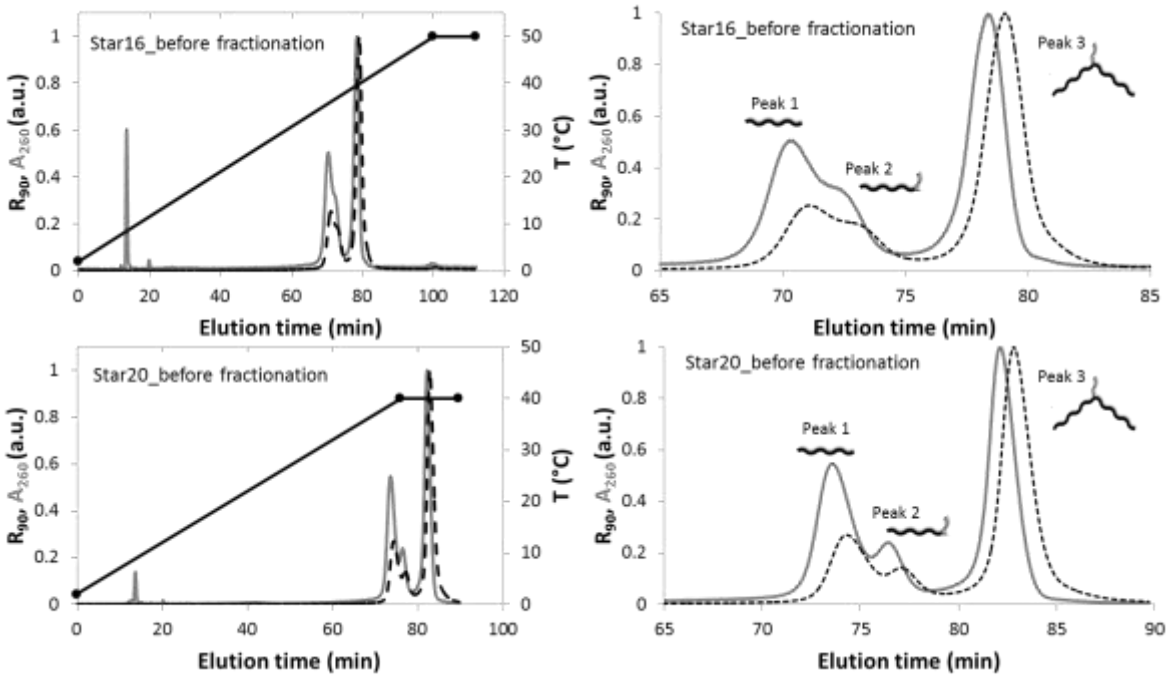


Figure 12. TGIC chromatograms of Star16 and Star20 before purification by fractionation recorded with UV and RALS detector. On the right hand side the expanded chromatograms are reported in order to observe the presence of the three peaks due to stars and impurities.

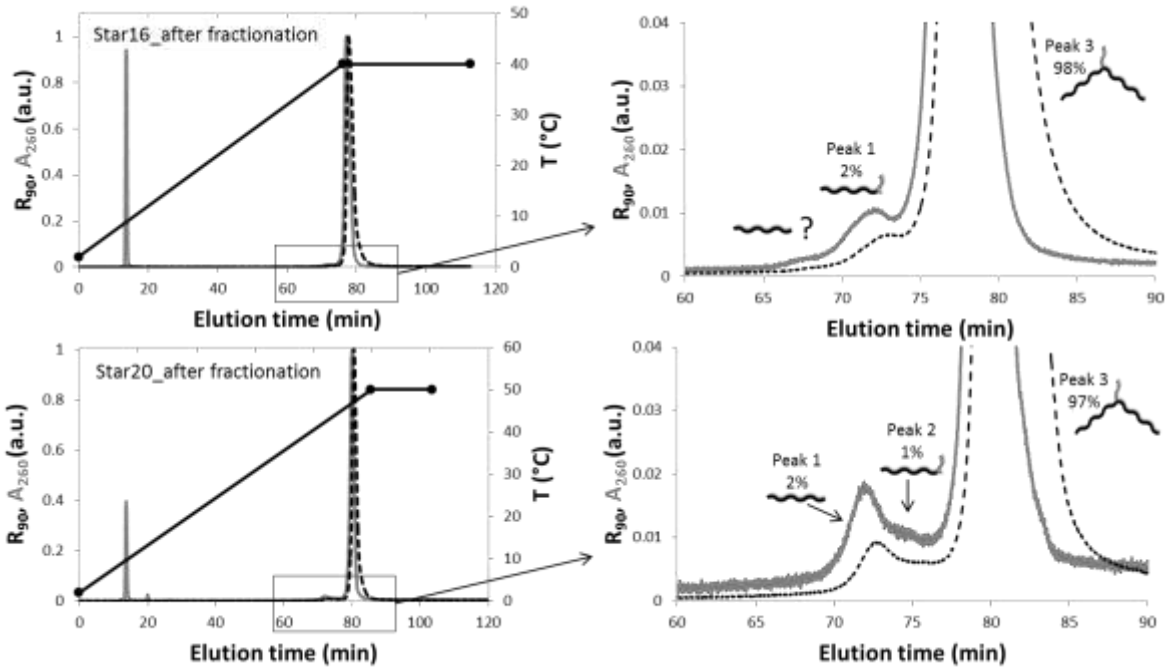


Figure 13. TGIC chromatograms of Star16 and Star20 after purification by fractionation recorded with UV detector and RALS detector. On the right hand side the expanded chromatograms are reported in order to observe the presence of trace amounts of remaining impurities. The relative concentration (weight fraction) of each species was estimated by deconvolution of the chromatograms using a Gaussian distribution.

Conclusions

We have successfully used the "macromonomer" approach to synthesize a homologous series of three-arm stars in which the molar mass of two (long) arms are fixed at 90 000 $gmol^{-1}$ and the molar mass of the remaining (short) arm is varied from below the entanglement molecular weight (M_e) to above M_e. These stars have been used as model polymers to probe branched-polymer dynamics and in particular, to establish the chain-length of side-arm which precipitates a change in the rheological properties of the resulting polymers from "linear-like" to "star-like" and the results of these studies will be reported elsewhere. The advantage of the macromonomer approach is that living anionic polymerisation can be exploited for the synthesis of the arms, resulting in well-defined chain lengths and narrow molecular weight distribution, whilst the stars can be constructed by a simple (post-polymerization) condensation coupling reaction. In this way it is possible to produce a series of stars in which we can eliminate variation in all the molecular parameters except the molar mass of the "short" arm. We have compared the relative efficiency of using either Williamson or 'click' coupling reactions in producing the stars and found that whilst both methods are successful in producing stars, the 'click' coupling reaction is more efficient allowing reactions to be carried out at lower temperatures and to give stars with a higher degree of coupling. However, we did find that since coupling reactions between polymer chains require very small quantities of catalyst, the 'click' coupling reactions were variable in their success but almost quantitative chain coupling could be achieved in the presence of higher ratios of catalyst. The "crude" stars were purified by fractionation and the products subjected to both size exclusion chromatography (SEC) and temperature gradient interaction chromatography (TGIC). Whilst the former suggested that the fractionation process had been a complete success, TGIC revealed the presence of traces of impurity. Once again this reinforces the need to use TGIC as a complementary technique to SEC in the characterisation of model polymers for structure-property correlation studies.

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