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Synthesis and temperature gradient interaction chromatography of model asymmetric star polymers by the “macromonomer” approach

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A B S T R A C T

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 g mol^{-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.

1. 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 [49]. The term “living”

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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 3–128 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 and Iatrou [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.

2. Experimental

2.1. 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) 1.4 M 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].

2.2. Characterisation

^1H 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 × 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