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# Synthesis and Characterization of Well-Defined Regular Star Polyisoprenes with 3, 4, 6 and 8 Arms

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## Abstract

Three series of regular well-defined star polyisoprenes (PIs) with 3, 4 and 6 arms (each series: same arm molecular weight) have been synthesized by anionic polymerization high vacuum techniques and chlorosilane chemistry. In addition, three linear PIs with practically the double arm molecular weight of the corresponding series (2-arm star PIs) have been synthesized, as well as one 8-arm star PI. All intermediate (arms) and final (stars) products have been characterized by Size Exclusion Chromatography (SEC), SEC-Multi-Angle Laser Light Scattering (SEC-MALLS) and Nuclear Magnetic Resonance (NMR) spectroscopy. The  $T_g$  of the star PIs was determined by differential scanning calorimetry. These model polymeric materials are essential for polymer physics and polymer physical chemistry in order to establish the structure/property relationships.

**Keywords:** High Vacuum Techniques, Star-Branched Polymers, Star Polyisoprene, SEC

## 1. Introduction

Polymers with narrow molecular weight distribution and with well-defined architecture are essential for establishing structure/properties relationships. These relationships are necessary to achieve one of the ultimate goals of polymer chemistry i.e. designing molecules with predetermined properties (Hadjichristidis, 1999). In recent years, well-defined macromolecular architectures were developed such as miktoarm star (Hadjichristidis et al, 1999),  $\alpha$ ,  $\omega$ -branched (Gido et al, 1996 and Chrissopoulou et al, 1999), exact graft (Paraskeva & Hadjichristidis, 2000 and Nikopoulou et al, 2009), block-double graft (Velis & Hadjichristidis, 2000) and lately dendrimers (Trollsa & Hedrick, 1998; Bosman et al, 1999 and Roovers & Comanita, 1999) and dendritic polymers (Hawker, 1999; Voit, 2000 and Chalari & Hadjichristidis, 2002).

Star polymers are defined as polymer having more than

three chains radiating from a core. The regular symmetric stars have attracted the attention of scientists since they constitute the simplest form of branching. The earliest attempt to synthesize star molecules was that of Schaeffgen and Flory in 1948 (Flory, 1948), who polymerized  $\epsilon$ -caprolactam in the presence of either cyclohexanonetetracaproic or dicyclohexanoneoctacarboxylic acid and obtained tetra- and octa- chain star-shaped polyamides.

Fourteen years later, Morton and co-workers (Morton et al, 1962) took advantage of the living character of anionic polymerization to synthesize four-arm star polystyrenes (PS) by neutralizing living polystyryllithium with tetrachlorosilane. Although the produced materials were mixtures of three- and four-arm PS, this methodology eventually led to the preparation of star polymers with up to 128 arms (Roovers et al, 1993).

In 1963, Orofino and Wenger (1963) first used tri(chloromethyl) benzene as a linking agent to prepare three-arm star PS. Mayer (1974) used 1,2,4,5-tetra(chloromethyl)benzene to prepare four-arm star di- and triblock copolymers of styrene and isoprene. It is difficult to extend the functionality ( $f$ ) of the stars beyond  $f = 6$  with chloromethylbenzene derivatives.

Hadjichristidis (1999) was the first to demonstrate the validity of divinylbenzene (DVB) as a linking agent by preparing and properly characterizing PS stars with 6 to 15 arms. The DVB method was introduced by Hadjichristidis (Hadjichristidis, 1999), but unfortunately does not allow one to accurately control the number of the arms of the stars, not does it yield polymers with a uniform number of arms (Hadjichristidis, 1999) As a result, multifunctional chlorosilane compounds became the linking agents of choice (Zelinski & Wofford, 1965; Roovers & Bywater, 1972; Hadjichristidis & Roovers, 1974; Roovers & Bywater, 1974; Hadjichristidis et al, 1978; Hadjichristidis & Fetters, 1980; Roovers et al, 1983; Nguyen et al, 1986; Zhou et al, 1992 and Roovers et al, 1993).

Star-branched polymers have been widely investigated from both experimental and theoretical viewpoints because their behaviours and properties in solution, melt and solid state are quite distinct from those of the corresponding linear analogues (Higashihara et al, 2005).

Star-branched polymers are generally categorized in to the following two types: regular star-branched polymers having the same arm segments and asymmetric (also called mikto arm, derived from the Greek word, meaning mixed) star-branched polymers having different arm segments. The regular star includes star-branched polymers consisting of the same homopolymers or block copolymers. The asymmetric star-branched polymer further subdivides into four types according to the asymmetric architecture: (1) chemical structure asymmetry, (2) molecular weight asymmetry, (3) functional group asymmetry, and (4) topological asymmetry.

In order to synthesize star-branched polymers with well-defined structures, the use of a living polymerization system is essential. The living anionic polymerization of styrene, 1,3-butadiene, isoprene, alkyl methacrylates and their derivatives is still the best living system from the view point of the following features (Higashihara et al, 2011). Firstly, the molecular weight can precisely be controlled in a wide range from  $10^3$  to even  $10^6$  g/mol. Secondly, extremely narrow molecular weight distributions; the  $M_w/M_n$  values 1.05 or even smaller are possible. Finally, the living polymers have active chain-end anions which are highly reactive but stable under appropriate conditions. Such characteristics are ideally suited for the synthesis of well-defined star-branched polymers.

In this paper we describe the synthesis and characterization of 2-arm (linear), 3-arm, 4-arm, 6-arm and 8-arm star-branched PIs with arm-first methodology by using well-known anionic polymerization high vacuum techniques and chlorosilane chemistry. We report, for the first time, the synthesis of three different series of star PIs with controlled MW and narrow MW distribution. The star-branched PIs and their precursors have been characterized by Size Exclusion Chromatography (SEC), SEC-Multi-Angle Laser Light Scattering (SEC-MALLS) and Nuclear Magnetic Resonance (NMR) spectroscopy. The thermal behaviour of the polymers was analyzed by Differential Scanning Calorimetry (DSC). These model PIs are used for linear and non-linear rheology (Snijkers et al, in press), Small Angle Neutron Scattering (SANS) (Beaucage et al, in press) and other studies in order to find the influence of the structure on the properties.

## 2. Materials and Methods

### 2.1. Materials

The purification of the solvents (benzene, Panreac, 99%, and *n*-hexane, Merck, 99%) and the terminating agent (methanol, 99.9% Aldrich), to the standards required for anionic polymerization, was performed using well-established high-vacuum procedures (Hadjichristidis et al, 2000) while toluene (Merck) was used as received. The initiator for all polymerization, *sec*-Butyllithium (*s*-BuLi), was prepared from *sec*-butylchloride (99.9% Aldrich) and lithium dispersion (99% high sodium, Aldrich). The linking agents, trichloro-methylsilane ( $\text{Cl}_3\text{CH}_2\text{Si}$  99% Aldrich), tetrachlorosilane ( $\text{SiCl}_4$  99% Aldrich), and 1,2-bis(trichlorosilyl)-ethane (97% Aldrich) (6-SiCl) are liquid and easily purified by distillation over  $\text{CaH}_2$ , where it was allowed to stand overnight with continuous stirring, followed by distillation (middle fraction) and dilution with hexane in calibrated ampules. Tetra(methylchlorosilylethyl)silane  $\{\text{Si}[\text{CH}_2\text{CH}_2\text{SiCl}_2(\text{CH}_3)]_4\}$  (8-SiCl), prepared by hydrosilylation of tetra vinylsilane with dimethylchlorosilane in the presence of the Karstedt platinum catalyst, was diluted in purified *n*-hexane. *n*-BuLi in hexane (1.6 M, Aldrich) for purging the reactors was used as received. Butadiene (Bd, bp:  $24^\circ\text{C}/760\text{ mmHg}$ ), used as end capping agent, was condensed in a graduated cylinder with *n*-BuLi at  $-78^\circ\text{C}$  (dry ice/isopropanol bath), stirred for 30 min at  $-10^\circ\text{C}$  (ice/salt bath), then distilled into another flask containing new *n*-BuLi (1.6 M solution in hexane) and allowed to stand at  $-10^\circ\text{C}$  until the viscosity was slightly increased, due to polymerization (clean system). It was finally distilled at  $-78^\circ\text{C}$  in a calibrated ampule and diluted with purified benzene in a ratio of  $[\text{monomer}]/[\text{solvent}]$  lower than 0.2.

#### 2.1.1. Purification of Monomer

The monomer (Isoprene, 99% Aldrich; bp:  $34^\circ\text{C}/760\text{ mm}$

Hg) was dried over finely ground CaH<sub>2</sub> on the vacuum line overnight. It was then distilled over *n*-BuLi where it remains with continuous stirring for 30 min at 0 °C. This step was repeated twice before the pure monomer was distilled in pre-calibrated ampoules equipped with break-seals.

## 2.2. Measurements

### 2.2.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

<sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) spectra were recorded in chloroform-d (CDCl<sub>3</sub>) at 25 °C with a Varian Unity plus 300/54 NMR spectrometer

### 2.2.2. Size Exclusion Chromatography (SEC)

SEC experiments were performed at 25 °C with a Waters model 510 pump, a Waters model 410 differential refractometer, and three Styragel columns having a porosity range from 10<sup>3</sup> to 10<sup>6</sup> Å. The carrier solvent was a mixture of chloroform/triethylamine (95/5, v/v) at a flow rate of 1.0 mL/min. Calibration was performed with seven standard polystyrene (PS) samples covering the molecular weight range from 2.0 to 350 kg mol<sup>-1</sup>. The *M<sub>n</sub>* was obtained after applying a correction coefficient for PI. The instrument was used to determine the polydispersity factor ( $I = M_w/M_n$ ) of all samples and the *M<sub>w</sub>* of the linear precursors.

### 2.2.3. Size Exclusion Chromatography -Multi-Angle Laser Light Scattering (SEC-MALLS)

SEC-MALLS measurements were conducted by using Pk+ResiPore (Polymer Laboratories) instrument. This equipment consisted of a Diode Array Detector (DAD) 260 nm (Agilent Technologies 1260 Infinity), refractive index detector and a multi-angle light scattering detector (Wyatt Technology Corporation, USA). The mobile phase was THF at a flow rate of 1 mL/min.

### 2.2.4. Differential Scanning Calorimetry (DSC)

The thermal behaviour of these polymers was analyzed using a TA Instruments DSC, model 2920. Approximately 8 to 10 mg of each sample was heated at 10 °C/min to 150 °C and then equilibrated at 20 °C. After it cooled down to -120 °C, further heated at 10 °C/min to 50 °C. The glass transition temperatures were recorded on second heating cycles.

## 2.3. Synthesis

### 2.3.1. Synthesis of Tetra(methyldichlorosilylethyl) Silane

Tetra(methyldichlorosilylethyl) silane {Si[CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (8-SiCl) was prepared by a known procedure

(Hadjichristidis et al, 1978). It was diluted in *n*-hexane and subdivided into ampoules with break-seals. The concentration of the silicon-chlorine groups was determined by acid-base titration: an ampoule containing a known amount of 8-SiCl solution was ruptured in excess water and the generated acid was titrated with 0.025M sodium hydroxide (NaOH) solution.

### 2.3.2. Synthesis of Regular Star-Branched PIs

Polymerizations and linking reactions were carried out in benzene in sealed vacuum systems. Reaction apparatus was made as shown in Figure 1. Ampoules containing *sec*-BuLi (initiator), isoprene (monomer), butadiene (for end capping), linking agent and degassed methanol (for termination) were connected to the apparatus. The apparatus (Figure 1) was attached to the vacuum line through the ground joint (A), checked for pinholes, flame dried and pumped for 1 h in order to remove the volatile species such as air and humidity. 2-3 mL of a solution of *n*-BuLi in hexane

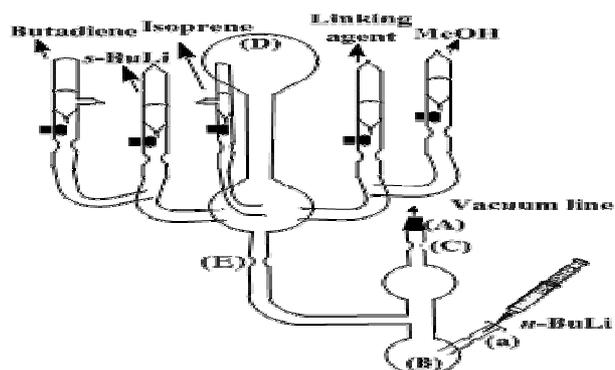


Figure 1. Glass Home-Made Apparatus for the Synthesis of Star PIs

(2.5 M) was then injected in the flask (B) through the septum and the tube holding the septum was removed by heat sealing at (a). The apparatus was pumped for another half hour in order to remove hexane and air inserted in the apparatus during the injection, followed by distillation of the benzene solvent into the flask (B). The amount of solvent was chosen such that the final polymer concentration was 10%. The reactor was removed from the vacuum line by heat sealing at (C). The inner wall of the reactor was purged with *n*-BuLi solution; this solution was transferred back to the flask (B) and placed in a water bath at 50 °C. Due to the presence of the vacuum inside the apparatus, benzene refluxes and condenses over the whole reactor, rinsing traces of *n*-BuLi from the glass walls. As a consequence, all *n*-BuLi inserted along with the products of reaction impurities were collected in flask (B) of the purge section. The apparatus was tilted. A water bath at 25 °C was placed under the purge section and an ice-water bath under the flask (D). Due to the vacuum in the apparatus, the solvent was distilled into the main reactor but the non-

volatile species, that is, *n*-BuLi and its reaction products with impurities, remain in flask (B). The purge section was removed by heat sealing of the constriction (E) leaving a clean reactor filled with an appropriate amount of pure solvent. First, the break-seal of the isoprene monomer was ruptured, by moving the pair of magnets. The monomer was poured in the flask (D), followed by addition of the initiator. The polymerization was left to proceed for 24 hrs and then ampoule containing butadiene was ruptured for end capping. The reaction flask was kept at room temperature for few hours and aliquot was taken for SEC.

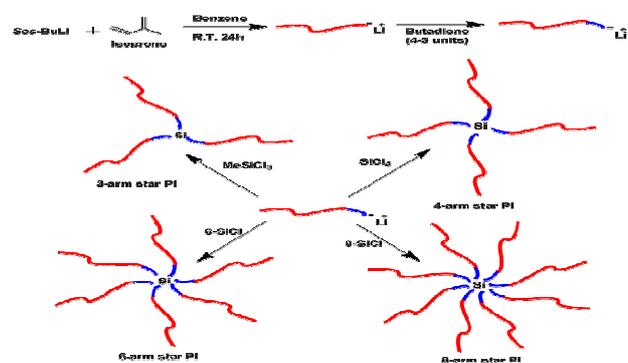
Narrow molecular weight distribution polyisoprenyllithium was obtained by using *sec*-butyllithium as the initiator and benzene as the solvent at room temperature. The linking agent was then added. The ratio of polyisoprenyllithium to silicon chlorine bonds, depending on the arm MW, was between 1.2 and 1.9 in order to ensure complete coupling. Excess of polyisoprenyllithium was terminated by breaking methanol ampoule. Fractionations of the polymers were carried out by adding methanol (non-solvent) to polymer solutions in toluene. The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of linear PIs chains were determined by SEC (PS standards and correction coefficient for PI). The glass transition temperatures for final star-branched polymers were determined by DSC.

### 3. Results and Discussion

#### 3.1. Synthesis and Characterization of 3, 4, 6 and 8-Arm Star PIs

The synthesis of the star-branched PIs was achieved by using anionic polymerization high vacuum techniques and chlorosilane chemistry (Scheme 1). First a narrow molecular weight linear living polyisoprene was prepared, in benzene at 25 °C, with *sec*-BuLi as the initiator. A small fraction was removed and terminated with degassed MeOH (arm of the star). The living polyisoprenyllithium was end-capped with a few units of butadiene (Bd) prior to reaction with the chlorosilane linking agent. Polyisoprenyllithium should be end-capped with few units of butadiene to minimize the steric hindrance (higher reactivity) of the end monomeric unit before the reaction with the linking agent. 3-arm, 4-arm, 6-arm, and 8-arm star PIs were prepared by reacting the living arms with methyltrichlorosilane (MeSiCl<sub>3</sub>), tetrachlorosilane (SiCl<sub>4</sub>), 1,2-bis(trichlorosilyl)ethane (6-SiCl) and tetra(methyl dichlorosilyl)ethylsilane (8-SiCl) respectively. About 10-20% (3, 4, 6-arm PI) to 50% (8-arm PI) excess of the living PI, end-capped with Bd, was used in order to force the linking reaction to completion. The linking reaction was monitored by comparison of the high molecular weight "star" peak and the low molecular weight "arm" peak of SEC traces. The excess living polymer was terminated with degassed meth-

anol. The polymers were extensively fractionated (solvent/non solvent: toluene/methanol) to remove the excess arm material. Two representative examples (3-arm PI,  $M_{n,arm} = 46 \text{ kg mol}^{-1}$  and 4-arm PI,  $M_{n,arm} = 38 \text{ kg mol}^{-1}$ ) are given in Figure 2.



6-SiCl: [Si(Cl<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(Cl<sub>3</sub>)]; 8-SiCl: [Si(CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>); Red are Polyisoprene Chains and Blue Is Butadiene

Scheme 1. General Reaction Scheme for the Synthesis of 3-arm, 4-arm, 6-arm, and 8-arm Star PIs

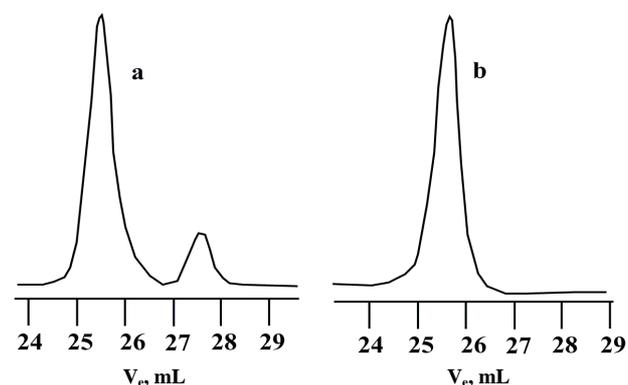


Figure 2. SEC traces of 3-arm PI (arm 46 kg/mol) before (a) and after fractionation (b)

Figure 3 shows the SEC traces of arm (10.5 kg/mol) and the corresponding star PIs with 2, 3, 4 and 6 arms. The molecular characteristics for the arms and the corresponding stars are given in Table 1. For all samples, the polydispersity index (PDI:  $M_w/M_n$ ) was lower than 1.1.

#### 3.2. Microstructural Characterization of Star PI by <sup>1</sup>H NMR Spectroscopy

The relative amounts of 1,4- vs. 3,4-enchainment of PIs was determined using <sup>1</sup>H NMR in CDCl<sub>3</sub> by comparison of peak integration at δ 5.1 and 4.75 ppm respectively (Quirk & Hsieh, 1996). <sup>1</sup>H NMR spectra revealed that all PIs have a high 1,4-content (92 to 94%). Representative NMR spectra are given in Figure 4. Also, NMR spectrum doesn't show signal at δ 5.8 ppm which indicates that there is no formation of 1,2-vinyl microstructure.

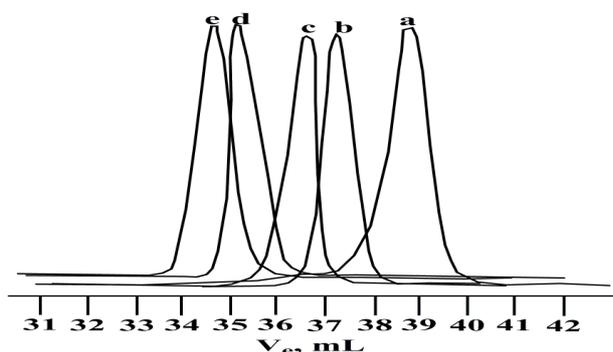


Figure 3. SEC Traces of Linear (a: 10.5kg/mol arm) and 2-arm (b: 23 kg /mol), 3-arm(c: 30.27K), 4-arm(d:39.76K) and 6-arm (e:64.05K) star PIs

Table 1. Molecular Characterization Results for Star Polyisoprenes (PIs) and the Corresponding Arms

Sr. No.	1,4-PIs	Arm (SEC)			Fractionated Star PIs (SEC-MALLS)	
		$M_n$ [kg/mol(cal.) <sup>a</sup> ]	$M_n$ [kg/mol (SEC) <sup>b</sup> ]	$M_w/M_n$	$M_n$ [kg/mol]	$M_w/M_n$
1	Linear	100	96	1.01	89.21	1.02
2	3-arm star	50	46	1.01	132.7	1.03
3	4-arm star	50	46	1.01	181.7	1.01
5	6-arm star	50	46	1.01	267.7	1.01
6	8-arm star	60	55	1.01	415.4	1.01
7	Linear	74	68	1.01	68.13	1.02
8	3-arm star	35	38	1.03	101.0	1.01
9	4-arm star	35	38	1.03	133.2	1.01
10	6-arm star	35	38	1.03	201.4	1.01
11	Linear	22	23	1.01	21.41	1.02
12	3-arm star	10	10.5	1.02	30.27	1.02
13	4-arm star	10	10.5	1.02	39.76	1.03
14	6-arm star	10	10.5	1.02	64.05	1.02

a.  $M_n$  = g of monomer/ moles of initiator ; b.  $M_n$  SEC-PS/1.6

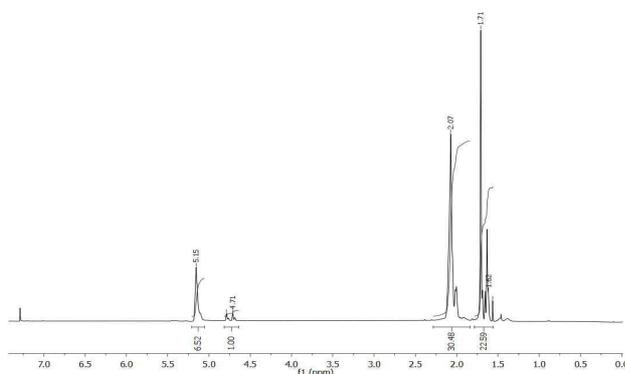


Figure 4. <sup>1</sup>H NMR spectra for 8-arm star PI (arm 55 kg/mol) (93 % 1,4-microstructure)

### 3.3. Isomeric Composition by <sup>13</sup>C NMR Spectroscopy

The <sup>13</sup>C NMR spectra of PIs are rich in microstructural information. For example, C1 (CH<sub>2</sub>) carbon is observed at  $\delta$  32.08 and 39.70 ppm for *cis*-1,4- and *trans*-1,4-microstructural units, respectively. The C5 (CH<sub>3</sub>) resonances are observed at  $\delta$  = 23.25, 15.76 and 18.74 ppm for the *cis*-1,4, *trans*-1,4- and 3,4 units, respectively. 6-arm star PI (arm 38 kg/mol) shows 76% *cis*-1,4-, 18% *trans*-1,4-, and 6% 3,4-microstructures.

### 3.4. Thermal Transition Study of Star PIs by DSC

The Differential Scanning Calorimetry (DSC) was used to determine the  $T_g$  of all star PI polymers. As expected, all

polymers have practically the same  $T_g$  (-61.0 to -62.0°C), since they possess almost the same microstructure and their MW is higher than the critical one (10 kg/mol).

## 4. Conclusion

By using well established chlorosilane chemistry approaches and anionic polymerization high vacuum techniques we have successfully synthesized, for the first time, three series of star-branched PI containing 2 (linear), 3, 4, 6 and 8 arms, with arm molecular weights ranging from 10.5 to 46 kg/mol. The synthetic methodology involves the end capping of living polyisoprene (PILi) with a few units of butadiene, followed by the linking reaction of an excess of PI(Bd)<sub>2-4</sub>Li with an appropriate chlorosilane to produce the

corresponding regular star-branched polymers. The excess of the arm was removed from the final reaction product by repeated fractionations with toluene/methanol (solvent/non-solvent methodology). All intermediates and final star PIs were characterized by SEC, SEC-MALLS and NMR. The thermal behaviour of the star polymers was analyzed using differential scanning calorimetry. Such series of model polymers are useful and essential in establishing the structure/properties relationships of polymeric materials.

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