

Hexaarm Star-Shaped Polystyrenes by Core-First Method

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The hexafunctional initiator $C_6[(CH_2)_2p-C_6H_4CH(Cl)Me]_6$ is synthesized by $Fe(\eta-C_5H_5)^+$ induced hexabenzoylation of C_6Me_6 followed by regiospecific acetylation, $NaBH_4$ reduction and chlorination, and allows the living cationic polymerization of styrene which yields hexaarm star-shaped polymers.

Star-branched polymers are a category of polymeric architectures which have received much attention in recent years, given their unique solution and bulk properties.¹⁻³ End functionalised star polymers can serve as useful intermediates in polymer synthesis, for instance, as precursors in the synthesis of dendritic polymers,⁴ and as cross-linking agents.¹⁻³ Much effort has been directed toward elaborating star-branched polymers with well-defined structures. Most applications of star molecules require samples that exhibit a low fluctuation of the number and size of the arms.

There are two synthetic methods leading to star-branched polymers. The 'arm-first' method is based on the synthesis of a linear 'living' polymer and its treatment with a polyfunctional deactivating reagent.^{1a-c} The star central core may also be built upon copolymerization of a 'living' linear polymer with a difunctional monomer but, in the latter case, some fluctuation in star functionality cannot be avoided.^{1c,d,2} The 'core-first' method uses a polyfunctional initiator from which branches can be grown.³ If all of the active sites of the initiator give rise to branches, the functionality of the resulting star will thus be defined by the initiator.

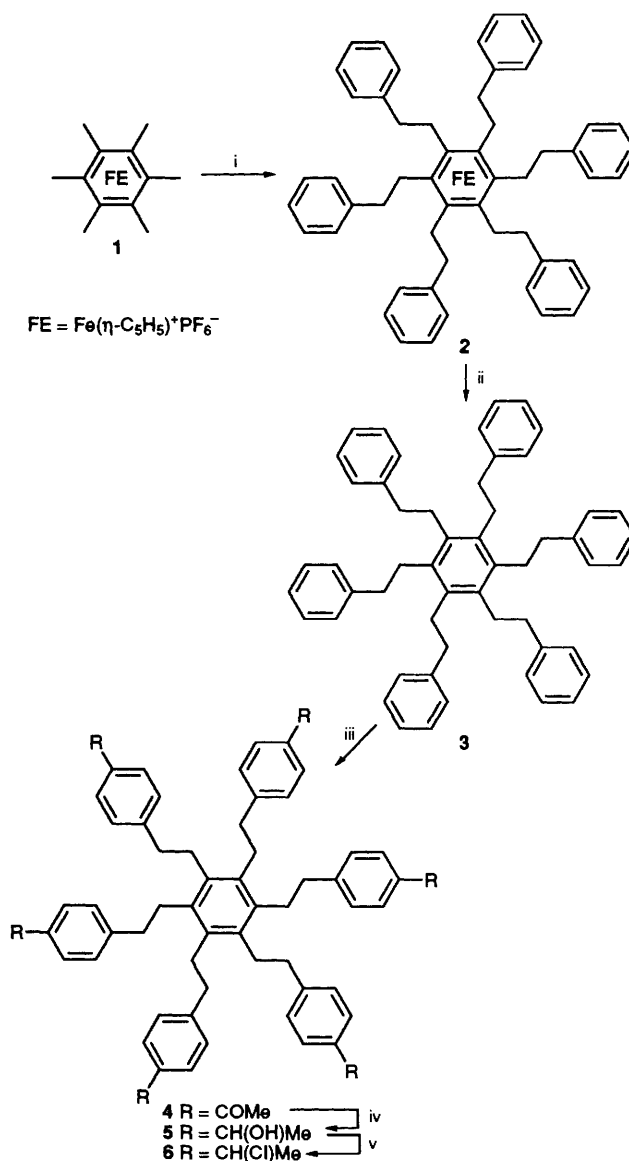
The lack of polyfunctional initiators prompted us to address this topic. We wish to elaborate compounds of a precise number of identical functional groups that could serve to prepare star-shaped polymers *via* the core-first method. The $Fe(\eta-C_5H_5)^+$ induced perfunctionalization of polymethylaromatics offers opportunities for devising a variety of initiators.⁵ We report here our first results based on this strategy which uses the one-pot hexabenzoylation of $[Fe(\eta-C_5H_5)(C_6Me_6)]^+[PF_6]^-$, **1** (Scheme 1). Subsequent to the appropriate regiospecific parafunctionalization of the outer phenyl rings, star-shaped polystyrene samples have been synthesized by living cationic polymerization of styrene.⁷ There has been so far only one report of 'core-first' synthesis of hexabranch polymers.^{3e}

The hexafunctional reagent **6**, which has been designed as cationic initiator of styrene polymerization, is synthesized by hexafunctionalization of $[Fe(\eta-C_5H_5)(C_6(CH_2CH_2Ph)_6)]^+[PF_6]^-$, **2**. This compound is obtained by the one-pot hexabenzoylation of **1** subsequent to clean photodecomplexation (UV Hg lamp)⁸ of **2** in MeCN giving $C_6(CH_2CH_2Ph)_6$, **3** in 86% yield, after oxidation (H_2SO_4) of the ferrocene formed and extraction with ether. The reaction of **3** with $MeCOCl + Al_2Cl_6$ in CH_2Cl_2 at 20 °C for 12 h gives the hexaketone $C_6(CH_2CH_2p-C_6H_4COMe)_6$, **4** in 86% yield; the subsequent $NaBH_4$ reduction of **4** in $MeOH-CH_2Cl_2$ at 20 °C for 12 h gives the hexaol $C_6[CH_2CH_2p-C_6H_4CH(OH)Me]_6$, **5** in 72% yield. Reaction of **5** with $SOCl_2$ at 20 °C for 12 h gives $C_6[CH_2CH_2p-C_6H_4CH(Cl)Me]_6$, **6** in 100% yield.

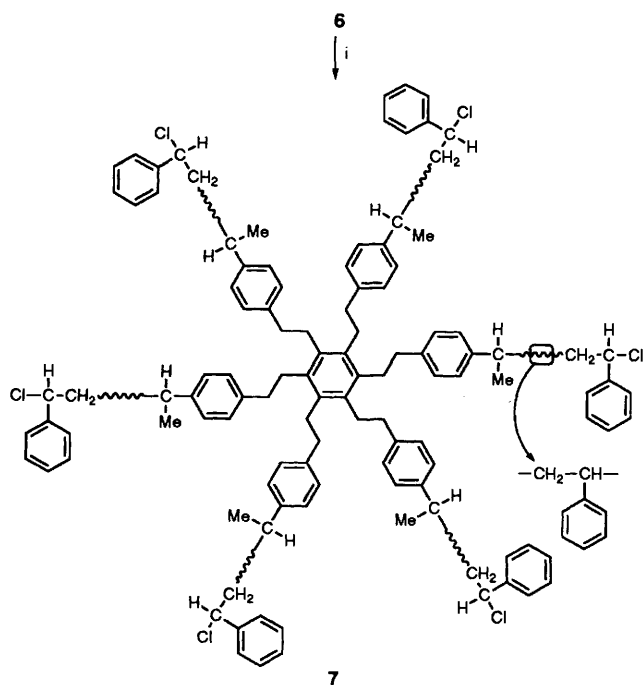
When carried out in the presence of **6**, 5 equiv. of $SnCl_4$ and 2 equiv. of $Bu^+N^+Cl^-$, the cationic polymerization of styrene gave rise to the expected star-shaped polymers. The polymerization process is performed in CH_2Cl_2 at -15 °C (Scheme 2). Depending upon the amount of styrene introduced and the reaction time, polystyrene stars whose molecular weights range from a few thousands to 40 000 $g\ mol^{-1}$ are obtained. Polymers with 60 styrene units per arm, which corresponds to

a total molecular mass of 36 000 $g\ mol^{-1}$, are accessible within one hour of polymerization (Fig. 1). Characterization of the stars by size exclusion chromatography (SEC) equipped with light scattering detectors yields the actual molar masses (\overline{M}_w and \overline{M}_n) of the samples and shows that all of them exhibit polydispersity indexes close to unity ($\overline{M}_w/\overline{M}_n \approx 1.1$).

These polymers were also characterized by NMR: from the intensity of the signal corresponding to the terminal PhCHCl unit and that of the signal due to styrene units, it is possible to calculate the number average molar mass of each sample.



Scheme 1 Reagents and conditions: i, Bu^+OK , $PhCH_2Br$, DME, 40 °C; ii, hv, MeCN, room temp.; iii, $MeCOCl$, $AlCl_3$, CH_2Cl_2 , room temp.; iv, $NaBH_4$; v, $SOCl_2$



Scheme 2 Reagents and conditions: i, SnCl_4 , $\text{Bu}_4\text{N}^+\text{Cl}^-$, styrene, CH_2Cl_2 , -15°C

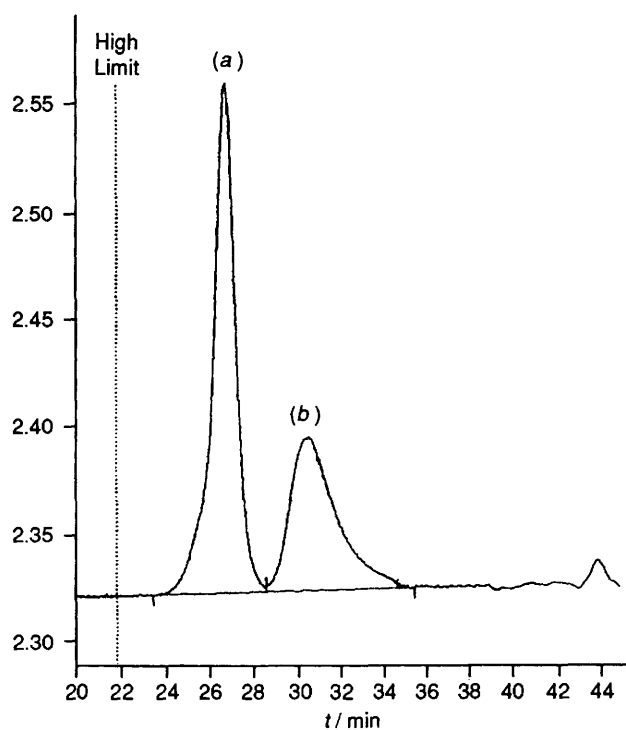


Fig. 1 GPC trace (a) of the six-armed polystyrene (average molecular weight obtained by light scattering $\bar{M}_n = 38000 \text{ g mol}^{-1}$) and (b) of a linear polystyrene used as internal standard ($\bar{M}_n = 6200 \text{ g mol}^{-1}$). Both polymers were grown as a mixture ($\bar{M}_w/\bar{M}_n \approx 1.1$ for both).

Values obtained by this technique lie in close agreement with those derived *via* SEC.

In conclusion, the good control of molar masses of the samples as well as the excellent polydispersity indexes obtained confirm the efficiency of our hexafunctional initiator. These results pave the way for the synthesis of other types of star-shaped polymers and for the development of star-branched block copolymers. More generally, branched polymers with various topologies should be accessible using the $\text{Fe}(\eta\text{-C}_5\text{H}_5)^+$ induced perfunctionalization of polymethylaromatics.[†]

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Footnote

[†] Subsequent to the 'freeze-drying' of 0.3 g of **6** (1 equiv.), 50 ml of CH_2Cl_2 are introduced at -15°C under N_2 ; 0.15 g of $\text{Bu}_4\text{N}^+\text{Cl}^-$ (2 equiv.), 1.4 ml of SnCl_4 (5 equiv.) and 5.5 ml of styrene (180 equiv.) are subsequently added at -15°C . The reaction mixture is allowed to stir between 15 min. and 1 hour depending on the polymer size, then quenched by 5 ml of methanol containing 1 ml of concentrated aqueous NH_3 . The reaction mixture is filtered and concentrated and excess methanol is added so as to precipitate the polymer. Filtration and drying yields a polymer suitable for SEC analysis. The chromatogram of this polymer ($\bar{M}_n = 36000$) is shown in Fig. 1. Other polymers of different \bar{M}_n are similarly obtained by varying the amount of styrene and the reaction time.

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