

# Synthesis and Characterization of Ferrocene-Containing Hyperbranched Poly(aryolarylene)s

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**Abstract** Ferrocene-containing hyperbranched poly(aryolarylene)s are prepared in satisfactory yields by one-pot copolycyclotrimerization of bis(aryolacetylene)s with a ferrocene-containing monoyne. The ferrocene content of the polymers can be varied by changing the monomer feed ratio, and copolymers with up to 41 mol% of ferrocene moiety can be readily prepared. All the polymers are thermally stable, losing little of their weights when heated to 340 °C.

**Keywords** Cyclotrimerization · Ferrocene · Hyperbranched polymer

## 1 Introduction

Synthesis of organometallic polymers has received much attention in recent years because of the expectation that their novel electrical, magnetic, optical, and catalytic properties will enable them to find an array of high-technology applications [1–4]. So far, the most widely studied organometallic polymers are those with metallocenes [5–9]. The first metallocene-containing polymer can be traced to the polymerizations of vinylferrocenes reported by Arimoto and Haven in 1995 [10]. Besides utilization as

side chains, the metallocene can be an integral part of the polymer backbone. For example, the ring-opening polymerizations of silicon-bridged silaferrocenophanes yield poly(ferrocenylsilane)s, which show an array of novel functional properties and have served as processable polymer precursors to ceramic materials [11].

Recently, we succeeded in exploring a new synthetic route for the construction of processable hyperbranched poly(aryolarylene)s by diyne polycyclotrimerization initiated by the simple base, piperidine [12]. Thanks to its ionic mechanism, the polycyclization is strictly regioselective and highly functionality-tolerant. With triarylbenzene units as the branching centers, the polymers are readily crosslinkable by UV irradiation with high photosensitivities, and can generate photopatterns with nanometer resolution. In order to endow the polymers with new functionalities, in this paper, we report the synthesis of organometallic hyperbranched poly(aryolarylene)s by copolycyclotrimerization of bis(aryolacetylene)s with a ferrocene-containing monoyne (Scheme 1). We choose ferrocene as one of the building blocks because of its high stability as well as its novel material properties [13–16]. A wealth of ferrocenyl dendrimers has been synthesized [17–21]. There have however, been very few reports on the synthesis of ferrocene-containing hyperbranched polymers [22–26], although the study of hyperbranched polymers is a hot topic of current interest [27–34].

This article is dedicated to Professor Didier Astruc.

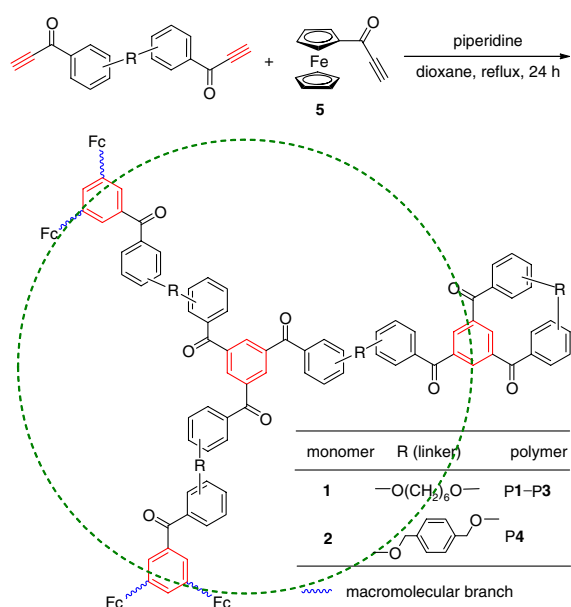
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## 2 Experimental

### 2.1 Materials

Monomers **1** and **2** were prepared according to our previous publications [12]. All the chemicals used in this study



**Scheme 1** Copolycyclotrimerization of Bis(aroylacetylene)s **1** and **2** with Ferrocenyl-Containing Monoynes **5**

were purchased from Aldrich. 1,4-Dioxane, tetrahydrofuran (THF), dichloromethane (DCM), and piperidine were distilled over sodium benzophenone ketyl or calcium hydride prior to use. All other solvents and reagents were used as received without further purification.

## 2.2 Instrumentation

The molecular weights of the polymers were estimated by a Waters Associates gel permeation chromatograph (GPC) system. IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using dichloromethane- $d_2$  or chloroform- $d$  as solvents and tetramethylsilane (TMS) as the internal reference ( $\delta = 0$ ). Mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole spectrometer operating in a chemical ionization (CI) mode using methane as the carrier gas. Thermal stability was evaluated on a Perkin-Elmer thermogravimetric analyzer TGA 7 at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  under nitrogen.

## 2.3 Synthesis of Ferrocenylcarbonylacetylene (**5**)

Into a 250 mL two-necked round bottom flask was dissolved 1 g (4.7 mmol) of ferrocenecarboxaldehyde in 40 mL of THF under nitrogen. The flask was cooled to  $0\text{ }^\circ\text{C}$  with an ice bath and 20 mL of 0.5 M ethynylmagnesium bromide (10 mmol) was slowly added. The

solution was stirred at room temperature for 12 h and the reaction was quenched by 40 mL of saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The solution was extracted with dichloromethane several times and dried over anhydrous  $\text{MgSO}_4$ . Evaporation of the solvent gave red crude product **7**. Without further purification, **7** was dissolved in dichloromethane (100 mL) at room temperature and 7.58 g (65.4 mmol) of activated manganese (IV) oxide was added. The mixture was stirred overnight and filtered through a short silica gel column to remove the insoluble materials. Monomer **5** was further purified by silica gel column chromatography using chloroform as eluent. Red solid; yield 74.7% (0.83 g). Characterization data: IR (thin film),  $\nu$  ( $\text{cm}^{-1}$ ): 3229 ( $\equiv\text{C-H}$  stretching), 3103 (Ar-H stretching), 2091 ( $\text{C}\equiv\text{C}$  stretching), 1618 ( $\text{C=O}$  stretching), 1449 ( $\text{C=C}$  ring stretching), 1273, 832, 758.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 4.95 [t, 2H, Ferrocene (Fc)-H], 4.64 (t, 2H, Fc-H), 4.28 (s, 5H, Fc-H), 3.27 (s, 1H,  $\equiv\text{CH}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 180.28 ( $\text{C=O}$ ), 81.26, 79.53, 76.49, 73.51, 70.50. MS (CI):  $m/e$  237.9 [ $\text{M}^+$ , calcd for  $\text{C}_{13}\text{H}_{10}\text{FeO}$ : 238.01].

## 2.4 Polymerization

All the polymerization reactions were carried out in nitrogen atmosphere using standard Schlenk technique (Scheme 1). Typical procedures for the synthesis of P1 from **1** and **5** are given below as an example.

In a 15 mL Schlenk tube with a three-way stopcock on the sidearm was placed 50 mg of **1** (0.134 mmol) and 32 mg of **5** (0.134 mmol) under nitrogen in a glovebox. Distilled dioxane (0.80 mL) was injected into the tube using a hypodermic syringe, followed by addition of a dioxane (0.15 mL) solution of piperidine (0.267 M). The solution was stirred and refluxed for 24 h. Afterwards, the polymerization mixture was added dropwise to 300 mL methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and was collected by filtration. The isolated polymer was washed with methanol and dried under vacuum at room temperature to a constant weight. Characterization data: Red powder; yield 67%.  $M_w$  22900;  $M_w/M_n$  4.3 (GPC, polystyrene calibration). IR (thin film),  $\nu$  ( $\text{cm}^{-1}$ ): 3080, 3009 (Ar-H stretching), 2940, 2861 ( $\text{CH}_2$  stretching), 1659 ( $\text{C=O}$  stretching), 1579, 1442 ( $\text{C=C}$  ring stretching), 1273, 1028, 1004, 749.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  (ppm): 8.76, 8.64, 8.58, 8.49, 8.41, 3.38, 8.32, 7.93, 7.52, 7.38, 7.12, 4.96, 4.91, 4.86, 4.65, 4.25, 4.13, 4.00, 1.82, 1.55.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 197.68, 194.71, 159.34, 158.61, 138.10, 137.66, 133.95, 132.55, 130.30, 129.55, 122.83, 121.13, 120.16, 118.14, 117.23, 114.77, 73.12, 71.49, 70.40, 68.11, 67.47, 29.08, 27.66, 25.82, 24.44.

Other polymers (P2–P4) are prepared by similar procedures, using different amounts of **5** or diyne monomer (**2**). Their characterization data are shown below:

**P2** Red powder; yield 54%.  $M_w$  15000;  $M_w/M_n$  3.3 (GPC, polystyrene calibration). IR (thin film),  $\nu$  ( $\text{cm}^{-1}$ ): 3082, 3015 (Ar–H stretching), 2940, 2867 ( $\text{CH}_2$  stretching), 1661 ( $\text{C}=\text{O}$  stretching), 1580, 1442 ( $\text{C}=\text{C}$  ring stretching), 1273, 1005, 750.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  (ppm): 8.76, 8.64, 8.58, 8.49, 8.42, 8.38, 8.32, 8.28, 7.93, 7.50, 7.38, 7.34, 7.12, 4.91, 4.86, 4.64, 4.25, 4.19, 4.02, 1.82, 1.55.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 197.58, 194.70, 159.33, 138.08, 137.91, 137.65, 133.96, 133.57, 130.29, 129.48, 122.70, 121.11, 120.13, 117.22, 114.78, 73.10, 70.33, 68.09, 67.46, 29.07, 27.64, 25.80, 24.42.

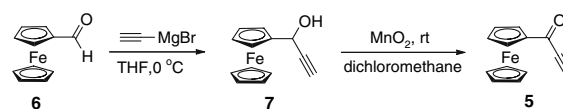
**P3** Red powder; yield 55%.  $M_w$  11400;  $M_w/M_n$  3.0 (GPC, polystyrene calibration). IR (thin film),  $\nu$  ( $\text{cm}^{-1}$ ): 3084, 3015 (Ar–H stretching), 2941, 2867 ( $\text{CH}_2$  stretching), 1661 ( $\text{C}=\text{O}$  stretching), 1579, 1441 ( $\text{C}=\text{C}$  ring stretching), 1273, 1005, 750.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  (ppm): 8.86, 8.76, 8.64, 8.58, 8.49, 8.41, 8.38, 7.93, 7.50, 7.38, 7.14, 4.96, 4.91, 4.86, 4.65, 4.31, 4.25, 4.19, 4.02, 1.82, 1.55.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 197.76, 195.08, 194.67, 159.30, 158.58, 139.82, 139.57, 138.06, 137.88, 137.63, 134.50, 133.94, 133.49, 132.89, 132.36, 131.77, 131.26, 129.54, 122.63, 121.00, 119.98, 118.18, 117.31, 114.83, 73.08, 71.48, 70.37, 68.07, 29.04, 27.63, 25.77, 24.04, 22.00.

**P4** Red powder; yield 64%.  $M_w$  7600;  $M_w/M_n$  3.2 (GPC, polystyrene calibration). IR (thin film),  $\nu$  ( $\text{cm}^{-1}$ ): 3084, 3014 (Ar–H stretching), 1649 ( $\text{C}=\text{O}$  stretching), 1599, 1449 ( $\text{C}=\text{C}$  ring stretching), 1251, 1000, 843, 755.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  (ppm): 8.77, 8.67, 8.58, 8.53, 8.47, 8.39, 8.30, 8.28, 8.13, 8.11, 7.89, 7.86, 7.50, 7.05, 5.16, 4.92, 4.88, 4.64, 4.29, 4.26.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 197.8, 193.9, 162.7, 139.7, 138.6, 136.1, 133.1, 132.1, 131.2, 129.5, 127.8, 115.9, 114.7, 90.2, 73.1, 71.5, 70.4.

### 3 Results and Discussion

#### 3.1 Monomer Synthesis

To enrich the research field of organometallic hyperbranched polymers, we synthesized a monoyne with ferrocene moiety (**5**), with an aim that its copolymerization with bis(aryolacetylene)s (**1** and **2**) will furnish organometallic hyperbranched polymers. The monoyne was synthesized by nucleophilic addition of ferrocenecarboxaldehyde with Grignard reagent followed by oxidation of the resulting alcohol with activated  $\text{MnO}_2$ . The monomer was characterized spectroscopically with satisfactory results (Scheme 2).



**Scheme 2** Synthesis of Ferrocene-Containing Monoyne **5**

#### 3.2 Polymerization

Table 1 summarizes the polymerization results of diynes **1** and **2** with monoyne **5**. All the polymerizations undergo smoothly, yielding polymers with high molecular weights in moderate yields. We change the ratio of **1–5** from 1:1 to 1:3 in order to tune the content of ferrocene in the resulting copolymers. With an increase in monoyne concentration from 0.14 to 0.42 M, the molecular weight of the polymer decreases by more than two-fold. It is understandable because **5** functions as an end-capping reagent and hampers the growth of the polymer chains.

#### 3.3 Structural Characterization

The molecular structures of the polymers are characterized by spectroscopic methods and all give satisfactorily analytical data corresponding to their expected molecular structures. An example of the  $^1\text{H}$  NMR spectrum of **P1** is shown in Fig. 1; for comparison, the spectra of its monomers are also shown in the same figure. The spectrum of **P1** shows no resonance peaks of the ethynyl protons (a and e) of **1** and **5** at  $\delta$  3.44 and 3.26 (Fig. 1). Three peaks associated with the cyclopentadienyl ring absorptions of the ferrocene are observed at  $\delta$  4.91, 4.66, and 4.24. The polymerization also shifts the resonances of the phenyl protons of **1** at  $\delta$  7.77 and 7.62 to  $\delta$  7.38. New peaks appear at  $\delta$   $\sim$  8.43–7.91, which are assignable to the proton resonances of the new benzene rings formed by the polymerization.

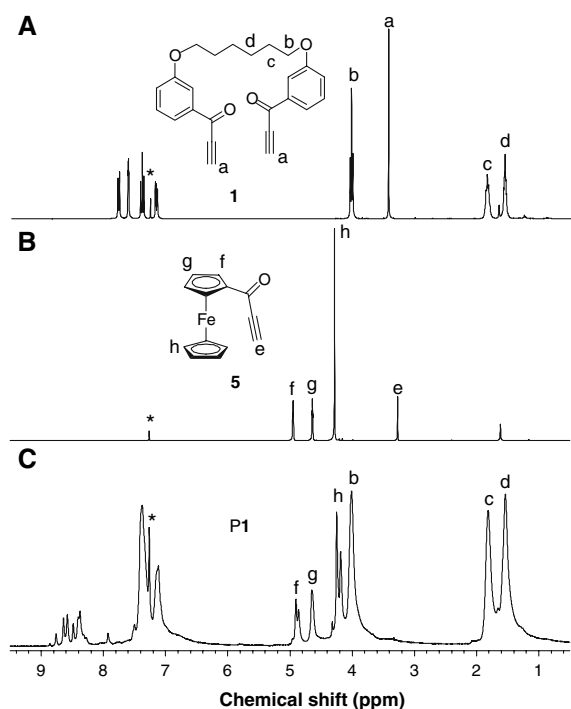
**Table 1** Copolymerization of diynes **1** and **2** with monoyne **5**<sup>a</sup>

Polymer	Diyne	$[\text{M}_{\text{II}}]:[\text{5}]$	Yield (%)	$M_w^b$	PDI <sup>b</sup>	mol% of <b>5</b> <sup>c</sup>
<b>P1</b>	<b>1</b>	1:1	67	22,900	4.3	24.3
<b>P2</b>	<b>1</b>	1:2	54	15,000	3.3	30.8
<b>P3</b>	<b>1</b>	1:3	55	11,400	3.0	41.1
<b>P4</b>	<b>2</b>	1:2	64	7,600	3.2	30.5

<sup>a</sup> Catalyzed by piperidine in dioxane under reflux for 24 h in nitrogen.  $[\text{Diyne}] = [\text{M}_{\text{II}}] = 0.14$  M,  $[\text{piperidine}] = 42$  mM (**P1–P3**);  $[\text{M}_{\text{II}}] = 0.10$  M,  $[\text{piperidine}] = 30$  mM (**P4**). Abbreviation: PDI = polydispersity index

<sup>b</sup> Determined by GPC in THF on the basis of a polystyrene calibration

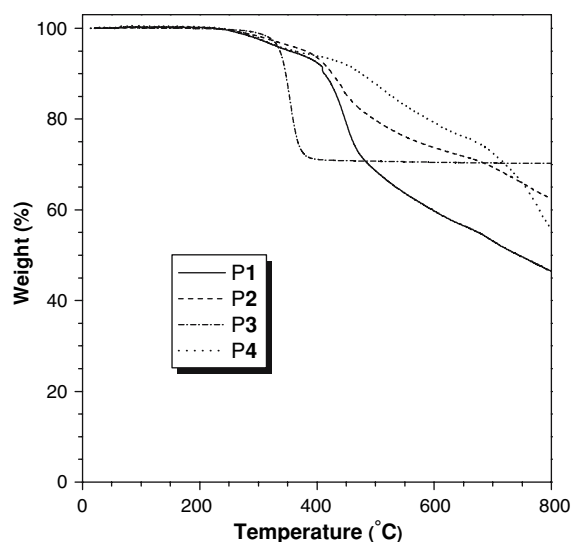
<sup>c</sup> Determined by  $^1\text{H}$  NMR analysis



**Fig. 1** <sup>1</sup>H NMR spectra of (a) diyne **1**, (b) monoynne **5**, and (c) their copolymers P1 in chloroform-*d*. The solvent peaks are marked with asterisks (\*)

### 3.4 Thermal Properties

The thermal properties of the hyperbranched polymers are investigated by thermogravimetric analysis (TGA) under nitrogen (Fig. 2). All the copolymers are thermally stable and degrade at high temperature (340–380 °C). It is noteworthy that after pyrolyzed at 800 °C, the amount of



**Fig. 2** TGA thermograms of hyperbranched poly(aroylarylene)s P1–P4 recorded under nitrogen at a heating rate of 20 °C/min

residue left for the polymers is high (43–70 %), suggesting that they are promising candidates as precursors for ceramic materials [23, 24].

## 4 Conclusion

In summary, in this study, we have successfully prepared a series of ferrocene-containing hyperbranched polymers. Copolycondensation of bis(aroylacetylene)s with a ferrocene-containing monoynne **5** undergo smoothly in refluxed dioxane, giving hyperbranched poly(aroylarylene)s in satisfactory yields. The ferrocene content can be varied with ease by changing the monomer feed ratio and copolymer with a ferrocene content up to 41 mol% can be readily prepared. All the polymers enjoy good thermal stability and degrade at high temperature ( $\geq 340$  °C).

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