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# Construction of Hyperbranched Polyphenylenes Containing Ferrocenyl Units by Alkyne Polycyclotrimerization

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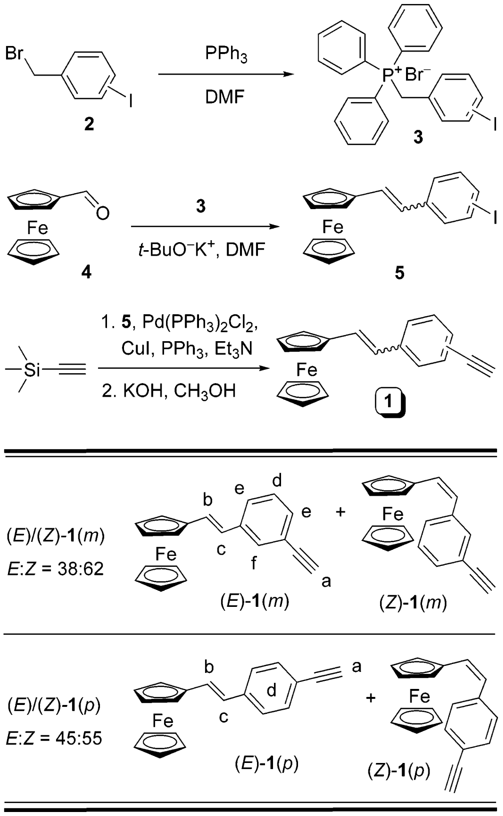
ABSTRACT: Copolycyclotrimerizations of [(*E*/*Z*)-2-(1-ferrocenyl)vinyl]-*m*/*p*-phenylacetylene [(*E*/*Z*)-**1**(*m*/*p*)] with 1,8-nonadiyne (**I**) were studied. The conformation of the vinyl unit of **1** affected the polycyclotrimerization reaction dramatically: while (*Z*)-**1** failed to give any polymeric products, its *E* isomer underwent polymerization smoothly, producing hyperbranched copolymers *hb*-P**1**/**I** in good to high yields (up to 100 wt %). The hyperbranched copolymers are soluble in common organic solvents and are thermally stable, losing little of their weights when heated to high temperatures (up to 466 °C). The incorporation of the ferrocenyl moiety endowed the copolymers with redox activity.

## Introduction

Dendrimers containing electrochemically active moieties have attracted much attention due to their potential applications as multielectron redox catalysts, electron reservoirs, electrode modifiers, ion sensors, and biomimics of the redox processes in the living system. Thanks to the enthusiastic efforts of polymer chemists, a variety of redox-active dendrimers have been synthesized.[1] Among them, most are ferrocenyl dendrimers since ferrocene exhibits stable redox properties and can be readily functionalized. There have, however, been very few reports on the synthesis of ferrocene-containing hyperbranched polymers,[2] although the study of hyperbranched polymers is a hot topic of current interest.[3,4]

We are interested in creating new polymers with novel structures and unique properties. Alkyne has been our favorite monomer. Utilizing the triple-bond building blocks, we have successfully generated, via polycyclotrimerization and polycoupling, hyperbranched polyarylenes and polyynes with excellent thermal stability, high photoluminescence efficiency and strong optical nonlinearity,[5] in addition to a large number of linear polyenes (or polyacetylenes) through metathesis and addition polymerizations.[6] In this work, we intend to synthesize new hyperbranched polymers containing ferrocene moieties. We prepared ferrocenyl monoynes **1** (Scheme 1) and studied their copolycyclotrimerizations with diyne **I** (Schemes 2 and 3). In this paper, we report the polymerization behaviors of **1** as well as the structures and properties of the resultant copolymers *hb*-P**1**/**I**.

**Scheme 1**



## Experimental Section

**Materials.** Toluene (BDH) and THF (Lab-Scan) were distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Triethylamine (RdH) was distilled under normal pressure and kept over potassium hydroxide under nitrogen. DMF (Aldrich) was dried over, and distilled from, calcium hydride under normal pressure. Dichloromethane (DCM; Lab-Scan) was dried over molecular sieves and distilled from calcium hydride under dry nitrogen. Copper(I) iodide, 3-iodobenzyl bromide, 18-crown-6, dichlorobis(triphenylphosphine)palladium(II), 4-iodobenzyl bromide, potassium *t*-butoxide, ferrocene carboxaldehyde, tetraphenyltin, tantalum(V) bromide, 1,8-nonadiyne, trimethylsilylacetylene, chloroform, potassium iodide, triphenylphosphine, acetone, methanol, hexane, and potassium hydroxide were all purchased from Aldrich and used as received without further purification. Intermediates **3** were prepared from *m*/*p*-iodobenzyl bromide (**2**) and triphenylphosphine in DMF (cf., Scheme 1).

**Instrumentation.** $^1$H and $^{13}$C NMR spectra were measured on a Bruker ARX 300 spectrometer using tetramethylsilane (TMS; $\delta$

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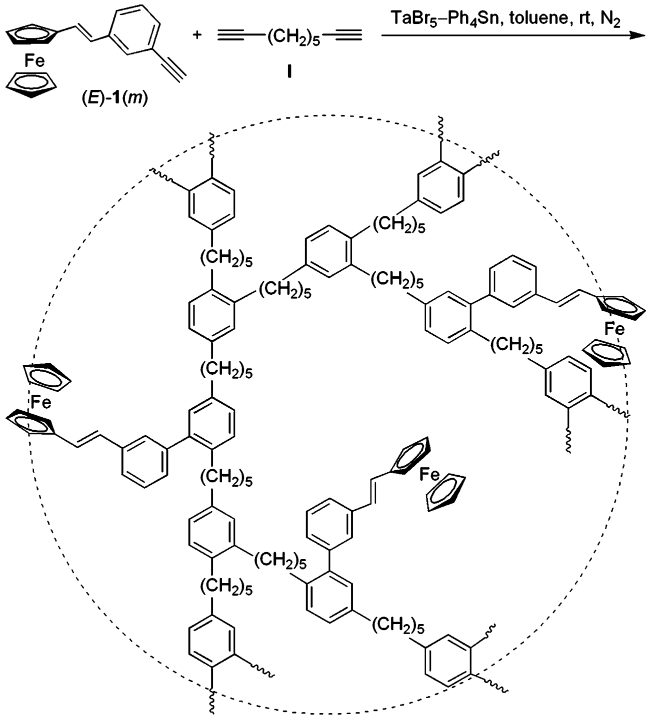
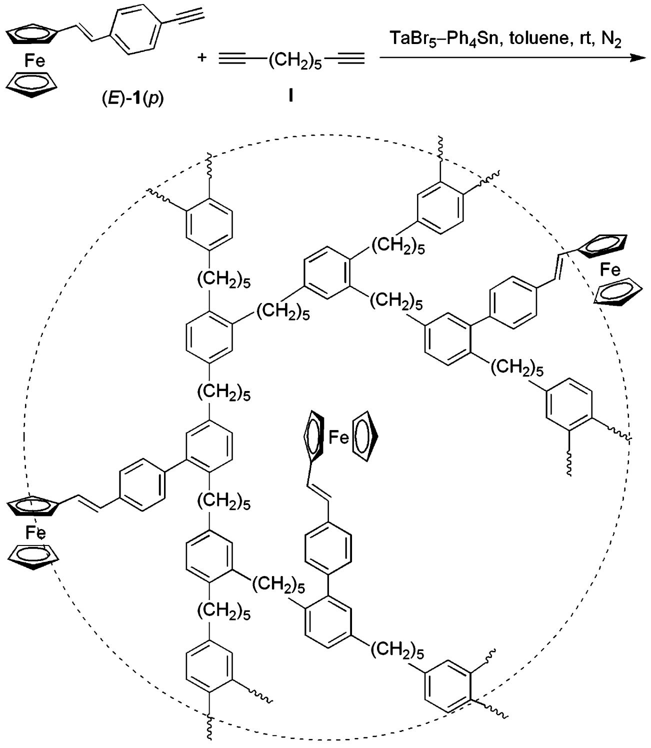
**Scheme 2**



Hyperbranched poly(ferrocenylarylene)s *hb*-P**1**(*m*)/**I**

**Scheme 3**



Hyperbranched poly(ferrocenylarylene)s *hb*-P**1**(*p*)/**I**

$= 0$ ppm) as internal standard. IR spectra were taken on a Perkin-Elmer 16 PC spectrometer. Mass spectra were recorded on a Finnigan TSQ 7000 triple quadrupole spectrometer operating in a chemical ionization (CI) mode using methane as carrier gas. UV–vis absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Thermal transitions of the polymers were investigated using a Setaram differential scanning calorimeter DSC92 under nitrogen at a scanning rate of 10 °C/min, and their thermal stabilities were evaluated on a Perkin-Elmer TGA 7 at a heating rate of 20 °C/min under nitrogen. Molecular weights of the polymers were estimated by a Water 510 GPC system equipped with a RI detector and a UV detector with its working wavelength set at 254 nm, using monodisperse polystyrenes as calibration standards and THF as eluent at a flow rate of 1.0 mL/min.

Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW 1830 powder diffractometer using monochromatized X-ray beam from a nickel-filtered Cu $K_\alpha$ radiation ($\lambda = 1.5406$ Å). Crystal X-ray diffraction intensity data were collected at 295 or 100 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo $K_\alpha$ radiation. Single crystals of (*E*)-**1**(*m*) and (*E*)-**1**(*p*) were both grown from chloroform. The intensity data was processed using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (Version 6.10). Cyclic voltammograms were recorded on a Princeton Applied Research model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag/AgNO$_3$ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to ferrocenium-ferrocene (Cp$_2$Fe$^{+/0}$).

**Monomer Synthesis.** The monoyne comonomers (**1**) were prepared according to the reaction routes given in Scheme 1.

**[(*E*/*Z*)-2-(1-Ferrocenyl)vinyl]-*m*-iodobenzene [(*E*/*Z*)-5(*m*)].** Ferrocene carboxaldehyde (**4**; 2.14 g, 10.0 mmol), **3** (5.8 g, 10.4 mmol), and a catalytic amount of 18-crown-6 were dissolved in 100 mL of DMF under nitrogen. The solution was cooled to 0−5 °C with an ice bath, to which 2.8 g of potassium *t*-butoxide (25 mmol) was added. The mixture was stirred under nitrogen at room temperature for 2 days. The reaction mixture was poured into a large amount of water (~700 mL). The precipitate was collected and further purified by a silica gel column using hexane as eluent. The brown red mixture of *E*- and *Z*-isomers of the product was obtained in 84.5% yield (3.5 g) and used directly for the next step of the reaction.

**[(*E*/*Z*)-2-(1-Ferrocenyl)vinyl]-*p*-iodobenzene [(*E*/*Z*)-5(*p*)].** The intermediates were prepared by the procedures similar to those described above for their *m* isomers, i.e., (*E*/*Z*)-**5**(*m*). The products were obtained in 81% as a brown red mixture of *E*- and *Z*-isomers.

**[(*E*/*Z*)-2-(1-Ferrocenyl)vinyl]-*m*-phenylacetylene [(*E*/*Z*)-1(*m*)].** To a 250 mL flask were added 3.35 g of *(E*/*Z)*-**5**(*m*) (8 mmol), 40 mg of copper(I) iodide, 40 mg of triphenylphosphine, and 120 mg of dichlorobis(triphenylphosphine)palladium in the glovebox. Triethylamine (200 mL) and 3 g (30 mmol) of trimethylsilylacetylene were then injected. The resultant mixture was stirred at room temperature for 40 h. The precipitate was removed by filtration. After removal of the solvent, the crude product was purified on a silica gel column using hexane as eluent. The isolated mixture of *E*- and *Z*-isomers of [(*E*/*Z*)-2-(1-ferrocenyl)vinyl]-*m*-(phenyl)-trimethylsilylacetylene was used directly for the next step of the reaction.

To a 250 mL flask were added the product obtained above, 3.0 g of potassium hydroxide (54 mmol), 50 mL of THF, and 180 mL of methanol. The resultant mixture was stirred at room temperature for 23 h. The reaction mixture was then poured into a large amount of water. The brown red precipitate was collected and further purified by a silica gel column using hexane as eluent very carefully. The *E*- and *Z*-isomers of the product were successfully separated and isolated.

**(*E*)-1(*m*).** Red brown powder (0.50 g, 20%). $^1$H NMR (300 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 7.62 (s, 1H), 7.41 (d, 2H), 7.32 (m, 1H), 6.89 (d, 1H), 6.69 (d, 1H), 4.49 (s, 2H), 4.31 (s, 2H), 4.16 (s, 5H), 3.11 (s, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 139.1, 130.6, 129.8, 129.5, 129.2, 129.0, 127.1, 126.5, 125.3, 123.1, 84.3, 83.4, 77.6, 69.9, 67.7. MS (CI): *m*/*e* calcd for C$_{20}$H$_{16}$Fe 312.19, found 312.05 (M$^+$).

**(*Z*)-1(*m*).** Red brown sticky liquid (0.81 g, 32.5%). $^1$H NMR (300 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 7.51 (s, 1H), 7.34 (d, 2H), 7.23 (m, 1H), 6.38 (s, 2H), 4.18 (s, 2H), 4.14 (s, 2H), 4.11 (s, 5H),

**Table 1. Copolymerization of [(*E*)-2-(1-Ferrocenyl)Vinyl]-*m*/*p*-phenylacetylene [(*E*)-1(*m*/p)] with 1,8-Nonadiyne (I)**[a]

| no. | [**I**]/[**1**] (mol/mol) | yield (wt %) | solubility[b] | content of Fc unit (mol %)[c] | $M_w$ [d] | $M_w/M_n$ [d] |
|---|---|---|---|---|---|---|
| | | | Copolymerization of (*E*)-**1**(*m*) with **I** | | | |
| 1 | 39.90 | gel | × | | | |
| 2 | 26.60 | gel | × | | | |
| 3 | 19.95 | gel | × | | | |
| 4 | 16.63 | 68.1 | √ | 5.21 | 63 100 | 9.34 |
| 5 | 13.30 | 72.9 | √ | 6.25 | 135 000 | 1.92 |
| 6 | 9.97 | 86.2 | √ | 6.92 | 31 300 | 7.65 |
| 7 | 6.65 | 100.0 | √ | 6.81 | 18 000 | 5.57 |
| 8 | 4.99 | 100.0 | √ | 9.09 | 13 500 | 3.20 |
| 9 | 3.33 | 100.0 | √ | 16.00 | 3400 | 2.30 |
| 10 | 1.66 | 42.3 | √ | 46.30 | 1500 | 1.92 |
| 11 | 0.67 | 50.0 | √ | 66.67 | 1200 | 1.69 |
| 12 | 0 | 56.3 | √ | 100 | 800 | 1.46 |
| | | | Copolymerization of (*E*)-**1**(*p*) with **I** | | | |
| 13 | 53.2 | gel | × | | | |
| 14 | 39.9 | 82.0 | √ | 5.59 | 24 900 | 6.99 |
| 15 | 6.65[e] | 54.5 | √ | 4.70 | 19 800 | 2.14 |

[a] Carried out in toluene at room temperature for 30 min unless otherwise specified, using $TaBr_5$-$Ph_4Sn$ as catalyst; $[TaBr_5] = [Ph_4Sn] = 10$ mM; [**1**] = 20 mM. [b] Tested in common solvents (chloroform, DCM, toluene, THF, DMF, DMSO, etc.); symbols: × = insoluble; √ = completely soluble. [c] Fc = 1-ferrocenyl. Calculated from eq 1 using $^1H$ NMR spectral data. [d] Estimated by GPC in THF on the basis of a polystyrene calibration. [e] Monomer (*E*)-**1**(*p*) was added into the reaction mixture after **I** had been polymerized for 10 min.

3.12 (s, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 139.5, 133.0, 130.9, 129.1, 126.5, 125.3, 123.1, 122.6, 84.3, 81.6, 77.8, 70.2, 69.5.

**[(*E*/*Z*)-2-(1-Ferrocenyl)vinyl]-*p*-phenylacetylene [(*E*/*Z*)-1(*p*)]:** The monomers were prepared by the procedures similar to those described above for their *m* isomers, i.e., (*E*/*Z*)-**1**(*m*). The *E*- and *Z*-isomers of the product were isolated by careful column separation.

**(*E*)-1(*p*).** Red brown powder (0.23 g, 28.9%). $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 7.45 (d, 2H), 7.39 (d, 2H), 6.89 (d, 1H), 6.69 (d, 1H), 4.47 (s, 2H), 4.31 (s, 2H), 4.16 (s, 5H), 3.13 (s, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 139.0, 133.1, 132.5, 129.3, 127.1, 126.5, 126.3, 125.7, 120.6, 84.6, 83.5, 77.8, 70.0, 67.8.

**(*Z*)-1(*p*).** Red brown powder (0.28 g, 35.2%). $^1H$ NMR (300 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 7.40 (d, 2H), 7.30 (d, 2H), 6.38 (s, 2H), 4.18 (s, 4H), 4.11 (s, 5H), 3.09 (s, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$), $\delta$ (TMS, ppm): 139.3, 132.3, 130.9, 129.9, 129.1, 126.9, 120.7, 84.4, 81.4, 77.6, 69.8, 69.2.

**Polymerization Reaction.** All polycyclotrimerization reactions and manipulations were carried out under nitrogen using standard Schlenk techniques in a vacuum line system or in an inert atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done in an open atmosphere. A typical experimental procedure for the preparation of hyperbranched copolymer *hb*-P**1**(*m*)/**I** no. 7 (Table 1) is given below as an example.

Into a thoroughly baked and carefully evacuated 15 mL Schlenk tube with a three-way stopcock on the sidearm was placed 29 mg of $TaBr_5$ (0.05 mmol) and 22 mg of $Ph_4Sn$ (0.05 mmol) under nitrogen in a glovebox. Freshly distilled toluene (2 mL) was injected into the tube using a hypodermic syringe. The monomer solution was prepared in another tube by dissolving (*E*)-**1**(*m*) (32 mg, 0.1 mmol) and 1,8-nonadiyne **I** (0.10 mL, 0.67 mmol) in 3 mL of freshly distilled toluene under nitrogen. The two tubes were aged at room temperature for 15 min, and the monomer solution was then transferred to the catalyst solution using a hypodermic syringe. The resultant mixture was stirred at room temperature under nitrogen for 30 min, after which the reaction was quenched by adding a few drops of methanol into the reaction mixture. The mixture was added dropwise to 500 mL of methanol through a cotton filter under stirring. The polymer precipitate was allowed to stand overnight and was then collected by filtration. The isolated polymeric product was washed with methanol and dried under vacuum at room temperature to a constant weight. A brown yellow powdery product of *hb*-P**1**(*m*)/**I** was obtained in 100% yield. Its characterization data are given in the figures and tables in the Results and Discussion.

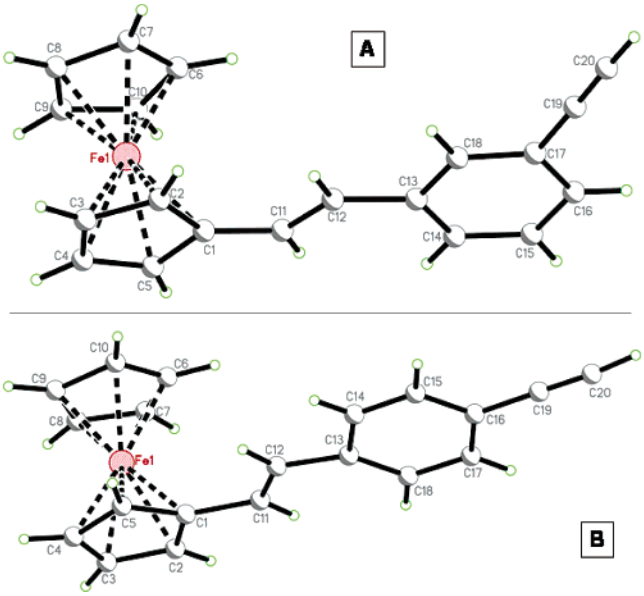


**Figure 1.** Molecular structures of (A) (*E*)-**1**(*m*) and (B) (*E*)-**1**(*p*) with atom-labeling schemes for Tables S1-S5 and S6−S10, respectively, in the Supporting Information.

## Results and Discussion

**Monomer Preparation.** Monomers **1**(*m*) were prepared by Wittig reaction and palladium-catalyzed coupling, followed by base-catalyzed desilylation (cf., Scheme 1). This synthetic route is different from that reported by Buchmeiser et al.[7] The starting materials used here are readily available and the reaction conditions are mild. Similar to the observation of Buchmeiser et al.,[7] two conformers, namely, *E*- and *Z*-isomers, are formed in the Wittig reaction due to the peculiarity of the double bond, and they are very difficult to separate. The isomers were thus not separated at this stage but used directly in the following reactions. The (*E*)- and (*Z*)-isomers of **1**(*m*) were isolated by column separation using hexane as eluent. Their ratio was found to be 38:62 (*E*/*Z*) but not 50:50 as reported before,[7] probably due to the different reaction conditions employed in our study.

As we are interested in knowing how a structural change in the monomer affects its polymerization behavior, another set of monomers, (*E*/*Z*)-**1**(*p*), were prepared by the similar synthetic procedures. The ratio of the *E*- to *Z*-isomers is found to be 45:55, indicating that the regiostructure of the phenyl ring influences the stereochemistry of the reaction.

Although $^1H$ NMR spectra can prove the conformation of the monomers, we still tried to grow their crystals in an effort to further verify their molecular structures. Single crystals with quality suitable for crystallographic data collection were obtained for the monomers with *E* conformation, viz., (*E*)-**1**(*m*) and (*E*)-**1**(*p*), and their OPTEP drawings are shown in Figure 1. The crystal analysis substantiates that the monomers indeed possess *E* conformation, although they both show disorder of the carbon double bond (C11−C12) in the ratio of around 1:1. The same disorder has been reported for other ferrocenyl compounds before.

**Polymer Synthesis.** All the polymerizations were carried out in toluene at room temperature for 30 min using $TaBr_5$−$Ph_4Sn$ as catalyst (cf., Schemes 2 and 3). According to our previous observation, there is a concentration window for the diyne monomers such as **I**, with the optimal concentration being 0.6 M when $TaBr_5$ was used as catalyst.[5d] However, in the copolymerization here, the monoyne (*E*)-**1**(*m*) may serve as a terminating species. With this in mind, we increased the concentration of diyne **I** at the beginning (up to 0.78 M), while keeping the monoyne concentration fixed at 0.02 M (Table 1, no. 1). The polymerization proceeded quickly: the color of the reaction mixture changed to dark brown from pale yellow in ~8 min with heat liberation, pushing the temperature of the reaction mixture to rise to ~70 °C. In about 10 s, the reaction mixture became a chunk of gel, which was not soluble in any solvents. This excludes the possibility of alkyne cyclooligomerization because the resultant oligomers should be soluble. It is known that the tantalum mixtures are incapable of initiating the metathesis polymerizations of terminal alkynes. The high molecular weight of the reaction product substantiates that the metathesis polymerization was an unlikely event. It can thus be concluded that the polymer was formed via the expected alkyne polycyclotrimetization mechanism.

We decreased the diyne concentration step by step. As the concentration of **I** was dropped to 0.32 M, completely soluble polymeric product was obtained in ~68% yield (Table 1, no. 4). This concentration is higher than the favorite concentration (0.27 M) when the catalyst was $TaCl_5-Ph_4Sn$.[5b] The monoyne (*E*)-**1**(*m*) can terminate the growth of the active propagating branch, so its presence can help hamper the formation of cross-linking networks to some extent, thus leading to an increase in the up-limit of the concentration window of diyne **I**. For the purpose of comparison in the structure characterization, we prepared homopolymer of **I** (or *hb*-P**I**) at the concentration of 0.27 M under the conditions same to those used for the synthesis of other copolymers except for that comonomer (*E*)-**1**(*m*) was not used.

We further decreased the concentration of diyne **I**. To our surprise, we could still get hyperbranched copolymers in 100% yield, even when the concentration of **I** was lowered to 0.094 M (Table 1, no. 8). In our previous studies on the diyne homopolymerization, we found that the isolation yields of the polymers and their molecular weights were low when the diyne concentrations were lower than 0.13 M. We have ascribed the low polymer yields and molecular weights to the termination of the branch growth by the intramolecular cyclization of the active propagating species with the diyne molecules at the low concentrations in the homopolymerization. Monoyne **1** is bulkier than diyne **I**. When the monoyne is added into the reaction mixture, it will hinder the termination of the propagating species by one diyne molecule but promote the reactions of the propagating species with two diyne monomers or other species with two independent triple bonds due to its steric effect. This steric effect also makes the propagating species difficult to terminate by the monoyne in the early stage since the species are still relatively small and cannot provide enough space for the termination reaction to occur.

We synthesized another monomer, (*E*)-**1**(*p*), to further test the synthetic route and reaction conditions. As discussed above, the monoyne comonomer can hamper the formation of cross-linking networks to some extent. Monoyne (*E*)-**1**(*p*) should be more active to react with the propagating species than its *m* isomer (*E*)-**1**(*m*) because the former is less bulky than the latter. The up-limit of concentration window of **I** should thus be higher. We investigated the copolycyclotrimerization of **I** with (*E*)-**1**(*p*) at a diyne concentration of 0.78 M, which is much higher than 0.32 M, the up-limit for (*E*)-**1**(*m*) under similar reaction conditions. As a nice surprise, the polymerization product was completely soluble in common solvents (Table 1, no. 14), proving that our consideration was correct. However, further increasing the diyne concentration resulted in the formation of insoluble gel (Table 1, no. 13).

What would happen if the ferrocenyl monoyne **1** is added into the polymerization solution of diyne **I** at a later stage rather than from the beginning? To answer this question, we conducted an experiment in which the ferrocene comonomer was added to the reaction mixture after the polymerization reaction of **I** had proceeded for 17 min (Table 1, no. 15). The resultant mixture was then stirred at room temperature for another 14 min. Using the normal purification procedures, a soluble polymeric product was isolated, whose properties will be compared with those of other polymers in the characterization section (vide infra).

In the copolycyclotrimerization of diethynylbenzene (diyne) with phenylacetylene or 1-ethynyl-3-toluene (monoyne), insoluble gel was formed when the initial molar ratio of diyne to monoyne exceeded 1.[8] As can be seen from Table 1, although the molar ratio of diyne to monoyne is changed in a wide range (16.63−0.67), soluble polymeric products can still be obtained when (*E*)-**1**(*m*) is used as monoyne comonomer. The ratios are generally higher than 1. This shows that the molecular structure of starting monomers can greatly influence their polycyclotrimerization behaviors. Even just changing the position of the substituents on the benzene ring, the up-limit ratio of diyne to monoyne is increased from 16.63 to 39.9 when (*E*)-**1**(*m*) is replaced by (*E*)-**1**(*p*).

The data given in Table 1 are all about the copolycyclotrimerizations of diyne **I** with monoynes (*E*)-**1**(*m*) and (*E*)-**1**(*p*), whose vinyl groups are *E* or trans in conformation. We have tried to use their *Z*- or *cis*-isomers (*Z*)-**1**(*m*) and (*Z*)-**1**(*p*) to do the copolymerization reaction but failed to obtain any polymeric products. This is probably due to the too high steric hindrance for the *Z*-isomers to undergo the alkyne polycyclotrimerization reaction.

**Structural Characterization.** We used spectroscopic methods to analyze the molecular structures of hyperbranched copolymers *hb*-P**1**(*m*)/**I**. Figure 2 shows typical examples of their IR spectra; the spectra of monomer (*E*)-**1**(*m*) and homopolymer *hb*-P**I** are also given in the same figure for comparison. The monomer shows $\equiv C-H$, $C\equiv C$, and $\equiv C-H$ bands at 3296, 2124, and 619 $cm^{-1}$, respectively (Figure 2A), which completely disappear in the spectra of the hyperbranched copolymers (Figure 3, panels B−D), indicative of a complete consumption of the carbon triple bonds by the polycyclotrimerization reaction. The ferrocene-associated vibration bands at 3121, 1633, 1112, and 958 $cm^{-1}$ are still observed in the spectra of the copolymers, proving that the polycyclotrimerization is harmless to the ferrocenyl groups. The intensity of these ferrocene-associated bands becomes weaker when the molar ratio of the ferrocene unit in the copolymer is decreased.

Examples of the $^1H$ NMR spectra of the copolymers are shown in Figure 3; also for comparison, the spectra of (*E*)-**1**(*m*) and *hb*-P**I** are given in the same figure. The resonance peaks of the protons of the ethynyl groups in monoyne **1** and diyne **I** at $\delta$ 3.10 (peak a) and 1.97 (data not shown), respectively, completely disappear after the polymerization reaction. The signal of the two methylene groups linked to the carbon triple bond shifts from $\delta$ 2.03 in **I** to $\delta$ 2.59 in *hb*-P**1**(*m*)/**I** as the methylene groups are now bonded to the benzene rings newly formed by the polycyclotrimerization reaction. The resonance peaks at $\delta$ 1.65 assigned to other methylene groups experience almost no

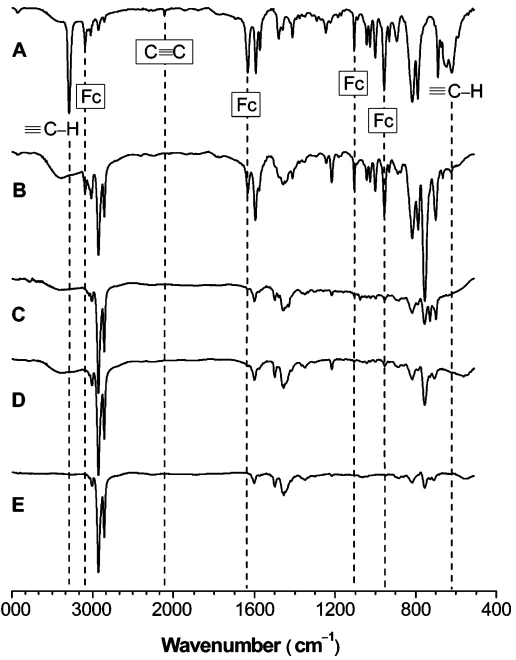


**Figure 2.** IR spectra of monomer (*E*)-**1**(*m*) (A) and its hyperbranched copolymers *hb*-P**1**(*m*)/**I** nos. 11 (B), 7 (C) and 5 (D; the numbers of the polymers correspond to those in Table 1). The spectrum of the homopolymer of 1,8-nonadiyne (*hb*-P**I**) is given in panel E for comparison, which was prepared under the conditions given in Table 1, footnote *a* with [**1**] = 20 mM replaced by [**I**] = 0.27 M.

change. A broad peak appears with its center at $\delta$ 6.93, which should comprise the resonance signals from the protons of the double bonds in the ferrocenyl unit (peaks b and (c) and the newly formed benzene rings.

Close inspection of the spectra reveals that the two peaks in the upfield are not symmetric but contain shoulder bands (Figure 3). These shoulders arise from the resonances of the methylene protons of the tetrahydronaphthalene (or tetralin) rings formed by the end-capping dimerization reaction.[5d] The three resonance peaks of the protons of the cyclopentadienyl (Cp) rings in the ferrocene units can be easily seen in the spectra of the copolymers at $\delta$ 4.51, 4.31, and 4.16, well corresponding to those of monomer (*E*)-**1**(*m*). The intensities of the three peaks are decreased when the feed ratio of **I** is increased. As can be seen from the spectrum of *hb*-P**I**, there are no resonance signals from the homopolymer that interfere with the ferrocene-associated peaks (Figure 4E).

The molecular compositions of the hyperbranched copolymers can be calculated from their $^1$H NMR spectra. As discussed above, the resonance peaks in the chemical shift range of $\delta$ 3.9−4.8 are assigned to the protons of the ferrocenyl (Fc) moieties from monoyne (*E*)-**1**(*m*), while those between $\delta$ 2.2 and 3.0 are associated with the resonance of the protons of the benzyl (Bz) groups derived from the two methylene groups located in the vicinity of the triple bonds in monomer **I**. This allows us to calculate the molar ratio of the ferrocenyl moiety ($R_{\mathrm{Fc}}$) in the copolymer by the following equation:

$$R_{\mathrm{Fc}} = \{(A_{\mathrm{Fc}}/9)/[(A_{\mathrm{Fc}}/9) + (A_{\mathrm{Bz}}/4)]\} \times 100\% \qquad (1)$$

where $A_{\mathrm{Fc}}$ and $A_{\mathrm{Bz}}$ denote the integrated areas of the resonance peaks of the Fc and Bz groups in the chemical shift regions of $\delta$ 3.9−4.8 and $\delta$ 2.2−3.0, respectively. The calculated results are summarized in Table 1. The $R_{\mathrm{Fc}}$ values in copolymers *hb*-P**1**(*p*)/**I** can be calculated by the same equation, which are also listed in Table 1 (nos. 14 and 15).

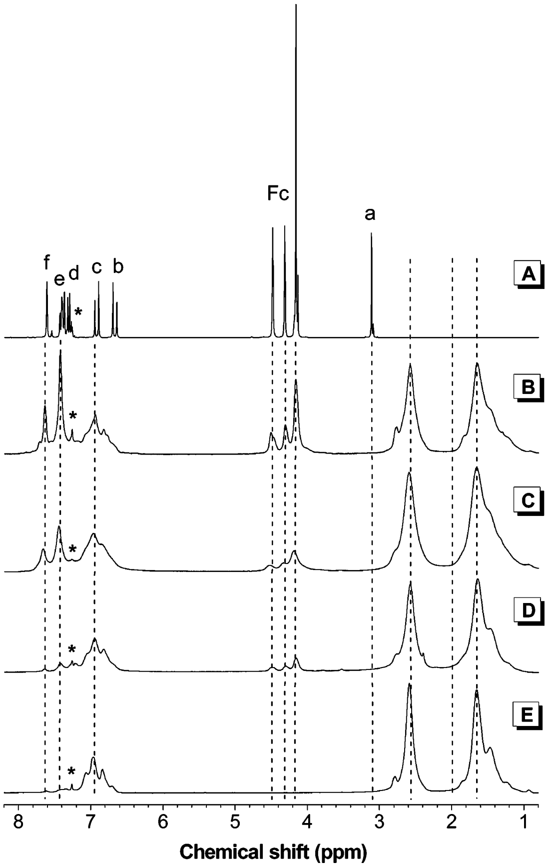


**Figure 3.** $^1$H NMR spectra of chloroform-*d* solutions of monomer (*E*)-**1**(*m*) (A) and its hyperbranched copolymers *hb*-P**1**(*m*)/**I** nos. 9 (B), **7** (C) and 4 (D; the numbers of the polymers correspond to those in Table 1). The labels of the resonance peaks of the protons of (*E*)-**1**(*m*) in panel A correspond to those given in Scheme 1. The spectrum of *hb*-P**I** is given in panel E for comparison. The solvent peaks are marked with asterisks.

The excellent solubility of the polymers enables us to further characterize their molecular structures in detail by $^{13}$C NMR spectroscopy. Figure 4 shows some typical examples of the $^{13}$C NMR spectra of the polymers as well as that of the monoyne. The acetylenic carbon atoms of (*E*)-**1**(*m*) resonate at $\delta$ 83.6 and 77.8. These peaks are absent in the spectra of the copolymers. New peaks appear in the aromatic region ($\delta$ ~143−126) in addition to the peaks coming from the benzene ring of (*E*)-**1**(*m*), proving the transformation of the acetylenic triple bonds to the aromatic double bonds by the polycyclotrimerization reaction. The carbon atoms of the Cp rings of the monomer give three main peaks at $\delta$ 84.3, 70.0 and 67.9, which experience little changes after polymerization. The peaks become weaker as the ratio of the ferrocenyl unit is decreased. The peak at $\delta$ 84.3 is difficult to discern in copolymer *hb*-P**1**(*m*)/**I** no. 4 (Figure 4D) because of its very low molar ratio of ferrocenyl unit (~5%). Homopolymer *hb*-P**I** shows no peaks of Cp carbon atoms (Figure 4E). This confirms that the two monomers have undergone the expected copolycyclotrimerization reactions.

The hyperbranched polymers are further characterized by UV analyses. Figure 5 shows an absorption spectrum of a copolymer, along with those of monomer (*E*)-**1**(*m*) and homopolymer *hb*-P**I**. The UV spectrum of 1,8-nonadiyne **I** is a flat line parallel to the abscissa with no absorption signals recorded in the whole spectral region of 200−900 nm because its isolated acetylenic triple bonds is known to absorb at <200 nm.[5b] Polymer *hb*-P**I**, however, absorbs in the UV region, giving three peaks at 230, 269, and 277 nm, which are associated with $\pi-\pi^*$ transitions

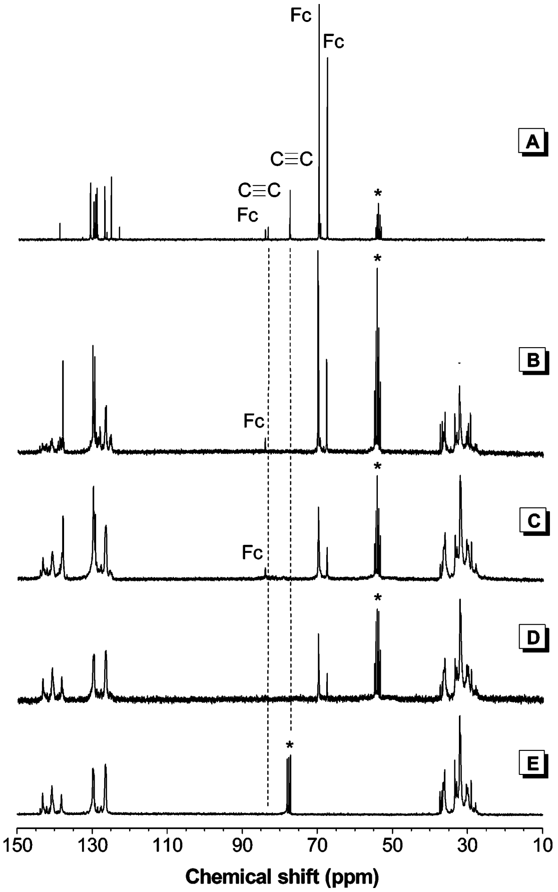


**Figure 4.** $^{13}$C NMR spectra of DCM-$d_2$ solutions of monomer (*E*)-**1**(*m*) (A) and its hyperbranched copolymers *hb*-P**1**(*m*)/**I** nos. 9 (B), 7 (C), and 4 (D; the numbers of the polymers correspond to those in Table 1). The spectrum of chloroform-*d* solution of homopolymer *hb*-P**I** is given in panel E for comparison. The solvent peaks are marked with asterisks.

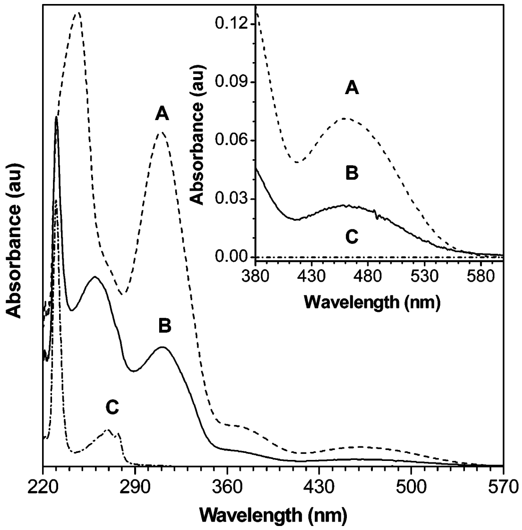


**Figure 5.** Absorption spectra of THF solutions of (A) monomer (*E*)-**1**(*m*) and (B) its hyperbranched copolymer *hb*-P**1**(*m*)/**I** no. 7 (sample from Table 1). (C) The spectrum of homopolymer *hb*-P**I** is given for comparison. Concentration (mg/mL): (A) 0.017; (B) 0.043; (C) 0.043.

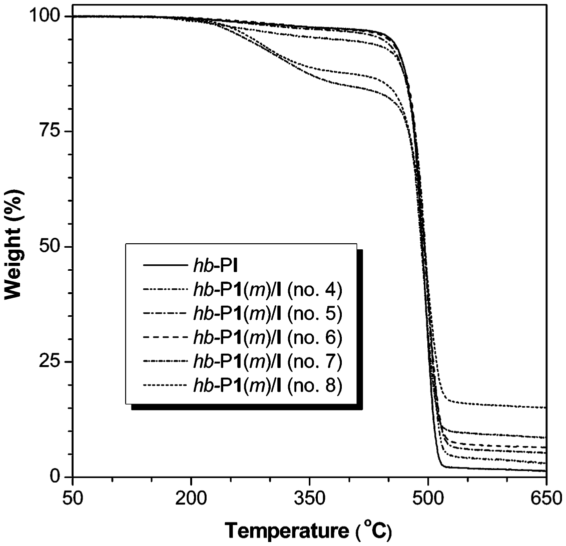


**Figure 6.** TGA thermograms of hyperbranched copolymers *hb*-P**1**(*m*)/**I** nos. 4−8 (the numbers of the polymers correspond to those in Table 1) and homopolymer *hb*-P**I** measured under nitrogen at a heating rate of 20 °C/min.

of the isolated trisubstituted benzene rings, with the peak at 230 nm assignable to the $E_2$ band and those at 269 and 277 nm to the *B* bands. The peak at 230 nm can be easily seen in the spectrum of the copolymer *hb*-P**1**(*m*)/**I**, while those at 269 and 277 nm are buried under the strong absorption peak of the ferrocenyl unit. The peak at 311 nm in the copolymer corresponds well with that in the monomer (*E*)-**1**(*m*). The peak at 436 nm is hardly recognizable in the spectrum of the copolymer but become clearly discernible after amplification (inset). The spectrum of *hb*-P**I** is still a flat line parallel to the abscissa after the spectral amplification, confirming that the peak at 436 nm is associated with the absorption of the ferrocenyl unit.

Summarizing all the spectral data discussed above, it can be concluded beyond doubt that the two alkyne monomers, that is, monoyne (*E*)-**1**(*m*) and diyne **I**, have been polymerized into hyperbranched polyphenylenes via the polycyclotrimerization mechanism.

The molecular weights of the soluble products were estimated by GPC. When the concentration of diyne **I** is decreased or the relative concentration of monoyne **1** is increased, the molecular weight of the copolymer and its polydispersity index are generally decreased (Table 1, nos. 4−12) except for one abnormal case (no. 5). Both the molecular weight and polydispersity index reach the lowest level in the absence of diyne **I**. Although GPC is not an accurate method for determining the molecular weights of hyperbranched polymers,[9] the results should be useful for comparison under the same measurement conditions. Clearly, monomer **1** can terminate the growth of some propagating branches.

**Polymer Properties.** We have previously found that the homopolymers of alkyldiynes are thermally very stable.[5b,5d] Figure 6 shows the TGA thermograms of hyperbranched copolymers *hb*-P**1**(*m*)/**I** and homopolymer *hb*-P**I** measured under nitrogen at a heating rate of 20 °C/min. Homopolymer *hb*-P**I** is highly resistant to thermolysis, with a 5% weight loss recorded at a temperature as high as 453 °C. The thermal behaviors of copolymers *hb*-P**1**(*m*)/**I** nos. 4−6 are similar to that of *hb*-P**I**, but copolymers nos. 7 and 8 show inferior performance. This is reasonable because polymers with higher molecular weights normally exhibit better thermal stability. The thermal stability of *hb*-P**1**(*m*)/**I** no. 9 is even poor (Table 2) due to its very low molecular weight. However, when the molar ratios of the ferrocenyl units become very high (>46%), the copolymers (nos. 10 and 11) become thermally stable. This is understandable because ferrocene is thermally very stable: it does not decompose when heated to >500 °C!

Copolymers *hb*-P**1**(*p*)/**I** are also thermally stable (Figure S2 in the Supporting Information) and their temperatures for 10%

**Table 2. Thermal and Electrochemical Properties of Hyperbranched Copolymers *hb*-P1(*m*/*p*)/I**

| *hb*-P**1**(*m*/*p*)/**I**[a] | Fc content (mol %) | $T_d$ (°C)[b] | $T_g$ (°C)[c] | $E_{1/2}$ (V)[d] | $\Delta E_p$ (mV)[e] |
|---|---|---|---|---|---|
| 4 | 5.21 | 462 | 64.3 | 0.61 | 77.3 |
| 5 | 6.25 | 464 | 67.5 | 0.59 | 58.7 |
| 6 | 6.92 | 466 | 70.6 | 0.58 | 78.6 |
| 7 | 6.81 | 324 | 69.2 | 0.58 | 62.4 |
| 8 | 9.09 | 334 | 69.5 | 0.59 | 63.9 |
| 9 | 16.00 | 274 | 73.6 | 0.58 | 64.4 |
| 10 | 46.30 | 432 | 89.1 | 0.57 | 62.7 |
| 11 | 66.67 | 391 | 103.9 | 0.57 | 57.3 |
| 14 | 5.59 | 443 | 98.8 | 0.58 | 62.1 |
| 15 | 4.70 | 443 | 61.2 | 0.59 | 65.3 |
| *hb*-P**I** | | 467 | 59.3 | | |
| (*E*)-**1**(*m*) | | | | 0.60 | 71.6 |

[a] The numbers for the copolymers correspond to those given in Table 1. The data for homopolymer *hb*-P**I** and monomer (*E*)-**1**(*m*) are shown for comparison. [b] Temperature for 10% weight loss determined by TGA under nitrogen at a heating rate of 20 °C/min. [c] Glass transition temperature ($T_g$) determined by DSC under nitrogen at a heating rate of 10 °C/min. [d] Voltages vs SCE, Pt working electrode, DCM solution containing 0.5 M [(*n*-Bu)$_4$N]PF$_6$, 25 °C, formal redox potential $E_{1/2} = (E_{pc} + E_{pa})/2$. [e] Difference between oxidation and reduction peaks in the cyclic voltammogram, $\Delta E_p = E_{pc} - E_{pa}$.

weight loss are as high as 443 °C (Table 2, nos. 14 and 15). It is of interest to note that these two polymers were prepared by different procedures (vide ante) but show exactly the same $T_d$ value. It can be conjured up that most of the ferrocenyl units are located on the peripheral shells of the hyperbranched copolymers, no matter whether the ferrocenyl monoyne is added at the beginning of the polymerization reaction or after the diyne has reacted for some time. The wrapping of the polymer cores by the bulky, stable ferrocenyl shell should make the copolymers resistant to thermolysis, which thus explains why copolymers *hb*-P**1**(*p*)/**I** nos. 14 and 15 share the same high thermal stability.

Hyperbranched homopolymer *hb*-P**I** undergoes glass transition at 59.3 °C. Incorporation of the rigid ferrocene units into the polymer structure increases the $T_g$ value. As can be seen from Table 2, in the series of copolymer *hb*-P**1**(*m*)/**I**, its $T_g$ almost monotonically increases with increasing the molar ratio of the ferrocenyl units (nos. 4−11). It seems that copolymer *hb*-P**1**(*p*)/**I** exhibits higher $T_g$ than its *m*-congener *hb*-P**1**(*m*)/**I**. The ferrocene content of *hb*-P**1**(*p*)/**I** no. 14 (∼5.6%) is lower than that of *hb*-P**1**(*m*)/**I** no. 5 (∼6.3%) but the $T_g$ (∼99 °C) of the former is much higher than that of the latter (∼68 °C). This is probably because the straight *p* regioisomer can offer more regular structure than does its bent *m* counterpart.

When the ferrocenyl content in the *hb*-P**1**(*m*)/**I** series is changed from 5.21% (no. 4) to 6.25% (no. 5) ($\Delta R_{Fc} \sim 1\%$), $T_g$ is changed from 64.3 to 67.5 °C ($\Delta T_g \sim 3$ °C). However, for a similar change in $R_{Fc}$ for *hb*-P**1**(*p*)/**I**, a much bigger change in $T_g$ (∼38 °C) is observed (cf., Table 2, nos. 14 and 15). What is the cause for this big change? As discussed above, *hb*-P**1**(*p*)/**I** no. 14 was prepared by a "normal" reaction procedure and exhibits a high $T_g$ value because of its regular molecular structure. On the other hand, *hb*-P**1**(*p*)/**I** no. 15 was prepared by adding the ferrocenyl monoyne into the polymerization mixture of the diyne after the latter had already reacted for some time. Most of the ferrocenyl units should thus be located on the periphery shell and would contribute little in terms of rigidifying of the core structure of the copolymer. This structural difference may account for the observed big difference in their $T_g$ values.

All the polymers, including homopolymer *hb*-P**I** and copolymers *hb*-P**1**(*m*)/**I** and *hb*-P**1**(*p*)/**I**, exhibit no sharp reflection peaks but diffuse halos centered at 2$\theta$ angles of ∼20° (Figures S3 and S4). These polymers are thus all amorphous glasses at room temperature. This agrees with the DSC results that no isotropization/crystallization transitions were detected during the heating/cooling scans of the polymer samples.

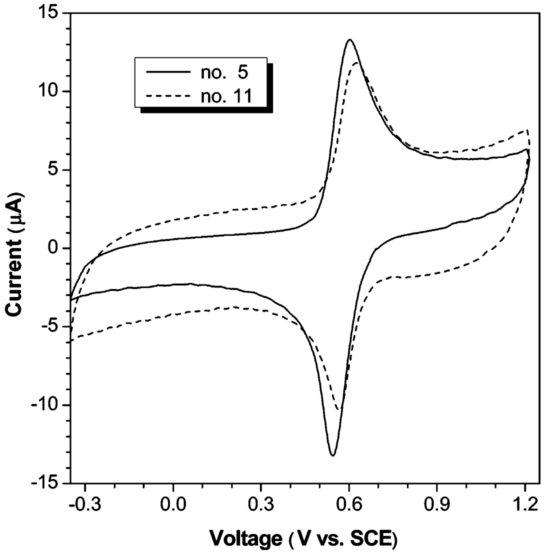


**Figure 7.** Cyclic voltammograms of hyperbranched copolymers *hb*-P**1**(*m*)/**I** nos. 5 and 11 (the numbers of the polymers correspond to those in Table 1) in DCM containing 0.5 M [(*n*-Bu)$_4$N]PF$_6$. Scan rate: 100 mV/s. Concentration (mg/mL): 1.52 (no. 5), 0.57 (no. 11).

It is well-known that transition-metal-catalyzed alkyne cyclotrimerization gives rise to the formation of 1,2,4- and 1,3,5-trisubstituted benzenes, with the 1,2,4-regioisomers being the major products.[10] The stereochemistry involved in the diyne polycyclotrimerization has been discussed in detail in our recent publications.[5] From Figure 3, we can easily determine that the newly formed aromatic rings are mainly 1,2,4-trisubstituted benzenes because their resonance peaks are centered at $\delta$ 6.95. It is known that an asymmetric 1,2,4-trialkylbenzene exhibits multiple peaks in the vicinity of $\delta$ 6.9, while its symmetric congener 1,3,5-trialkylbenzene gives a single peak in the upfield region.[11] On the basis of the spectral analysis, the main products of the polycyclotrimerization reactions are illustrated as 1,2,4-trisubstituted polyphenylenes as shown in Schemes 2 and 3.

The reversibility and oxidation potentials of the redox processes in the hyperbranched copolymers are estimated by cyclic voltammetry in DCM solutions. All the copolymers exhibit only single oxidation wave in the range −0.4 to 1.2 V (vs SCE). This indicates that all the ferrocenyl units in one polymer possess the same redox potential just as many ferrocene-containing dendrimers do because of the lack of direct interactions between the metal centers.[12] The potentials are summarized in Table 2, with representative cyclic voltammograms shown in Figure 7 as well as Figures S5 and S6 in the Supporting Information. The oxidation wave is reversible and occurs at a potential very close to that of the Fe$^{II/III}$ couple of ferrocenyl moieties. Compared with the potential of (*E*)-**1**(*m*), there are no big difference in the potentials of the hyperbranched copolymers, as ferrocenyl moiety is the only electroactive unit in the system. The electrochemical behaviors of copolymers *hb*-P**1**(*p*)/**I** nos. 14 and 15 are similar to those of copolymers *hb*-P**1**(*m*)/**I** nos. 4−11 (Table 2). This proves that the redox-active unit is the ferrocenyl group, whose electrochemical behavior is not affected to a great extent by the isomeric structure (*m* or *p*) of the benzene ring.

## Concluding Remarks

In this work, we have successfully expanded the scope of applicability of our previously developed polycyclotrimerization technique from organic to organometallic system. By copolycyclotrimerization of diyne **I** with ferrocenyl monoynes (*E*)-**1**(*m*/*p*), we succeeded in synthesizing ferrocene-containing hyperbranched polyphenylenes in high yields. The conformation of the monoyne was found to affect the alkyne polycyclotrimerization to a great extent, with the *Z*-isomer afforded no polymeric products at all. The hyperbranched copolymers obtained from the copolymerization of the *E*-isomers are solution processable and thermally stable. The electrochemical behavior of the ferrocenyl unit is practically not affected by the polymeric structure due to the hyperbranched topology. To the best of our knowledge, this is the first example in which a group of soluble, ferrocene-containing hyperbranched polymers are prepared by a simple, one-pot polymerization reaction. We are currently working on further extending the utility of the polycyclotrimerization technique to the preparation of other hyperbranched polymers containing various functional organometallic groups.

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**Supporting Information Available:** Figures showing supplementary NMR spectra, TGA thermograms, XRD patterns, and CV curves of the monomers and polymers, tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of monomers (*E*)-**1**(*m*) and (*E*)-**1**(*m*), and .cif files for both monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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