680 *Macromolecules* **2010**, *43*, 680–690
DOI: 10.1021/ma9012658

Macromolecules
ARTICLE

Ferrocene-Functionalized Hyperbranched Polyphenylenes: Synthesis, Redox Activity, Light Refraction, Transition-Metal Complexation, and Precursors to Magnetic Ceramics

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Received June 12, 2009; Revised Manuscript Received December 12, 2009

ABSTRACT: New catalyst systems for diyne polycyclotrimerization were developed. *E*-1-[2-(2,5-Diethynylphenyl)vinyl]ferrocene (**1**), a ferrocene-containing diyne, was polymerized by ruthenium- and rhodium-based catalysts, affording hyperbranched polyphenylenes (*hb*-P**1**) with high molecular weights (M_w up to $\sim 1.4 \times 10^5$) in high yields (up to 100%). Effects of reaction conditions on the polymerization process were investigated, and structures of the resultant polymers were characterized by spectroscopic methods. The polymers were soluble, thermally stable, and redox active. Complexation with cobalt carbonyls further metalized the polymers. Both the polymers and their cobalt complexes showed high refractive indices (RI up to ~1.81) at 300−1700 nm, large Abbé numbers (ν_D' up to ~681), and low optical dispersions (D' down to ~0.0015) in the telecommunication wavelength region. Pyrolyses of the polymers and their complexes furnished magnetic ceramics with high magnetizabilities (M_s up to ~83 emu/g).

Introduction

Organometallic polymers are hybrid macromolecules of organic and inorganic species. Thanks to their unique magnetic, electronic, catalytic, sensory, and optical properties,[1] the polymers have high potentials to find high-tech applications in an array of areas as functional materials, such as precursors to nonoxide ceramics.[2] Ferrocene (Fc) is the most prominent example of an organometallic molecule. It possesses special thermal and electrochemical properties and has been utilized as a versatile building block for the construction of functional macromolecules.[3,4] Silaferrocenophanes, for example, are a group of useful monomers for the syntheses of poly(ferrocenylenesilane)s, which show unique chemical and physical properties that are difficult, if not impossible, to access with "conventional" pure organic polymers.[5,6] Other linear and star polymers with Fc units in the backbones or skeletons or side chains have also been prepared.[7]

Our research groups have prepared hyperbranched poly(ferrocenylsilyne)s by desalt polycoupling of dilithiated Fc with trichlorosilane.[8] The polymers were obtained in high yields but are insoluble or only partially soluble unless long alkyl chains are attached to the branches of the polymers. Recently, we have developed new synthetic approaches to Fc-containing polymers. We have successfully prepared hyperbranched poly(ferrocenylphenylene)s with macroscopic processability by tantalum- and cobalt-catalyzed polycyclotrimerizations.[9] For example, through copolymerization of a ferrocenyl monoyne with an aromatic diyne, a hyperbranched polyphenylene (*hb*-PP) with its branch terminals capped by Fc groups was obtained (Chart 1). Homopolymerization of a Fc-containing diyne, on the other hand, afforded an *hb*-PP with Fc units in both corona and core (Chart 2). The *hb*-PPs can be further metalated through complexation with cobalt carbonyls. Upon pyrolysis at high temperatures, the *hb*-PPs and their cobalt complexes were ceramized in higher yields than their linear counterparts did, thanks to the "cage effect" of their three-dimensional molecular structures. When magnetized by an external magnetic field at room temperature, the ceramics exhibited high saturation magnetization (M_s up to ~126 emu/g) and near-zero remanence and coercivity.[9] Evidently, the ceramics are excellent magnetic materials with high magnetizabilities and low hysteresis losses. It is envisioned that further structural design and process optimization may lead to the generation of new polymers and ceramics that show even better performances and hence offer even more exciting possibilities.

The Ta-catalyzed polycyclotrimerizations are, however, totally intolerant of polar functional groups, and the reactions thus must be conducted under stringently moisture- and oxygen-free conditions. The polycyclotrimerization reactions proceed very rapidly, making the process control extremely difficult.[10] Although the Co catalysts can polymerize diyne monomers carrying certain polar groups, they need to be preactivated by UV irradiation. The resultant polymers generally have lower molecular weights and inferior optical and photonic properties than those prepared from the Ta catalysts, owing to the presence of catalyst residues as cobalt complexes in the polymers. Development of new catalyst systems for diyne polycyclotrimerization that are efficient, stable, and easy to handle would thus be very rewarding.

In this work, we extended our effort in the area on the synthesis of organometallic *hb*-PPs containing Fc groups. In our previously synthesized Fc-containing *hb*-PPs, the Fc units are at the branch ends (Chart 1) or in the skeleton and terminal (Chart 2) with relatively low Fc density.[9,10] In this study, we designed a diyne monomer (**1**), whose polymerization would produce an *hb*-PP

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Chart 1. Hyperbranched Polyphenylene with Peripherally Decorated Ferrocenyl Groups

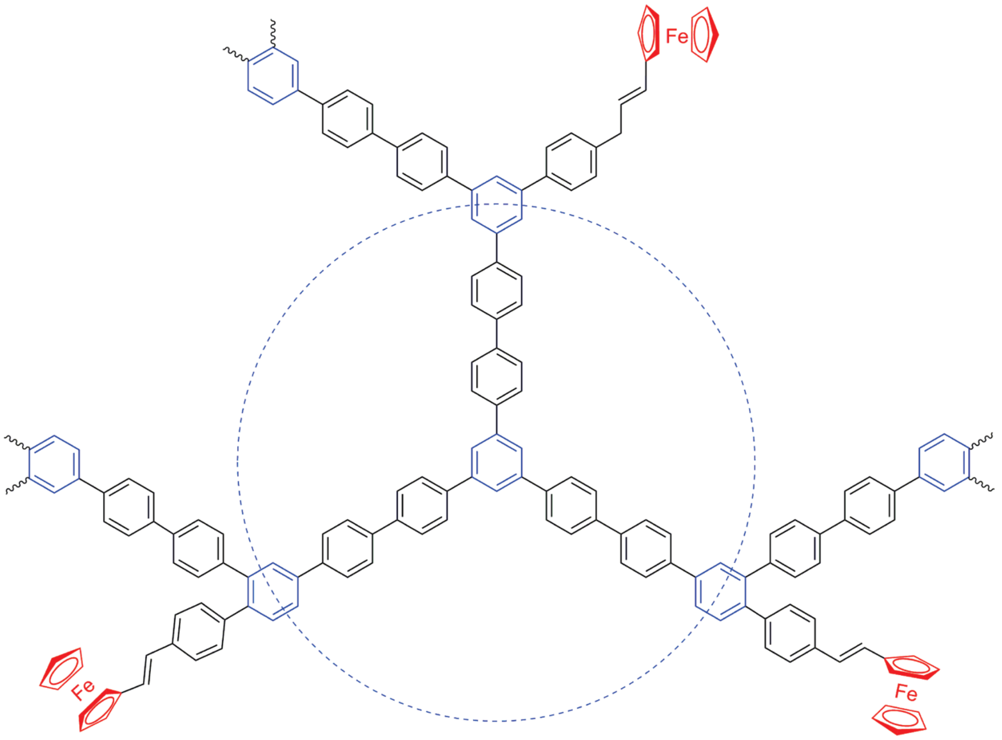
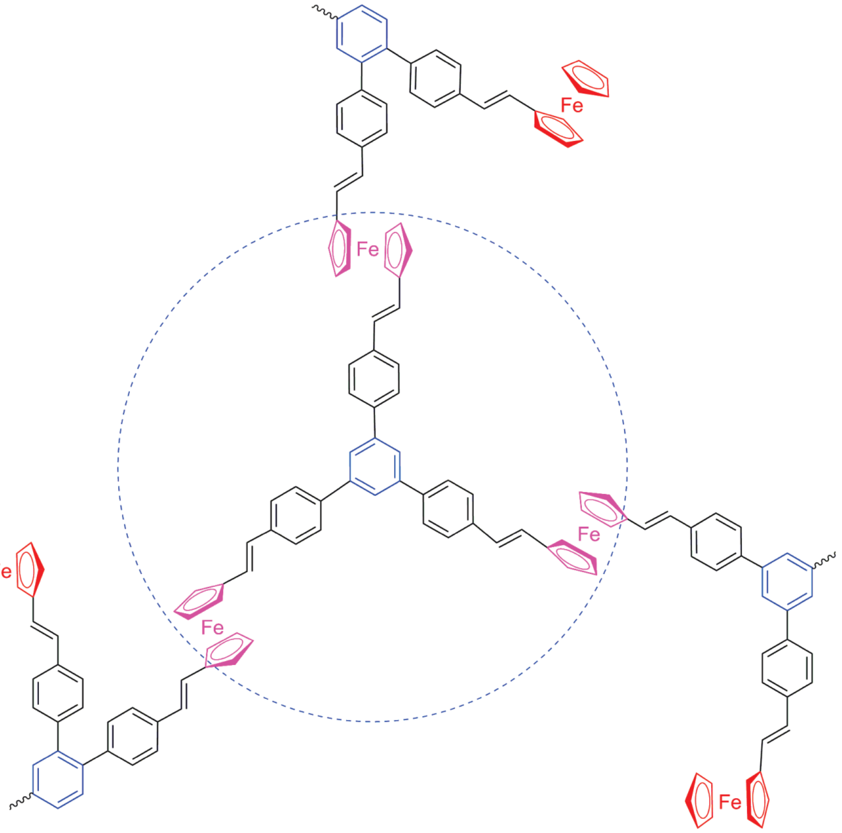
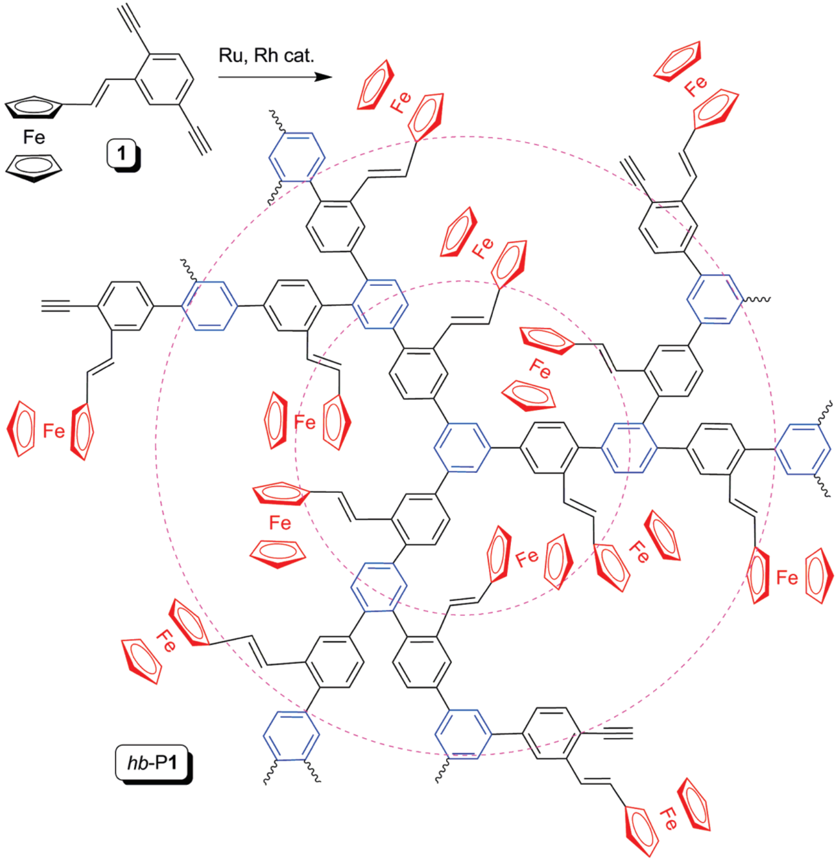


Chart 2. Hyperbranched Polyphenylene with Ferrocenyl Groups Embedded in Its Skeleton and Embellished around Its Periphery

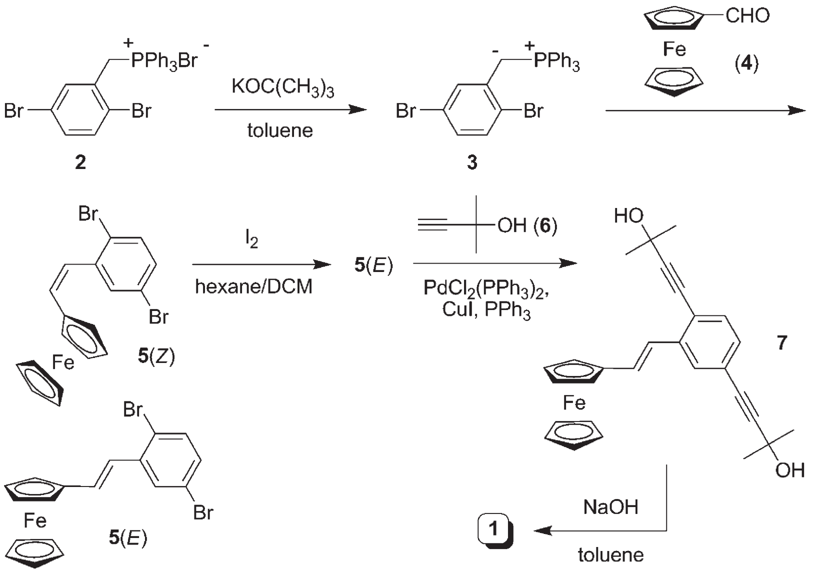


with the Fc groups as pendants to its repeat branches and with a high density of Fc units (*hb*-**P1**, Scheme 1). Whereas the Ta-catalyzed polycyclotrimerization of **1** was very fast and difficult to control, we successfully developed ruthenium- and rhodium-based catalysts to bring the polymerization reactions under control. The obtained *hb*-PPs were soluble and stable. The organometallic polymers showed high refractive indices and Abbé numbers. Their further metallization by cobalt carbonyls afforded cobalt−polymer complexes that served as precursors to magnetic ceramics with high magnetizabilities.

Scheme 1. Polymerization of (*E*)-1-[2-(2,5-Diethynylphenyl)vinyl]ferrocene (1) to Hyperbranched Polyphenylene (*hb*-P1) with Ferrocenyl Groups Attached to Its Repeat Branches as Pendant Groups



Scheme 2. Synthesis of (*E*)-1-[2-(2,5-Diethynylphenyl)vinyl]ferrocene (1)



Experimental Section

General information about materials and instrumentations, experimental procedures for the monomer synthesis and polymerization, and structural characterization data for the monomer and polymers are given in the Supporting Information.

Results and Discussion

Monomer Synthesis. To enrich the research area of hyperbranched organometallic polymers, we synthesized a diyne monomer carrying Fc moiety (**1**) according to the synthetic route shown in Scheme 2. An isomeric mixture of 1-[2-(2,5-dibromophenyl)vinyl]ferrocene (**5**) with *E*- and *Z*-conformations was prepared by Wittig reaction of **3** and ferrocenecarboxyaldehyde (**4**). Recrystallization from hexane separated the *E*-isomer from the mixture, while the *Z*-isomer left in the solution was transformed to the *E*-isomer quantitatively by iodine-catalyzed isomerization. Palladium-catalyzed cross-coupling of **5** with 2-methyl-3-butyn-2-ol (**6**)

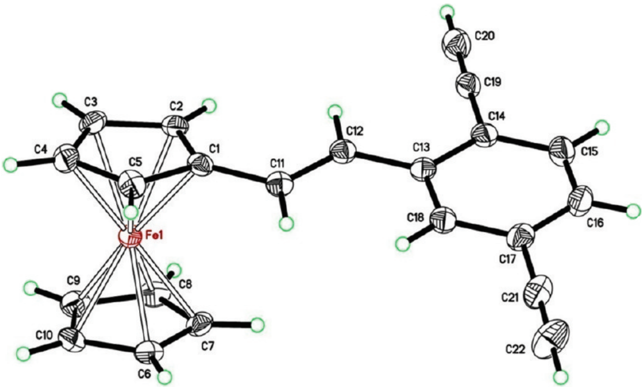


Figure 1. ORTEP drawing of monomer **1**.

Table 1. Polymerization of Monomer 1 by Tantalum Halides[a]

no.	catalyst	time (min)	yield (%)[b]	S[c]
1	$TaBr_5-Ph_4Sn$	30	53.6 (23.5)	Δ
2	$TaCl_5-Ph_4Sn$	30	71.7 (55.1)	Δ
3	$TaCl_5-Ph_4Sn$	10	47.0 (11.9)	Δ

[a] Carried out under dry nitrogen in toluene at room temperature with $[M]_0$ = 50 mM and [cat.] = 7.5 mM. [b] Yield of soluble fraction given in the parentheses. [c] Solubility (S) tested in common organic solvents such as tetrahydrofuran (THF), toluene, dichloromethane (DCM), and chloroform; Δ = partially soluble.

gave compound **7**, which afforded the desired diyne monomer **1** after the base-catalyzed deprotection.

The diyne monomer was characterized by spectroscopic methods, from which satisfactory analysis data corresponding to its expected molecular structure were obtained (see Experimental Section in the Supporting Information for details). We successfully obtained single crystals of **1**. Its ORTEP drawing is shown in Figure 1, and the crystal data are given in Tables S1−S5 in the Supporting Information. The crystal structure proves that the monomer indeed takes an *E*-conformation. The two cyclopentadienyl (Cp) rings of the Fc unit of **1** are arranged in a nearly parallel fashion. Because of the involved steric effect, the substituted Cp ring (C1−C5) and the benzene ring (C13−C18) are not on the same plane, which have lowered the extent of electronic communication or conjugation in the molecule.

Polymerization Behaviors. We first attempted to polymerize **1** by a mixture of tantalum halide and tetraphenyltin because this catalytic system was found to be effective for the polycyclotrimerizations of ferrocenyl diynes.[9] The polymerization reactions of **1** catalyzed by $TaBr_5-Ph_4Sn$ in toluene at room temperature gave a partially soluble product in 30 min (Table 1, no. 1). Changing the catalyst system to $TaCl_5-Ph_4Sn$ increased the polymer yield, but the solubility of the product was still poor. Our attempt to suppress the cross-linking reaction by shortening the reaction time did not succeed. The high catalytic activity of the tantalum halides led to fast polycyclotrimerization reactions and resulted in the formation of polymers with poor processability.

Although the above results were disappointing, we did not give up. We examined whether the diyne polycyclotrimerization reaction could be initiated by $Cp^*RuCl(PPh_3)_2$ complex, an effective catalyst for the polycyclotrimerization of arylene bipropiolate.[11] Delightfully, stirring a THF solution of **1** in the presence of $Cp^*RuCl(PPh_3)_2$ at 70 °C for 24 h gave a soluble polymer with an M_w value of 2000, albeit in a low yield (Table 2, no. 1). The yield and molecular weight of the polymer were increased when the reaction time was prolonged to 48 h. Although the yield was boosted when the temperature was increased to 150 °C, the solubility of the polymer was lowed.

Table 2. Polymerization of Monomer 1 by $Cp^*RuCl(PPh_3)_2$[a]

no.	solvent	temp (°C)	time (h)	yield (%)	S[b]	M_w[c]	M_w/M_n[c]
1	THF	70	24	16.5	√	2000	1.16
2	THF	70	48	50.3	√	2600	1.28
3	DMF	150	24	90.6	Δ		

[a] Carried out under nitrogen with $[M]_0$ = 100 mM and [cat.] = 5 mM. [b] Solubility (S) tested in common organic solvents such as THF, toluene, DCM, and chloroform; √ = completely soluble, Δ = partially soluble. [c] Estimated in THF by a gel permeation chromatography (GPC) equipped with refractive index (RI) and ultraviolet (UV) detectors on the basis of a linear polystyrene calibration.

Table 3. Polymerization of Monomer 1 by $[Rh(cod)(PPh_3)_2]PF_6$[a]

no.	[M] (mM)	[cat.] (mM)	solvent	time (h)	yield (%)	M_w[b]	M_w/M_n[b]
1	50	5	toluene	6	49.9	2000	1.18
2	50	5	DMF	6	86.9	2300	1.26
3	50	5	dioxane	6	86.7	2400	1.29
4	50	5	THF	6	79.0	2500	1.28
5	25	5	THF	6	100	2800	1.34
6	50	5	THF	6	79.0	2500	1.28
7	100	5	THF	6	46.6	2500	1.27
8	50	1.25	THF	24	18.1	2000	1.20
9	50	2.5	THF	24	51.9	2600	1.30
10	50	5	THF	24	98.5	2600	1.44
11	100	5	THF	6	46.6	2500	1.27
12	100	7.5	THF	6	74.0	3000	1.36
13	100	10.0	THF	6	97.0	3200	1.46

[a] Carried out at 70 °C under nitrogen. [b] Estimated in THF by a GPC equipped with RI and UV detectors on the basis of a linear polystyrene calibration.

Cationic rhodium(I) complexes are known as effective catalysts for chemo- and regioselective [2 + 2 + 2] cycloaddition reactions. Whereas synthetic chemists have frequently used them in the transformation of small molecules,[12] little effort has been made to utilize them in the polymer synthesis. We prepared $[Rh(cod)(PPh_3)_2]PF_6$ according to the literature procedures[13] and checked its catalytic activity for the polycyclotrimerization of **1**. The reaction conducted in toluene gave a soluble polymer in ~50% yield in a short time (Table 3, no. 1). Solvent exerted a strong influence on polymer yield. The polymerization reactions performed in polar solvents of DMF, dioxane, and THF produced polymers in much higher yields.

Encouraged by the success of polymerizing **1** by the organorhodium complex, we went on to optimize the reaction conditions. We first examined the effect of monomer concentration on the polymerization reaction. An increase in the monomer concentration led to a decrease in the polymer yield (Table 3, nos. 5 and 6). At a monomer concentration of 100 mM, the polymer yield was only half of that at 25 mM. On the contrary, increasing the catalyst concentration increased the polymer yield and molecular weight (Table 3, nos. 8−13). The results obtained in runs 5, 10, and 13 suggest that the optimal molar ratio of monomer to catalyst falls in the range from 5:1 to 10:1.

We followed the time course of the polycyclotrimerization reaction. The reaction conduced at the optimal monomer and catalyst concentrations afforded a polymer with an M_w value of 2500 in ~78% yield in 3 h (Table 4, no. 1), revealing a high catalytic activity of the rhodium complex. Prolonging the polymerization time increased the polymer yield, with a polymer obtained in a nearly quantitative yield in 24 h. The molecular weights of the polymers measured by GPC were all low. This may be caused by the problem associated with the GPC system calibrated by linear polystyrene standards,

Table 4. Time Course of the Polymerization of Monomer 1[a]

no.	time (h)	yield (%)	M_w[b]	M_w/M_n[b]
1	3	78.3	2500 (36 000);	1.28
2	6	79.0	2500 (32 000);	1.28
3	12	89.2	2500 (98 000);	1.31
4	24	98.5	2600 (137 000);	1.45

[a] Carried out in THF at 70 °C under nitrogen using [Rh(cod)(PPh_3)$_2$]PF_6 as catalyst. $[M]_0 = 50$ mM and [cat.] = 5 mM. [b] Estimated in THF by a GPC equipped with RI and UV detectors on the basis of a linear polystyrene calibration. Absolute value determined by static laser light scattering technique given in parentheses.

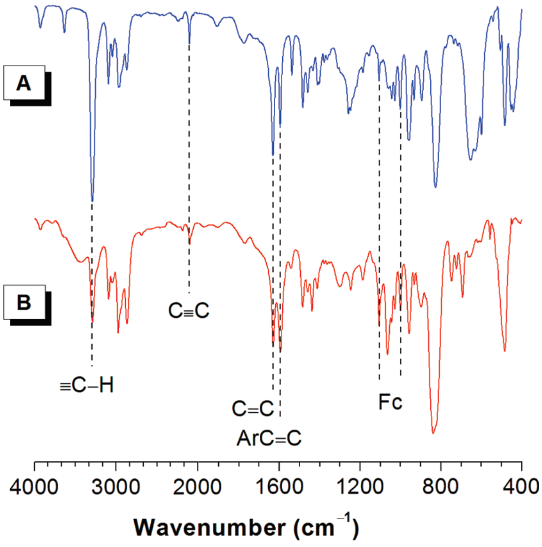


Figure 2. IR spectra of (A) monomer **1** and (B) its polymer *hb*-**P1** (sample taken from Table 3, no. 13).

which often underestimates the molecular weights of hyperbranched polymers due to their rigid, three-dimensional architectures.[14] The real molecular weights of the *hb*-PPs could be much higher than the relative values estimated by the GPC system.[15] Indeed, when we measured the molecular weights of the *hb*-PPs by the light-scattering technique, their absolute M_w values were found to be 12−50 times higher than their relative values (Table 4). It becomes clear that the homopolycyclotrimerization of **1** catalyzed by the Rh catalysts can produce soluble *hb*-PPs with high molecular weights in excellent yields.

Structural Characterization. The *hb*-PPs were characterized by spectroscopic techniques, and all the polymers gave satisfactory analysis data (see Experimental Section in the Supporting Information for details). An example of the IR spectrum of *hb*-**P1** is shown in Figure 2 along with that of its monomer **1**. The strong bands associated with ≡C−H and C≡C stretching vibrations of **1** are observed at 3289 and 2102 cm^{-1}, respectively. These absorption bands become weaker in the spectrum of *hb*-**P1**, indicating that most of the acetylenic triple bonds have been consumed by the polycyclotrimerization reaction. The unreacted terminal triple bonds in the *hb*-**P1** can undergo end-capping reactions, which offers a nice opportunity to decorate periphery of the polymer and endow it with new functionalities.[16] Absorption bands characteristic of monosubstituted Fc are observed at 1105 and 1000 cm^{-1}, confirming that the polycyclotrimerization reaction has proceeded as expected and has been harmless to the Fc group. The aromatic C=C skeleton vibration of **1** absorbs at 1594 cm^{-1}, which is intensified after polymerization. The spectrum of *hb*-**P1** also displays alkene C=C stretching vibration at 1630 cm^{-1}, indicating that the Rh catalyst has selectively transformed the ethynyl triple bonds of **1** into benzene rings, while leaving the vinyl double bonds intact.

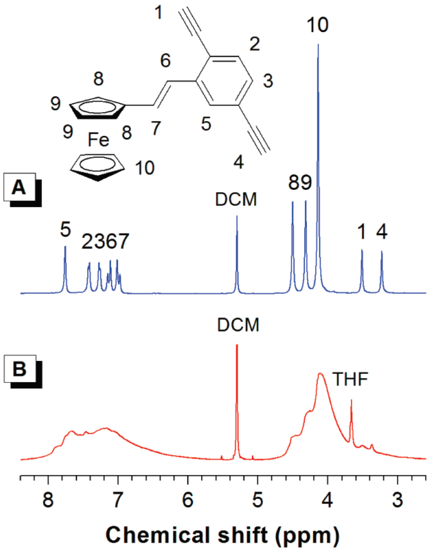


Figure 3. ^{1}H NMR spectra of (A) monomer **1** and (B) its polymer *hb*-**P1** (Table 3, no. 13) in DCM-d_2.

The ^{1}H NMR spectra of *hb*-**P1** and its monomer **1** are shown in Figure 3. The ethynyl protons of **1** resonate at δ 3.23 and 3.51. The resonance peaks of ethynyl protons become much weaker in intensity in the spectrum of *hb*-**P1**. This again proves that the acetylenic triple bonds have been consumed by the polycyclotrimerization. The resonance peaks of the Cp protons of the Fc units in **1** and *hb*-**P1** are located in the similar chemical shift region, but those of the latter are significantly broadened because of the rigid and irregular structure of the polymer. The broad peaks of *hb*-**P1** in the chemical shift region of δ 6.5−8.1 are associated with the resonances of the protons of the phenyl and vinyl groups originally present in the monomer as well as the protons of the 1,2,4- and 1,3,5-trisubstituted benzene rings newly formed during the diyne polycyclotrimerization reaction.

It is known that some organorhodium complexes can catalyze addition polymerizations of monoynes such as phenylacetylenes and 1-alkynes to yield linear polyenes.[17] The polyenes take predominant *Z*-conformation and show sharp resonance peaks at δ 5.8−6.1 in the ^{1}H NMR spectra.[18] No such peaks, however, are observed in the spectrum of *hb*-**P1**. This substantiates that the Rh complex used in this study catalyzed polycyclotrimerization reaction and that the resultant polymer has a hyperbranched molecular structure.

The UV spectra of monomer **1** and its polymer *hb*-**P1** in THF solutions are shown in Figure 4. The phenyl and ferrocenylvinylphenyl groups of **1** absorb at 270 and 330 nm. A broad absorption peak at 420−550 nm is also observed, which is assignable to the d−d transition within the ligand field formalism of conjugated ferrocene.[19] The absorption peaks are broadened in the spectrum of *hb*-**P1**. The polymer shows higher absorptivity in the spectral region of 370−550 nm due to the contribution from its conjugated molecular structure.

Thermal Stability and Redox Activity. The thermal properties of the Fc-containing polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under argon. Thanks to its rigid structure comprised of benzene rings, the *hb*-**P1** starts to lose it weight at a temperature above 300 °C (Figure 5). When pyrolyzed

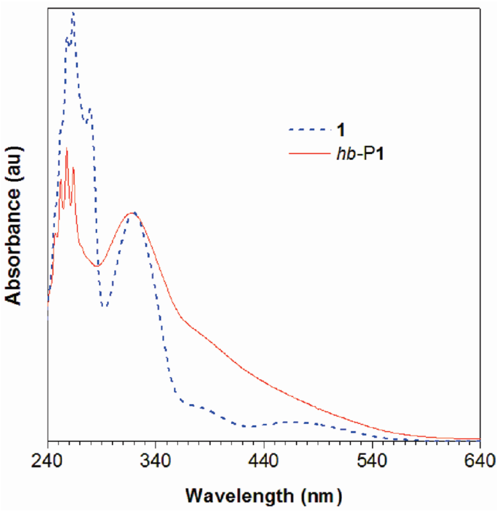


Figure 4. UV spectra of THF solutions (10 μg/mL) of monomer **1** and its polymer *hb*-**P1** (sample taken from Table 3, no. 13).

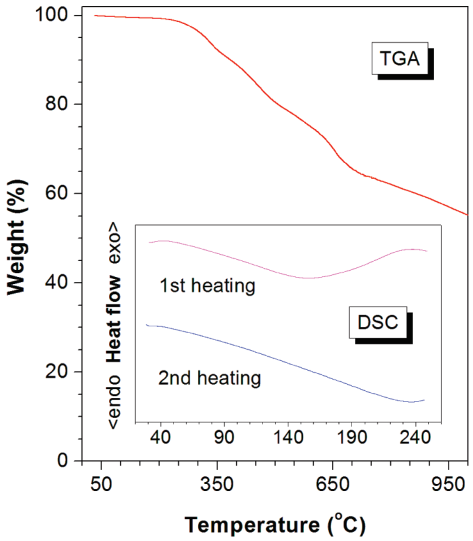


Figure 5. TGA and DSC thermograms of *hb*-**P1** (sample taken from Table 3, no. 13) recorded under argon at a heating rate of 10 °C/min.

at 1000 °C, the polymer carbonizes in ~56% yield, which is much higher than those of its linear congeners.[20] The high thermal stability of the polymer further verifies its hyperbranched structure because poly(phenylacetylene) $-[HC{=}CC_6H_5]_n-$ starts to lose its weight at 225 °C due to the instability of its linear polyene backbone.

Polymers containing acetylene moieties are known to undergo thermal polymerization upon heating. There exist acetylenic triple bonds in the periphery of *hb*-**P1**, and the polymer is expected to undergo facile thermal curing reaction. Indeed, when *hb*-**P1** is heated in a DSC cell, it begins to release heat from ~150 °C and shows a peak at ~240 °C due to the thermally induced cross-linking associated with the alkyne polymerization (Figure 5, inset). The second heating scan of the DSC analysis offers a monotonic curve, with no exothermic peak detected in the same temperature region, indicating that the thermal curing process is irreversible.

Electrochemical properties of *hb*-**P1** were investigated by cyclic voltammetry. For comparison, the redox behavior of monomer **1** was also studied under the similar experimental conditions. The data obtained at different scan rates are shown in Figure 6 and summarized in Table 5. It is well-known that in a fully reversible redox system $\Delta E_p = (E_p^a - E_p^c) = 59/n$ (where n is the number of electron transferred during the redox process) and $i_p^c/i_p^a = 1$ (where i_p^c and i_p^a are the peak currents of cathode and anode, respectively).[21] Monomer **1** shows Fc/Fc^+ redox couples in the voltage region from −1.0 to 1.0 V (Figure 6A). The i_p^c/i_p^a value at a scan rate of 100 mV/s is equal to 0.99. The ratio changes little with the scan rate, indicative of an excellent reversibility.

Polymer *hb*-**P1** also shows a single oxidation peak in the voltage region from −1.0 to 1.0 V (Figure 6B). No high degree of Fc−Fc interaction is observed in the redox process, suggestive of a lack of electronic communication between the metallic species.[22] Unlike **1**, the i_p^c/i_p^a value of *hb*-**P1** is not equal to unity and varies with the scan rate, revealing that its redox process is not fully reversible. The $E_{1/2}$ value of *hb*-**P1**, however, is smaller than that of its monomer. Clearly, the Fc units are oxidized more easily when incorporated into the conjugated polymer structure.[23] The charges may have been stabilized by the delocalization effect in the conjugated polymer. The cathodic and anodic peak currents of the monomer and polymer are proportional to the square root of scanning rate (Figure 7). This suggests that the electric current is limited by the diffusion of the monomer or polymer species to the electrode surface.[24]

Metal Complexation and Light Refraction. The acetylene triple bond is a versatile ligand widely used in organometallic chemistry.[25] Examples of acetylene−metal reactions include facile complexations of one triple bond with $Co_2(CO)_8$ and of two triple bonds with $CpCo(CO)_2$.[26] The *hb*-PPs contain π-electron-rich benzene ring, ethylene double bonds, and residual ethynyl triple bonds, all of which can form complexes with cobalt carbonyls. Indeed, when *hb*-**P1** was admixed with octacarbonyldicobalt in THF at room temperature, the solution color was changed from red to brown with steady evolution of gas bubbles, clearly verifying the occurrence of the cobalt complexation reaction (Scheme 3). The mixture remained homogeneous throughout the complexation process, and the product was isolated by pouring the THF solution into hexane. The precipitate was soluble in THF, which enabled us to purify the complex by repeated precipitation. However, the complex became insoluble after being dried under vacuum, possibly due to the formation of supramolecular aggregates during the drying process.

Figure 8 shows the IR spectra of *hb*-**P1**$\{[Co(CO)_3]_2\}_x$ complex and its precursor polymer *hb*-**P1**. The spectrum of the cobalt−polymer complex shows no ≡C−H and C≡C stretching vibrations of *hb*-**P1** at 3287 and 2099 cm^{-1}. Very strong vibration bands typical of cobalt carbonyl absorptions are emerged at 2090, 2052, and 2023 cm^{-1}, duly verifying the integration of the metallic species into the polymer structure at the molecular level.[26] The absorption bands of the benzene ring, ethylene double bond, and Cp ring in the *hb*-**P1**$\{[Co(CO)_3]_2\}_x$ complex are significantly weakened in intensity and broadened in width, probably due to the perturbations caused by the interactions of these moieties with the cobalt carbonyls.

Polymers with high refractive indices (RI) are promising candidate materials for photonic applications. In our previous work, we have found that hyperbranched polyynes and their cobalt complexes show RI values as high as 1.713−1.861 in the long wavelength region.[16,27] Recent investigation reveals that hyperbranched poly[1,3,5-tri(aroxycarbonyl)phenylene]s are also a class of highly refractive polymers, whose RI values can be tuned by UV

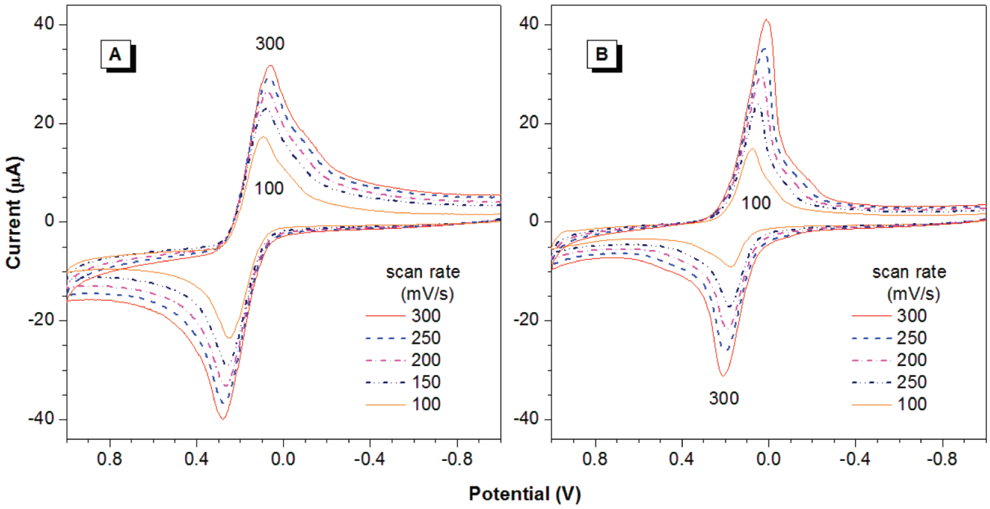


Figure 6. Cyclic voltammograms of (A) monomer **1** and (B) its polymer *hb*-**P1** (sample taken from Table 3, no. 13) measured at 25 °C in DCM containing 0.1 M of n-Bu$_4$NPF$_6$ at different scan rates. Concentration of **1** or *hb*-**P1**: 1.0 mg/mL.

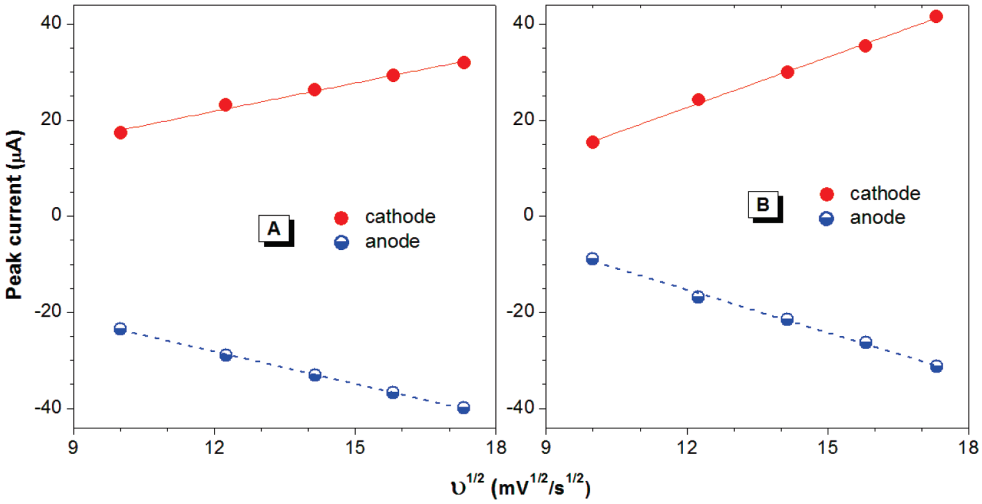


Figure 7. Plots of cathodic and anodic peak currents of (A) monomer **1** and (B) its polymer *hb*-**P1** (sample taken from Table 3, no. 13) against square root of the scan rate (υ).

Table 5. Electrochemical Properties of Monomer 1 and Its Polymer *hb*-P1[a]

υ (mV/s)	i_p^c (μA)	i_p^a (μA)	E_p^c (V)	E_p^a (V)	ΔE_p (V)	$E_{1/2}$ (V)	i_p^c/i_p^a
			Monomer **1**				
100	22.13	−22.29	0.092 26	0.2525	0.160 24	0.1724	0.99
150	26.90	−27.38	0.079 51	0.2642	0.184 69	0.1718	0.98
200	30.39	−31.16	0.078 67	0.2688	0.190 13	0.1737	0.98
250	33.32	−34.47	0.066 56	0.2772	0.210 64	0.1719	0.97
300	36.23	−37.47	0.062 17	0.2807	0.218 53	0.1714	0.97
			hb-P**1**				
100	15.31	−8.87	0.076 97	0.1745	0.097 53	0.1257	1.73
150	24.24	−16.96	0.047 87	0.1847	0.136 83	0.1163	1.43
200	29.96	−21.53	0.037 43	0.1927	0.155 27	0.1151	1.39
250	35.46	−26.24	0.019 88	0.2018	0.181 92	0.1108	1.35
300	41.51	−31.21	0.010 11	0.2109	0.200 79	0.1105	1.33

[a] Measured in DCM (~1 mg/mL) containing 0.1 M of n-Bu$_4$NPF$_6$ at room temperature. Abbreviations: υ = scan rate, i_p^c = cathodic peak current, i_p^a = anodic peak current, E_p^c = cathodic peak potential, E_p^a = anodic peak potential, ΔE_p = peak potential difference ($E_p^a - E_p^c$), and $E_{1/2} = (E_p^a + E_p^c)/2$.

irradiation.[28] The *hb*-**P1** and its organocobalt complex possess polarizable aromatic rings and metallic species, both fulfilling the requirement for exhibiting high RI values. Indeed, a thin solid film of *hb*-**P1** displays high refractive indices (n = 1.808−1.740) in the spectral region of 300−1700 nm (Figure 9). Its cobalt complex *hb*-**P1**$\{[\mathrm{Co(CO)_3}]_2\}_x$ shows similarly high RI values (1.704−1.681). These values are much higher than those of the commercially important plastics such as poly(methyl methacrylate) (PMMA, n ~ 1.49), polycarbonate (PC), and poly(ethylene terephthalate) (both n ~ 1.58).

For a material to be useful for technological applications, its optical dispersion should be small. The Abbé number (ν_D) of a material is a measure of the variation in its RI value with wavelength, which is defined as

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \tag{1}$$

where n_D, n_F, and n_C are the RI values at wavelengths of Fraunhofer D, F, and C spectral lines of 589.2, 486.1, and 656.3 nm, respectively. To evaluate the potential of a photonic material for real-world application, a modified Abbé number (ν_D') has been proposed, using the RI values at the nonabsorbing wavelengths of 1064, 1319, and 1550 nm in the IR spectral region.[29] The first two wavelengths are chosen in

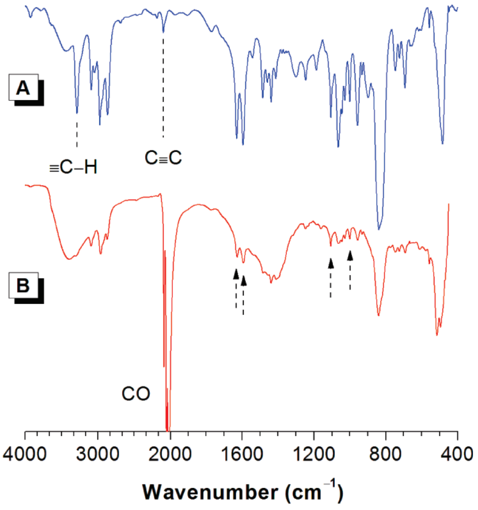


Figure 8. IR spectra of (A) *hb*-**P1** (Table 3, no. 13) and (B) its cobalt complex *hb*-**P1**$\{[Co(CO)_3]_2\}_x$.

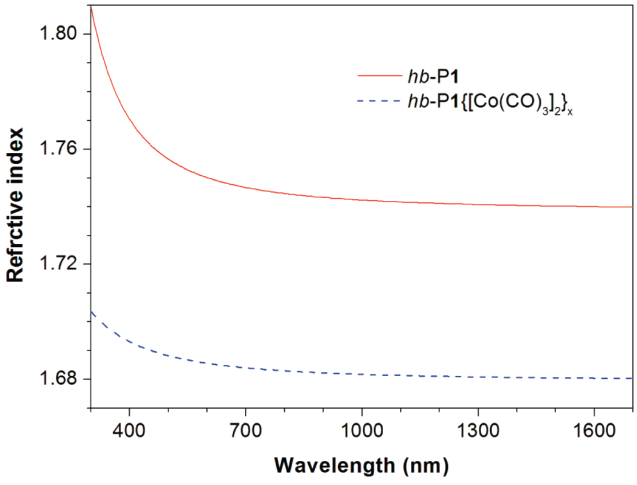


Figure 9. Refractive indices of thin films of *hb*-**P1** (sample taken from Table 3, no. 13) and its cobalt complex *hb*-**P1**$\{[Co(CO)_3]_2\}_x$.

view of the practical interest of commercial laser wavelengths (Nd:YAG), while the last one is the wavelength for telecommunication. The modified Abbé number is defined as

$$\nu_D' = \frac{n_{1319}-1}{n_{1064}-n_{1559}} \qquad (2)$$

where n_{1319}, n_{1064}, and n_{1550} are the RI values at 1319, 1064, and 1550 nm, respectively. The chromatic dispersion ($D^{(\prime)}$) is the constringence of the Abbé number ($\nu_D^{(\prime)}$):

$$D^{(\prime)} = \frac{1}{\nu_D^{(\prime)}} \qquad (3)$$

A large Abbé number thus corresponds to a low dispersion in the refractive index.[30] Generally, an organic polymer with a high RI value displays a low $\nu_D^{(\prime)}$ value (or high dispersion) and vice versa.[31] For example, poly(vinylcarbazole) shows a high refractive index (n = 1.675) but a low Abbé number (ν_D = 19), whereas Teflon or poly(tetrafluoroethylene) exhibits a low refractive index (n = 1.345) but a high Abbé number (ν_D = 83).[32] It has been extremely rare for a material to have both high n and ν_D values.

Scheme 3. Metalization via Complexation and Ceramization via Pyrolysis

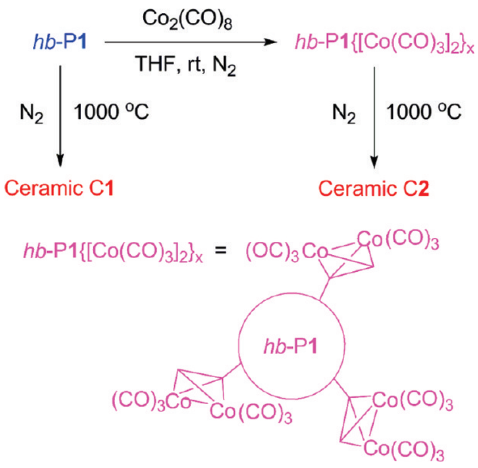


Table 6. Refractive Indices (n) and Chromatic Dispersions of *hb*-P1 and *hb*-P1$\{[Co(CO)_3]_2\}_x$[a]

material	$n_{632.8}$	ν_D	ν_D'	D	D'
hb-**P1**	1.7489	75.8	435.6	0.0132	0.00229
hb-**P1**$\{[Co(CO)_3]_2\}_x$	1.6851	163.3	680.8	0.00612	0.00147

[a] Data taken from Figure 9, unless otherwise specified. Abbreviations: n = refractive index (at 632.8 nm), ν_D = Abbé number (calculated from eq 1), ν_D' = modified Abbé number (calculated from eq 2), and $D^{(\prime)}$ = chromatic dispersion (calculated from eq 3).

The *hb*-**P1** and its cobalt complex belong to this group of rare materials, which show not only high refractive indices but also high Abbé numbers. The ν_D and ν_D' values for *hb*-**P1** are 75.8 and 435.6, corresponding to D and D' values of 13.2 × 10^{-3} and 2.29 × 10^{-3}, respectively (Table 6). The Abbé numbers of its cobalt complex are even higher (ν_D = 163.3 and ν_D' = 680.8), giving D and D' values as low as 6.12 × 10^{-3} and 1.47 × 10^{-3}, respectively. The chromatic dispersions of *hb*-**P1** and its complex are much lower than those of PMMA (D = 17.5 × 10^{-3}) and PC (D = 29.7 × 10^{-3}). Their D' values are also lower than those of poly(aroyltriazole)s recently synthesized in our research laboratories (D' = 6.1 × 10^{-3}–3.66 × 10^{-3}).[33] The very high refractive indices and extremely low optical dispersions of *hb*-**P1** and *hb*-**P1**$\{[Co(CO)_3]_2\}_x$ may enable them to find a variety of applications in photonics and holography, such as read-only memories in the near-IR region.[34]

Pyrolytic Ceramization to Nanostructured Magnetoceramics. We have found that hyperbranched organometallic polymers, in comparison to their linear counterparts, are better precursors to magnetic ceramics in terms of ceramization yield and magnetic susceptibility because the three-dimensional cages of the hyperbranched polymers enable better retention of pyrolytic species and steadier growth of magnetic crystallites.[26,35] Pyrolyzing *hb*-**P1** and its cobalt complex in a TGA furnace at 1000 °C under nitrogen gave ceramics **C1** and **C2**, as shown in Scheme 3. All the ceramics were magnetizable and could be readily attracted to a bar magnet, which prompted us to study their structures and properties in detail.

To get a first impression of the metalloceramics, we used scanning electron microscope (SEM) to examine their surface morphologies. Figure 10 shows the SEM images of **C1** and **C2**. The ceramics produced at 1000 °C in an atmosphere of nitrogen are compact but rough, with their surfaces decorated with small particles and clusters. Such a morphological

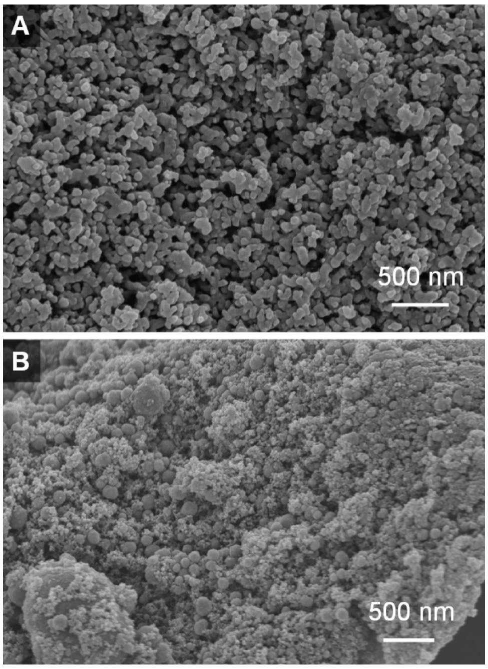


Figure 10. SEM micrographs of ceramics (A) C**1** and (B) C**2** prepared by pyrolytic ceramization of *hb*-P**1** and *hb*-P**1**$\{[Co(CO)_3]_2\}_x$ at 1000 °C under nitrogen.

Table 7. Chemical Compositions of the Magnetic Ceramics Estimated by XPS and EDX Analyses[a]

		XPS (%)				EDX (%)[a]			
ceramics	yield (%)	C	O	Fe	Co	C	O	Fe	Co
C**1**	55.0	93.20	5.32	1.22	0	88.92	5.42	5.66	0
C**2**	60.0	18.17	48.61	5.01	27.53	1.24	0.55	24.89	73.33

[a] Ceramics C**1** and C**2** obtained by pyrolyses of *hb*-P**1** and *hb*-P**1**$\{[Co(CO)_3]_2\}_x$, respectively, at 1000 °C for 1 h under nitrogen.

structure suggests a good heat resistance of the 3-dimensional *hb*-PP skeletons: only have some small amounts of volatile fragments been stripped off under the harsh conditions during the pyrolysis process.

We carried out X-ray photoelectron spectroscopy (XPS) and energy-dispersion X-ray (EDX) analyses to estimate the chemical compositions of the ceramics. XPS measurements give iron contents of 1.22% and 0% and cobalt contents of 5.01% and 27.53% on the surfaces of C**1** and C**2**, respectively (Table 7). In the bulk of C**1** and C**2**, the contents are respectively changed to 5.66% and 0% for iron and 24.89% and 73.33% for cobalt. This composition gradient of the transition metals from the bulk to the surface implies that the ceramization process is started from the formation of transition-metal nanocluster cores and ended by the wrapping with carbon coronas. To gain insights into the structures of the bulk, we investigated the ceramics by transmission electron microscope (TEM). As shown in Figure 11, the metal nanoparticles (dark grains) are of irregular round shape and well embedded in the carbon matrixes (light areas). The electron diffraction patterns of the metal nanoparticles show many diffraction spots, indicative of their crystalline nature.

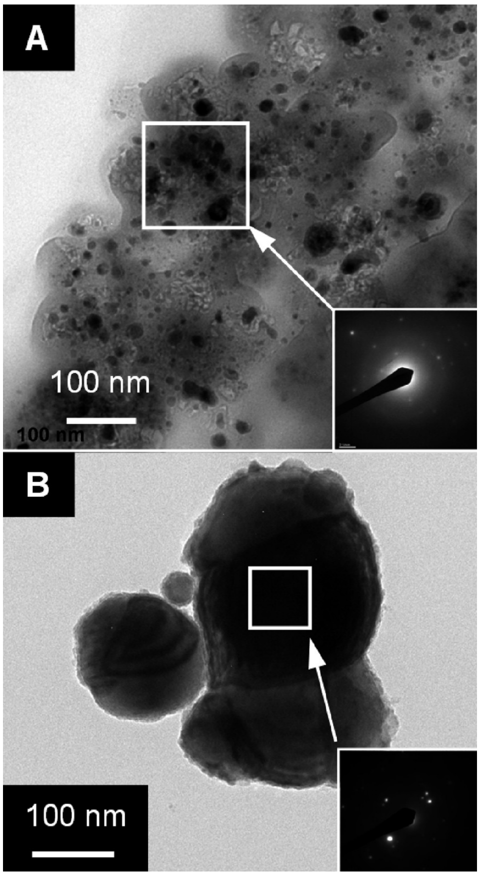


Figure 11. TEM images of ceramics (A) C**1** and (B) C**2**.

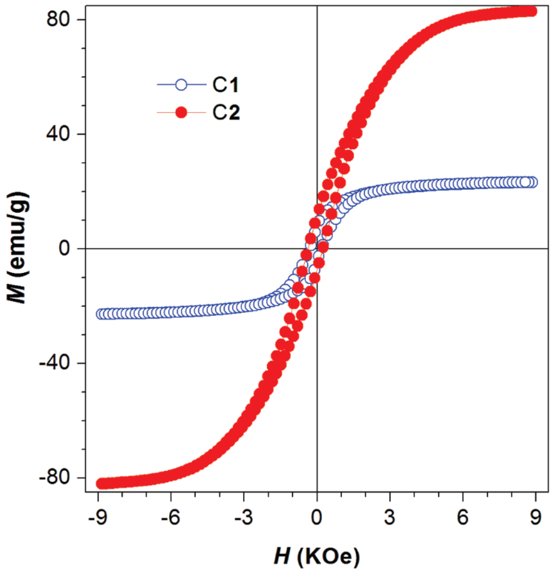


Figure 12. Plots of magnetization (M) vs applied magnetic field (H) at 300 K for ceramics C**1** and C**2**.

It now becomes clear that all the ceramic materials contain nanoscopic metallic nanoparticles, which are expected to be magnetically susceptible. Figure 12 shows the magnetization curves of the ceramics. Under an externally applied magnetic field, C**1** is magnetized and then quickly saturated at ∼23 emu/g. The magnetization of C**2** swiftly increases and ultimately levels off at a saturation magnetization (M_s) of ∼83 emu/g. Evidently, the cobalt nanoclusters in ceramic C**2** have helped to dramatically enhance its magnetizability, taking into account that the M_s value of maghemite (γ-Fe_2O_3) is 74 emu/g.[36] We have prepared magnetic ceramics from ferrocene-containing polyacetylenes and found that their M_s values are ∼17 emu/g.[37] Manners' group has obtained magnetic nanoparticles from the complexes of a linear poly(ferrocenylsilane) and $Co_2(CO)_8$, and their M_s values fall in the range of ~20−35 emu/g.[38] These comparisons prove that metal-containing hyperbranched polymers are better precursors to magnetic ceramics than their linear congeners.

Conclusions

In this work, effective, robust Ru- and Rh-based catalyst systems for diyne polycyclotrimerization were developed. New functional *hb*-PPs with high densities of Fc units and high molecular weights were synthesized in high yields. The polymers were soluble in common organic solvents, and their hyperbranched molecular structures were confirmed by spectroscopic analyses. The *hb*-PPs were film-forming, thermally stable, and redox active. They were further metalated through ready complexation with cobalt carbonyls. The *hb*-PPs and their cobalt complexes exhibit high refractive indices and low chromatic dispersions. Their pyrolytic ceramizations furnish ceramics with high magnetizabilities. These unique attributes make the polymers promising candidate materials for high-tech applications.

Acknowledgment. This work was partially supported by the Hong Kong Research Grants Council (603509, 603008, and HKUST13/CRF/08), the National Science Foundation of China (20974028 and 20634020), and the Ministry of Science & Technology (2009CB623605). We thank Prof. Chi Wu of the Chinese University of Hong Kong and Dr. Fanny L. Y. Shek of our University for their technical assistance. B.Z.T. thanks the support from the Cao Guangbiao Foundation of Zhejiang University.

Supporting Information Available: General information about the materials and instrumentations; experimental procedures for the monomer synthesis, polymerization reaction, cobalt complexation, and pyrolytic ceramization; characterization data for the monomer and its polymers; and crystal data of monomer **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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