

# Hyperbranched Polyynes: Syntheses, Photoluminescence, Light Refraction, Thermal Curing, Metal Complexation, Pyrolytic Ceramization, and Soft Magnetization

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Homopolycouplings of aryltriyne  $\text{Ar}(\text{C}\equiv\text{CH})_3$  and their copolycouplings with monoyne  $\text{Ar}'\text{C}\equiv\text{CH}$  are effected by  $\text{CuCl}$  in air under Glaser-Hay oxidative coupling conditions, giving soluble hyperbranched polyynes (*hb*-PYs). Hyperbranched poly[tris(4-ethynylphenyl)amine] emits bright blue light ( $\lambda_{\text{em}} = 440 \text{ nm}$ ) and shows high light refractivity ( $n = 1.770\text{--}1.861$ ). Its peripheral terminal triple bonds can be 100% end-capped by aromatic rings via palladium-catalyzed coupling with aryl iodides. The carbon-rich polyynes are readily curable (from  $\sim 150^\circ\text{C}$ ), thermally stable ( $T_d$  up to  $\sim 550^\circ\text{C}$ ), and pyrolytically carbonizable ( $W_r$  up to  $\sim 80\%$  at  $900^\circ\text{C}$ ). Complexations with cobalt carbonyls metallify the *hb*-PYs, and ceramizations of the cobalt–polyyne complexes afford soft ferromagnetic materials with high magnetizability ( $M_s$  up to  $\sim 118 \text{ emu/g}$ ) and low coercivity ( $H_c$  down to  $\sim 0.045 \text{ kOe}$ ).

Although a vast variety of nonconjugated polymers have been prepared from alkenes, we are interested in utilizing alkynes as building blocks to construct conjugated polymers with novel structures and unique properties.<sup>1–3</sup> Through metathesis polymerizations of *monoyne* ( $\text{RC}\equiv\text{CR}'$ ), we have generated linear polyynes  $[-(\text{RC}\equiv\text{CR}')_n-]$  that show such functional properties as liquid crystallinity, photoconductivity, electroluminescence, aggregatochromism, chemosensitivity, helical chirality, supramolecular assembly, and biological activity.<sup>1,2</sup> Employing polycyclotrimerizations of *diynes* [ $\text{R}(\text{C}\equiv\text{CH})_2$ ], we have created hyperbranched polyarylenes  $[>(\text{Ar}-\text{R}-\text{Ar})_n<]$  with excellent thermal stability, high photoluminescence efficiency, and strong optical nonlinearity.<sup>2,3</sup> In this work, we explored the possibility of using *triyne* [ $\text{R}(\text{C}\equiv\text{CH})_3$ ] as monomer units to assemble hyperbranched polyynes (*hb*-PYs; Scheme 1). Although a large number of linear polyynes [e.g., poly(aryleneethynylene)s] have been prepared,<sup>4,5</sup> hyperbranched polyynes have been rarely synthesized because of the difficulty in obtaining soluble polymers. Through structural design and reaction control, in this work, we succeeded in preparing a group of *hb*-PYs that are soluble, emissive, refractive, thermally curable, peripherally functionalizable, and molecularly metallizable. The metal–polyyne complexes can be readily converted to soft magneto-ceramics of high magnetizability.

With an interest in building a conjugated polyyne, we first prepared 1,3,5-triethynylbenzene (**1a**), an aryltriyne, by Pd-catalyzed coupling of silylacetylene with triiodobenzene followed by desilylation in an alkaline medium.<sup>4</sup> Polycoupling of the triyne was attempted under the Glaser-Hay conditions:<sup>5</sup> **1a** was added and mixed with  $\text{CuCl}$  and TMEDA in *o*-DCB, with an air stream bubbling through the resultant mixture. The polymerization proceeded rapidly and the mixture gelled quickly (Table 1, entry 1): the product was unfortunately insoluble. Introduction of long, flexible alkoxy groups has been a popular approach to boosting polymer solubility,<sup>6</sup> and we thus prepared

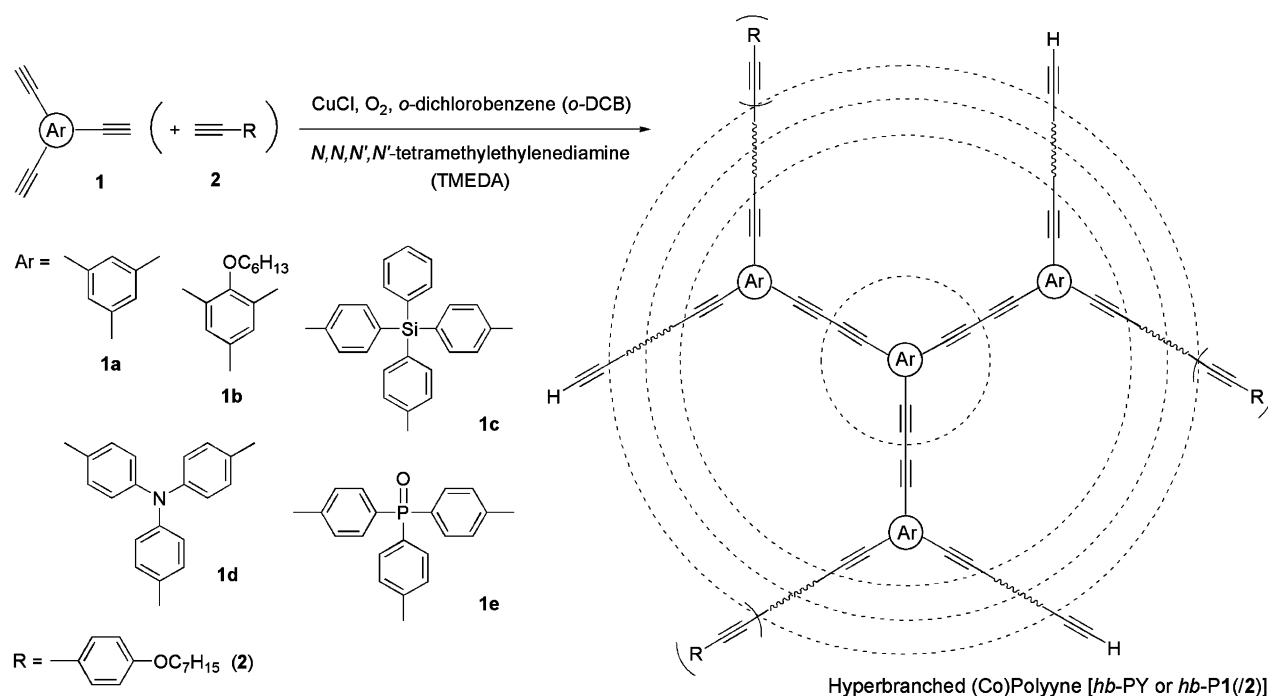
**1b**,<sup>4</sup> a congener of **1a** with a hexyloxy group, in the hope that its polymer would be soluble. Polycoupling of **1b** propagated steadily, giving a polymer (*hb*-**P1b**) with a high molecular weight ( $M_w = 30\,700$ ) in a high yield (76%). Delightfully, *hb*-**P1b** was completely soluble in common solvents such as THF, toluene, and chloroform. Nonplanar units can sometimes help improve polymer solubility<sup>6,7</sup> and three nonplanar aryltriyne monomers (**1c**–**1e**) were thus prepared.<sup>4</sup> Thankfully, two of their polymers, i.e., *hb*-**P1d** and *hb*-**P1e**, were soluble, although **1c** underwent cross-linking reaction.

Another strategy for solubility enhancement is to increase structural irregularity or randomness by copolymerization.<sup>7</sup> This approach worked well in this project: almost all of the copolycoupling reactions of the triynes (**1**) with monoyne **2**<sup>8</sup> afforded soluble copolyynes (*hb*-**P1/2**). Whereas the homopolycouplings of **1a** and **1c** easily run out of control, their copolycouplings with monoyne **2** were smooth, yielding copolyynes that were completely soluble in common solvents (cf., Table 1, entries 1 and 3 vs entries 6 and 8). The copolymerization of **1b** with **2**, however, practically failed. The reason for this failure is not understood and is under investigation in our laboratories.

All of the soluble *hb*-PYs were spectroscopically characterized, from which, satisfactory analysis data corresponding to their expected molecular structures were obtained (Supporting Information). An IR spectrum of *hb*-**P1d/2**, along with that of one of its monomers (**1d**), is given in Figure S1 as an example. From the comparison with the monomer spectrum, it is clear that the absorption bands of the copolyyne at 3293 and 2104  $\text{cm}^{-1}$  are associated with  $\equiv\text{C}-\text{H}$  and  $\text{C}\equiv\text{C}$  vibrations, respectively. The bands at 2207 and 2142  $\text{cm}^{-1}$  are related to  $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$  stretching,<sup>9</sup> confirming that the polycoupling reaction has taken place. The copolyyne exhibits  $\nu_{\text{as}}\text{CH}_3$  and  $\nu_{\text{as}}\text{CH}_2$  bands at 2924 and 2852  $\text{cm}^{-1}$ , respectively, proving that the monoyne bearing the alkoxy tail (**2**) has been copolymerized with the aryltriyne (**1d**). Figure S2A shows a  $^1\text{H}$  NMR spectrum of *hb*-**P1d**, a homopolyyne, whose peaks are readily assign-

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## SCHEME 1: Homopolycouplings of Triynes (1) and Their Copolycouplings with Monoynne (2)

TABLE 1: Syntheses<sup>a</sup> and Properties of Hyperbranched Polyynes (*hb*-PYs)

entry	monomer	time (min)	<i>hb</i> -PY	yield (%)	$M_w^b$	PDI <sup>b</sup>	$T_d^c$ (°C)	$W_r^d$ (%)
Homopolymer								
1	1a	8	<i>hb</i> -P1a	<sup>e</sup>	30 700	3.6	377	50.4
2	1b	20	<i>hb</i> -P1b	76.1				
3	1c	15	<i>hb</i> -P1c	<sup>e</sup>				
4	1d	10	<i>hb</i> -P1d	51.7	24 100	1.6	516	78.0
5	1e	10	<i>hb</i> -P1e	37.1	5 100	1.4	549	84.0 <sup>f</sup>
Copolymer								
6	1a/2	30	<i>hb</i> -P1a/2	46.9	17 900	4.7	412	60.3
7	1b/2	180	<i>hb</i> -P1b/2	<sup>g</sup>				
8	1c/2	30	<i>hb</i> -P1c/2	67.4	13 000	7.2	411	59.2
9	1d/2	30	<i>hb</i> -P1d/2	57.2	18 200	5.3	456	73.3
10	1e/2	17	<i>hb</i> -P1e/2	19.1	7 500	1.4	430	65.9

<sup>a</sup> Carried out at 50 °C with an air stream bubbling through the reaction mixtures; [1] = 80 mM; [CuCl] = 4 mM, [TMEDA] = 13.8 mM. For copolycoupling, [1]/[2] = 1:1.5. <sup>b</sup> Determined by GPC on the basis of a polystyrene calibration. (Linear polystyrene-calibrated GPC often underestimates the molecular weights of hyperbranched polymers<sup>2,3</sup> and the “real”  $M_w$  values of the polyynes thus could be much higher than the relative values given here in this table.). <sup>c</sup> Temperature for 5% weight loss. <sup>d</sup> Weight residue at 900 °C unless otherwise specified. <sup>e</sup> Gelation. <sup>f</sup> At 850 °C. <sup>g</sup> Trace amount.

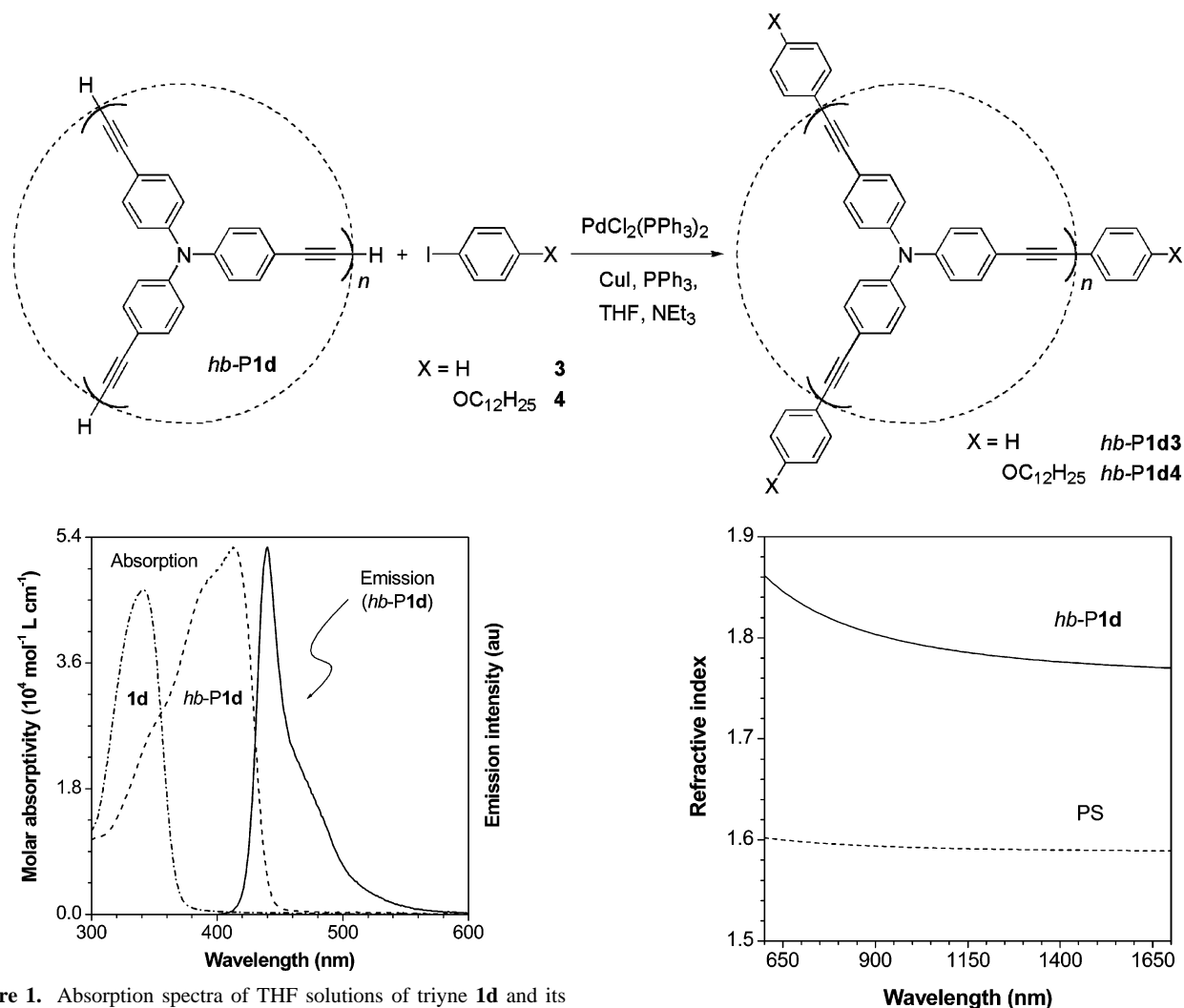
able: the resonance signals at  $\delta$  7.4, 7.0 (a), and 3.1 (b) are due to the absorptions of the aromatic and acetylenic protons, respectively. Chart S1 depicts <sup>31</sup>P NMR shifts of *hb*-P1e in different chemical environments, from which, the degree of branching (DB) of the phosphorus-containing polyynes is calculated to be 0.53, in agreement with theoretical prediction.<sup>10</sup> The DB determinations for other *hb*-PYs, however, remain a challenge, because of the difficulty in distinguishing the resonance peaks affiliated to their dendritic, linear, and terminal units.

As revealed by the spectroscopic analyses, both the homo- and copolyynes contain terminal triple bonds, which offers an opportunity to decorate the polymer peripheries by end-capping reactions. This is demonstrated by the coupling of *hb*-P1d with aryl iodides (Scheme 2). The coupling of iodobenzene (3) with the triple bonds proceeds smoothly at room temperature: the reaction product *hb*-P1d3 shows no vibration bands of terminal triple bonds, indicative of 100% end-capping. Although *hb*-P1d3 is soluble in the reaction solution, it becomes partially soluble after isolation, possibly due to  $\pi$ - $\pi$  stacking-induced supra-

molecular aggregation during the precipitation and drying processes. The coupling product of *hb*-P1d with 4, viz., *hb*-P1d4, remains soluble after isolation, thanks to its long dodecyloxy group. The solubility enables its structural characterization by “wet” methods. As can be seen from Figure S2B (Supporting Information), its NMR peaks nicely correspond to its expected molecular structure. No signal of terminal acetylene resonance is observed at  $\delta$  3.1, unambiguously attesting the completion of the end-capping reaction.

Triphenylamine (TPA) and its derivatives have often been used as hole-transporting materials in the fabrication of light-emitting diodes<sup>11</sup> and it is of interest to examine the electronic properties of the *hb*-PYs containing the TPA moiety, i.e., *hb*-P1d and *hb*-P1d/2. The absorption maximum ( $\lambda_{ab}$ ) of triyne 1d is located at 342 nm (Figure 1), which is 43 nm red-shifted from that of TPA,<sup>12</sup> thanks to the electronic communication of the peripheral triple bonds with the TPA core. The  $\lambda_{ab}$  of *hb*-P1d (413 nm) is further bathochromically shifted from that of 1d by 71 nm, indicative of extensive  $\pi$ -conjugation in the polyynes system. The polyynes emit a blue light of 440 nm upon

## SCHEME 2: Peripheral End-Capping through Terminal Acetylene Coupling with Aryliodide



**Figure 1.** Absorption spectra of THF solutions of triyne **1d** and its polymer **hb-P1d** ( $c = 0.012$  mg/mL) and emission spectrum of the **hb-P1d** solution ( $\lambda_{\text{ex}} = 368$  nm).

excitation. The blue emission is bright, whose luminance easily goes beyond  $1000 \text{ cd/m}^2$  when the polyynes are excited by a weak UV lamp with a power of merely  $30 \text{ mW/cm}^2$ . The absorption and emission spectra of copolymer **hb-P1d/2** resemble those of its homopolymer counterpart **hb-P1d** (Figure S3; Supporting Information), suggesting that the monoyne comonomer (**2**) exerts little effect on the electronic transitions of the copolymer. The optical properties of the **hb-PYs** are comparable to those of partially dialkoxylated linear poly(phenyleneethynylene)s,<sup>5,6,13</sup> but the former enjoy an obvious advantage of synthetic simplicity over the latter.

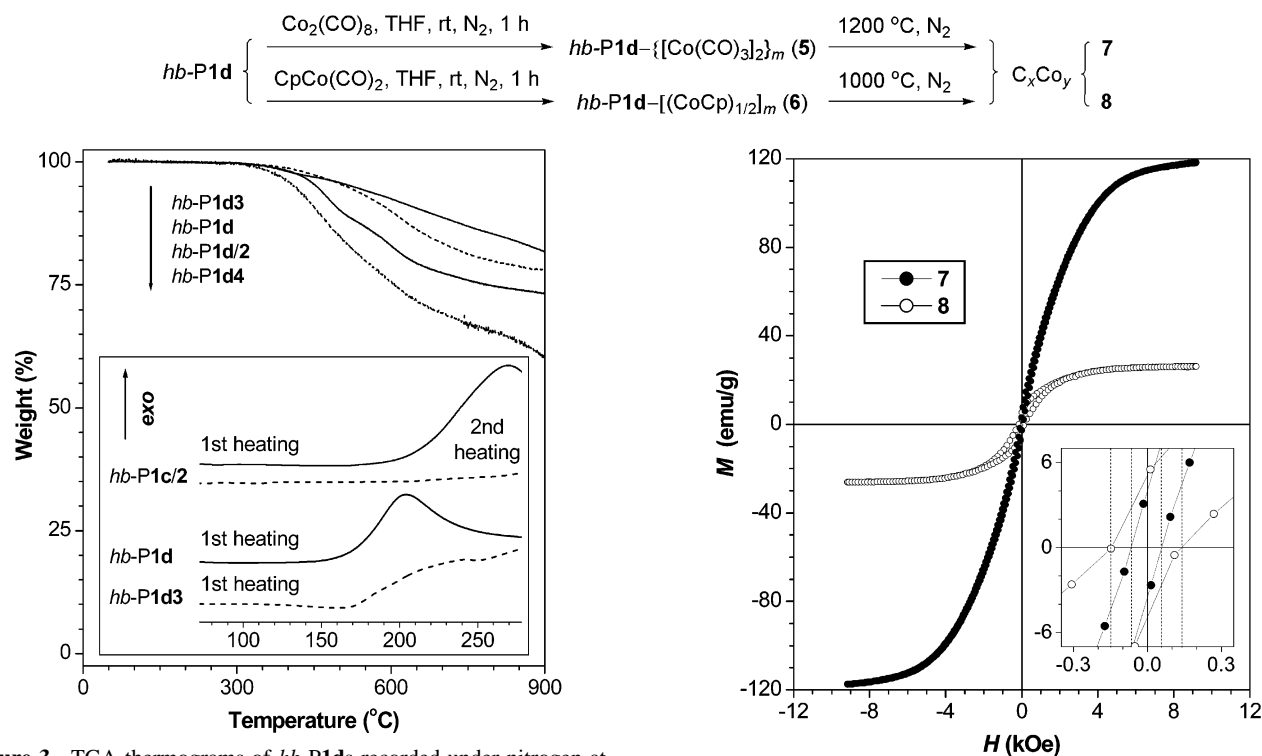
Advanced photonic devices are often composed of working units with high contrast of refractive index (RI). The RIs of existing polymers, however, vary in a small range (1.338–1.71),<sup>14</sup> which limits the scope of their photonic applications. Theory predicts that (macro)molecules consisting of groups with high polarizabilities and small volumes can exhibit high refractivities. Polyynes **hb-P1d** are comprised of electronically mobile aromatic rings and dimensionally slim triple-bond bars and are thus likely to possess high RIs. This is indeed the case: a thin film of **hb-P1d** shows RI values of 1.861–1.770 in the spectral region of 600–1700 nm (Figure 2), which are much higher than those of well-known “organic glasses” such as polystyrene ( $n = 1.602$ – $1.589$ ),<sup>15</sup> poly(methyl methacrylate) (1.497–1.489),<sup>14</sup> and polycarbonate (1.593–1.576).<sup>14</sup> The polyynes

**Figure 2.** Wavelength dependence of refractive index of a thin film of **hb-P1d**. Data for a thin film of polystyrene (PS) is shown for comparison.

film is transparent and shows high transmittance in the long wavelength region. The high light refractivity and optical transparency of the polyynes make it a promising candidate material for photonic applications.<sup>16</sup>

Polymers containing diyne moieties readily cross-link upon moderate heating<sup>17</sup> and many monoyne-terminated oligomers or prepolymers have been easily converted to thermoset networks.<sup>18</sup> The homo- and copolymers carry both di- and monoyne moieties and are thus expected to undergo facile thermal curing reactions. When **hb-P1c/2** is heated in a DSC cell, it starts to release heat at  $\sim 200$  °C due to the commencement of thermally induced alkyne polymerizations (Figure 3). The exothermic reaction peaks at  $\sim 270$  °C. The second heating scan of the DSC analyses detects almost a flat line parallel to the abscissa in the same temperature region, suggesting that all of the triple bonds have reacted during the first heating scan. The cross-linking reaction of **hb-P1d** starts from  $\sim 150$  °C and peaks at  $\sim 204$  °C. The easier curing of homopolymer **hb-P1d** over copolymer **hb-P1c/2** is probably because the former has more reactive terminal acetylene peripheries<sup>9a</sup> and sterically less crowded aryl cores. When the terminal acetylene groups of **hb-P1d** are end-capped by phenyl groups, the resulted **hb-P1d3** now contains only internal acetylene groups, which needs higher temperatures to drive its thermal curing to completion (Figure

## SCHEME 3: Complexation with Cobalt Carbonyls and Ceramization to Cobalt Magnets



**Figure 3.** TGA thermograms of *hb-P1ds* recorded under nitrogen at a heating rate of 20 °C/min. Inset: DSC thermograms of *hb-P1c/2*, *hb-P1d*, and *hb-P1d3* (nitrogen, 10 °C/min).

3), further manifesting the effect of the acetylene reactivity on the thermal curability of the polyynes.

The thermal curing makes the *hb-PYs* highly resistant to thermal decomposition. The temperature for 5% weight loss ( $T_d$ ) and the weight residue at 900 °C ( $W_r$ ) for the polyynes are high, being 377–549 °C and 50.4–78.0%, respectively (Table 1). Among the polyynes, *hb-P1e* is most stable, which loses little weight when heated to ~550 °C and retains 84% of its original weight when pyrolyzed at 850 °C. When the thermal stabilities of the *hb-P1d* family are compared, it is clear that the polyne end-capped by the robust phenyl ring (*hb-P1d3*) is more stable than its parent form (*hb-P1d*), whereas the polymers bearing the flexible alkoxy chains (*hb-P1d/2* and *hb-P1d4*) are less stable: the longer the alkoxy chain, the easier the polymer degradation (Figure 3).

Acetylene triple bond is a versatile ligand in organometallic chemistry.<sup>19</sup> Examples of acetylene–metal reactions include facile complexations of one triple bond with  $\text{Co}_2(\text{CO})_8$ <sup>20</sup> and of two triple bonds with  $\text{CpCo}(\text{CO})_2$ <sup>21</sup> (Scheme S1; Supporting Information). The *hb-PYs* contain many triple bonds and should be easily metallized through their complexations with the cobalt carbonyls. When a mixture of *hb-P1d* and octacarbonyldicobalt with a  $[\text{Co}_2(\text{CO})_8]/[\text{C}\equiv\text{C}]$  ratio of 1.5:1 is stirred in THF at room temperature, the solution color changes from yellow to brown accompanying CO gas evolution. The mixture remains homogeneous toward the end of the reaction, and the product (**5**; Scheme 3) is isolated in a high yield (94%) by pouring the THF solution into hexane.<sup>22</sup> Although **5** is completely soluble in the reaction mixture, it becomes insoluble after isolation, possibly due to the formation of supramolecular aggregates during the precipitation and drying process. Complex **5** is stable in air, whose IR spectrum shows strong vibration bands typical of cobalt carbonyl absorptions at 2090, 2055, and 2025  $\text{cm}^{-1}$ ,<sup>20c</sup> verifying the integration of the metallic species into the polyne structure at the molecular level.<sup>22</sup> Alternatively, *hb-P1d* can be

**Figure 4.** Plots of magnetization ( $M$ ) versus applied magnetic field ( $H$ ) at 300 K for magnetoceramics **7** and **8**. Inset: enlarged portions of the  $M$ – $H$  plots in the low strength region of the applied magnetic field.

cobalt-metallized via intra- and/or intermolecular complexations of its triple bonds with  $\text{CpCo}(\text{CO})_2$ , giving a hyperbranched polyne complex carrying cyclopentadienylcyclobutadienylcobalt ( $\text{CpCbCo}$ ) moieties (**6**).

We have previously 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 hyperbranched polymers enable better retention of pyrolyzed species and steadier growth of magnetic crystallites.<sup>23</sup> Will the hyperbranched polyne-cobalt complexes (**5** and **6**) serve as precursors to magnetic ceramics? The answer to this question is a firm yes. Pyrolyzing the complexes in a tube furnace at 1000 or 1200 °C for 1 h under a stream of nitrogen gives ceramic products **7** and **8** (Scheme 3) in ~42–65% yields. All of the ceramics are magnetizable and can be attracted to a bar magnet.

Figure 4 shows magnetization curves of the ceramics. With an increase in the magnetic strength of external field, the magnetization of ceramic **7** swiftly increases and ultimately levels off at a saturation magnetization ( $M_s$ ) of ~118 emu/g. This value is impressively high, taking into account that the  $M_s$  value of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) is 74 emu/g.<sup>24</sup> It is known that cobalt is ferromagnetic but its oxides ( $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ ) are paramagnetic at room temperature.<sup>25</sup> The high  $M_s$  value of **7** suggests that the cobalt nanocrystallites in the ceramic are wrapped by the carbeneous species (cf., Scheme 3), preventing the cobalt nanomagnets from being oxidized during and after the pyrolysis process. The  $M_s$  value of ceramic **8** is lower (~26 emu/g), which is understandable, because the cobalt content of its precursor complex (**6**) is low. Theoretically two triple bonds take one cobalt atom to form a  $\text{CpCbCo}$  unit in **6**, in comparison to the high cobalt/carbon stoichiometry in **5**, where one triple bond shares two cobalt atoms (cf., Scheme S1; Supporting Information). Manners and Ozin's groups prepared magnetic



ceramics from a complex of a linear polymer and  $\text{Co}_2(\text{CO})_8$  and found that their  $M_s$  values were in the range of  $\sim 20$ – $35$  emu/g.<sup>26</sup> The  $M_s$  value ( $\sim 118$  emu/g) of ceramic **7** fabricated from the complex of *hb*-**P1d** and  $\text{Co}_2(\text{CO})_8$  is up to  $\sim 6$ -fold higher, demonstrating that the hyperbranched macromolecular complexes are much better precursors to magnetic ceramics than the linear one.

The hysteresis loops of our magnetoceramics are small. From the enlarged  $H$ – $M$  plots shown in the insets of Figure 4, the coercivities ( $H_c$ ) of **7** and **8** are found to be 0.058 and 0.142 kOe, respectively. An  $H_c$  value as low as 0.045 kOe is observed in the magnetization of a ceramic made from the complex of *hb*-**P1d3** and  $\text{Co}_2(\text{CO})_8$  with a  $[\text{Co}_2(\text{CO})_8]/[\text{C}\equiv\text{C}]$  feed ratio of 1:1,<sup>27</sup> suggesting that the low coercivity is a general property of this new family of magnetic ceramics. A ferromagnetic material with a coercivity smaller than 0.126 kOe (or  $10^4$  A/m) is termed a soft magnet.<sup>25,28</sup> The high magnetizability ( $M_s \sim 118$  emu/g) and low coercivity ( $H_c \sim 0.06$  kOe) of **7** make it an excellent soft ferromagnetic material, which may find high-tech applications in various electromagnetic systems.

In summary, in this work, a group of hyperbranched (co)-polyyenes [*hb*-**P1(2)**] has been successfully synthesized through homopolycouplings of triynes (**1**) and their copolycouplings with a monoyne (**2**). By introducing asymmetric aryl cores or flexible alkoxy tails and through reaction condition control, the polyyenes are made soluble and hence processible. The *hb*-PYs are conjugated and luminescent. A thin film of *hb*-**P1d** shows very high refractivity ( $n = 1.770$ – $1.861$ ) in the spectral region useful for optical communications,<sup>29</sup> thanks to its polarizable aromatic rings and slender triple-bond rods. The triple bonds do not only offer the useful properties mentioned above but also confer a rich reactivity on the polyyenes. Employing an acetylene-halide coupling reaction, the terminal triple bonds of *hb*-**P1d** are completely end-capped by aromatic rings, demonstrating the feasibility of decorating the peripheral surfaces of the polyyenes by functional groups through simple polymer reactions. The complexation power of the triple bonds with cobalt carbonyl enables the polyyenes to metallify at room temperature, and their thermal polymerizability allows the polyyenes to cure at moderate temperatures (starting from  $\sim 150$  °C). The *hb*-PYs are strongly resistant to thermolysis ( $T_d$  up to  $\sim 550$  °C) and efficiently carbonized upon pyrolysis ( $W_r$  up to 84% at 850 °C). Ceramization of the polyyene-cobalt complexes yields soft ferromagnetic materials with high magnetic susceptibilities ( $M_s$  up to  $\sim 118$  emu/g) and low hysteresis losses ( $H_c$  down to  $\sim 0.045$  kOe). These multifaceted attributes already make the *hb*-PYs a group of promising specialty materials, although they are expected to show more functional properties, such as plasma resistivity and electron-beam writability for direct generations of nanopatterns.<sup>30</sup> These and other properties of the polyyenes are under investigation in our laboratories now and will be reported in due course.

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**Supporting Information Available:** Synthetic procedures and spectroscopic data of the polymers. Examples of the IR spectra of **1d** and *hb*-**P1d/2** and the NMR spectra of *hb*-**P1d** and *hb*-**P1d4**. Chart showing the structures of dendritic, linear, and terminal units of *hb*-**P1e** and their  $^{13}\text{P}$  chemical shifts. Scheme depicting the complexation reactions of cobalt carbonyls

with acetylenic triple bonds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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