

CHAPTER 10

Hyperbranched Acetylenic Polymers from Metal-Free and Regioselective Polycyclotrimerization of Arylene Bipropiolates: Synthesis, Characterization, and Photonic Properties

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10.1 Introduction

The study of hyperbranched polymers is a “young” but “hot” area of research. Hyperbranched polymers are expected to show size-, shape-, branch-, and surface-related properties,¹ which may enable them to find an array of technological applications as nanoscale catalysts, chemical sensors, molecular antennae, supramolecular assemblies, micelle mimics, drug-delivery carriers,

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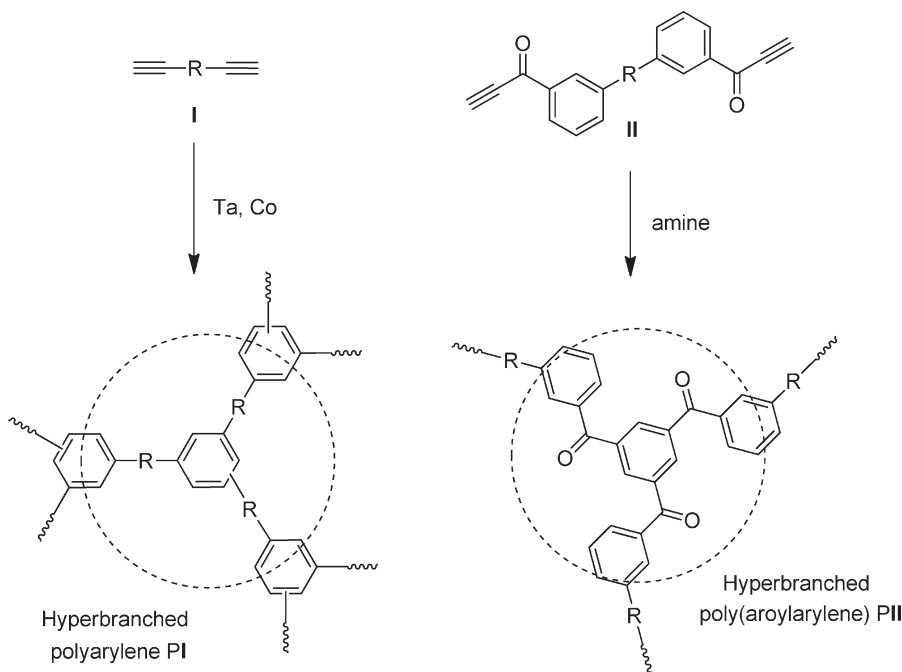
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immunodiagnostic probes, and so forth.² Various hyperbranched polymers have been prepared by different synthetic strategies.³ The most commonly used methods have been the condensation polymerizations of AB_n -type monomers, with A and B being mutually reactive functional groups and $n \geq 2$. However, the preparations of such multifunctional monomers often require nontrivial synthetic efforts.⁴ The monomers are difficult to keep and handle and easy to self-oligomerize during storage. The polymerization reactions are often initiated by *in situ* deprotection under harsh conditions and the incomplete deprotection results in the formation of imperfect polymers with low molecular weights (MWs) and degrees of branching (DBs).

Acetylene cyclotrimerization is a century-old reaction for effective transformation of triple bonds to benzene rings. Polycyclotrimerizations of diyne molecules are anticipated to result in the formation of hyperbranched polyarylenes.⁵ This simple A_2 -type polycyclotrimerization approach will circumvent the synthetic difficulties encountered in the AB_n -type condensation polymerizations and produce stable polymers consisting of robust aromatic rings. This possibility, however, has not been actively explored, because alkyne cycloadditions can easily run out of control to yield crosslinked gels.^{5,6}

We have embarked on a research program on the development of the polycyclotrimerizations of diynes (**I**) initiated by transition-metal catalysts into a useful synthetic protocol for the construction of hyperbranched polyarylenes (**PI**; Scheme 10.1).⁷ While crosslinking or gelation was involved in the diyne



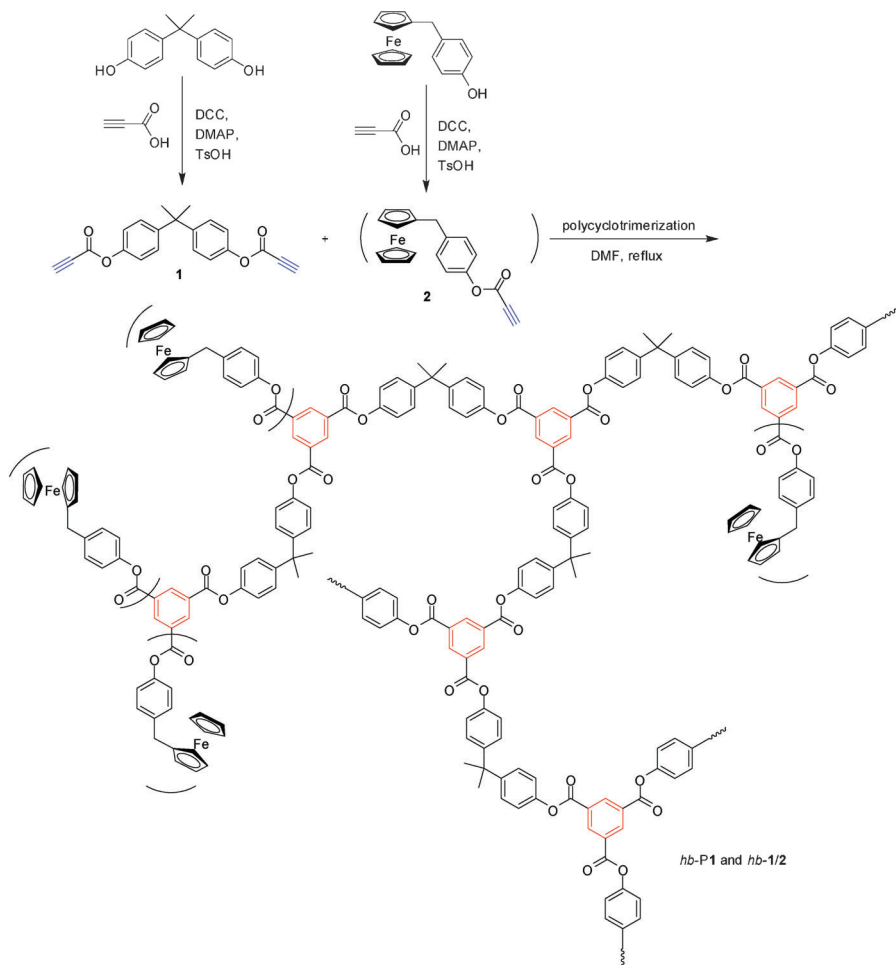
Scheme 10.1 [Copyright (2009) American Chemical Society]

polycyclotrimerization reactions, we succeeded in the preparation of hyperbranched polyarylenes with excellent solubility through optimization of polymerization conditions. The polymers have been found to exhibit a variety of unique properties.⁸ They are, for example, highly luminescent with fluorescence quantum yields up to unity, nonlinear-optically active when photoexcited by laser pulses, thermally very stable (T_d up to 500 °C), and readily graphitized in high yields upon pyrolysis.

The tantalum-catalyzed diyne polycyclotrimerization, however, has some drawbacks: the catalysts are completely intolerant of polar functional groups and polymerization reactions therefore must be conducted under stringently moisture- and oxygen-free conditions. The polycyclotrimerization reactions proceed very rapidly, making the process control very difficult. Although the cobalt-based catalysts can polycyclotrimerize diyne monomers carrying certain functional groups, the resultant polymers generally have lower MWs and poorer optical and photonic properties than those prepared from the tantalum catalysts due to the presence of the catalyst residues in the polymer structures after precipitation. Moreover, both Ta and Co catalysts produce hyperbranched polymers consisting of regiorandom structural units of 1,2,4- and 1,3,5-trisubstituted benzene isomers.

We have recently discovered that the polycyclotrimerizations of aroylacetylenes (**II**) catalyzed by secondary amines (e.g., piperidine) produce hyperbranched poly(1,3,5-triaroylarylene)s (**PII**) with high DBs in high yields (Scheme 10.1).⁹ The polycyclotrimerization is tolerant to polar functional groups and is strictly regioselective, furnishing polymers comprising of sole structural units of 1,3,5-trisubstituted benzene regioisomers. The aroylacetylene monomers (**II**), however, are difficult to prepare. It takes many synthetic steps to prepare the monomers and the reactions involve the use of toxic heavy-metal oxidants such as MnO_2 and CrO_3 .⁹ It would be nice if the polycyclotrimerization can be extended or applicable to the “simple” diyne monomers that can be readily prepared from commercially available starting materials by one-step reactions in one-pot procedures in an environmentally benign fashion.

Careful examination of the molecular structure of monomer **II** reveals that this polymerization works for electron-deficient diynes, whose acetylene triple bonds are linked with electron-withdrawing groups. If the carbonyl linkage between the triple bond and the aromatic ring in the aroylacetylene can be replaced by an ester group, it will make the monomer synthesis much easier. Acetylenecarboxylic acid or propiolic acid is a commercially available reagent and can be readily esterified with arylene diol to give bipropiolate (Scheme 10.2). If the bipropiolate monomer can be polymerized, it will pave the way to facile and economic syntheses of functional hyperbranched polymers. However, a propiolate derivative is less electron deficient than an aroylacetylene because an ester group is less electron-withdrawing than a carbonyl group, which makes it uncertain whether or under what conditions an arylene bipropiolate will undergo polycyclotrimerization reaction.



Scheme 10.2

In this work, we explore the utility of alkyne polycyclotrimerization of arylene bipropiolate as a useful tool for the preparation of hyperbranched polymers and their organometallic counterparts. In this chapter, we show that bipropiolate monomers can be effectively polycyclotrimerized in refluxed *N,N*-dimethylformamide (DMF) without adding any external catalysts, producing processable, regioregular, hyperbranched poly[1,3,5-tri(aryloxy)phenylene]s or *hb*-PTACPs with high DB value in high yields.¹⁰ Addition of ferrocene-containing propiolate during the polymerization results in the generation of *hb*-PTACPs with numerous ferrocene units on the surface. Structurally, the *hb*-PTACPs are polyesters but synthetically they are very difficult to access by the conventional polycondensation reactions of $A_2 + B_3$ monomers, with A_2 and B_3 being diol and triacid, respectively. Monomers of

trisubstituted benzene derivatives (B_3) are generally difficult to prepare. In particular, those that carry three electron-withdrawing ester groups at the 1,3,5-positions are difficult to make due to the well-known deactivating effect of the ester group. To make hyperbranched polymers with high MWs and DBs by the ($A_2 + B_3$)-type polycondensation reaction, strict stoichiometric balance is theoretically required but practically difficult to meet. Moreover, the $A_2 + B_3$ polycondensations are equilibrium reactions with small MW compounds such as water generated as byproducts. The polycyclotrimerization of the A_2 monomers is free of all these problems and is thus of great value in terms of synthetic methodology.

10.2 Experimental

10.2.1 Materials

Tetrahydrofuran (THF, Labscan), toluene (BDH), and 1,4-dioxane (Aldrich) were distilled in an atmosphere of dry nitrogen from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM) was distilled under nitrogen over calcium hydride. DMF was stirred with calcium hydride overnight, distilled under reduced pressure and kept under dry nitrogen. Other solvents such as dimethylsulfoxide (DMSO) and triethylamine were purified using standard procedures. Propiolic acid, bisphenol A (4,4'-isopropylidenediphenol), 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), *p*-toluenesulfonic acid monohydrate (TsOH), and all other chemicals were purchased from Aldrich and used as received without further purification. (4-Hydroxybenzyl)ferrocene (**2**) was prepared according to the literature.¹¹

10.2.2 Instrumentation

Relative number- ($M_{n,r}$) and weight-average ($M_{w,r}$) molecular weights and polydispersity indices (PDI or $M_{w,r}/M_{n,r}$) of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) system equipped with RI and UV detectors. THF was used as the eluent at a flow rate of 1.0 mL. A set of monodisperse linear polystyrenes was used as standards for MW calibration. Absolute weight-average molecular weights ($M_{w,a}$) of the polymers were measured by a commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ -digital time correlator (ALV5000) and a cylindrical 22 mW He-Ne laser ($\lambda = 632.8$ nm, uniphase) as a light source. The RI increment (dn/dc) was determined to be 0.292 mL/g in THF at 25 °C on an Optilab DSP (Digital Signal Processing) refractometer (Wyatt Technology; $\lambda = 632.8$ nm, $c \leq 1.0$ mg/mL).

IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using CDCl_3 , $\text{DMSO}-d_6$, or $\text{DCM}-d_2$ as deuterated solvents. Light transmission spectra were measured on a Milton Roy

Spectronic 3000 array spectrophotometer. MALDI-TOF spectra were recorded on a GCT Premier CAB048 mass spectrometer operating in a chemical ionization mode (CI) with methane as carrier gas. Elemental analyses were conducted with an Elementary Vario EL analyzer. Thermogravimetric analysis (TGA) measurements were carried out under nitrogen or in air on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C/min. RI values were measured on a Gaertner L116C ellipsometric thin-film thickness measurement system using 1 mW He-Ne laser beam ($\lambda = 632.8$ nm) as light source or determined on a J A Woollam variable-angle ellipsometry system with a wavelength tunability from 300 to 1700 nm. To fit the acquired Ψ and Δ curves with the data obtained from the 3-layer optical model consisting of crystalline silicon substrate, 2 nm SiO₂ layer and a uniform polymer film, the Levenberg–Marquardt regression algorithm was employed. The Cauchy dispersion law was applied to describe the polymer layer from visible to IR spectral region.

10.2.3 Monomer Preparation

Acetylene bipropiolate **1** was prepared by esterification of arylene diol with propiolic acid in the presence of DCC, DMAP, and TsOH (*cf.*, Scheme 10.2). The detailed experimental procedure for the synthesis of monomer **1** is given below as an example. In a 500 mL round-bottom flask were dissolved 3.26 g (14 mmol) of bisphenol A, 8.86 g (43 mmol) of DCC, 0.70 g (5.8 mmol) of DMAP, and 1.08 g (5 mmol) of TsOH in 240 mL of dry DCM/THF (3:1 v/v). The solution was cooled to 0 °C with an ice-water bath, into which 2.0 g (28.6 mmol) of propiolic acid (**4**) dissolved in 20 mL of DCM/THF (3:1 v/v) was added under stirring *via* a dropping funnel. The reaction mixture was stirred overnight. After filtering out the solid, the solution was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using chloroform/hexane (1:2 v/v) as eluent.

Characterization Data for 4,4'-Isopropylidenediphenyl Bipropiolate (1): White solid; yield 53.2% (2.52 g). IR (thin film), ν (cm⁻¹): 3266, 2934, 2124, 1730, 1634. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.26 (d, 2H), 7.05 (d, 2H), 3.06 (s, 1H), 1.67 (s, 3H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 151.0, 148.5, 147.7, 127.9, 120.6, 76.6, 74.3, 42.6, 30.8. HRMS (MALDI-TOF): *m/z* 333.1080 [(M + H)⁺, calcd 333.3493]. Anal. Calcd for C₂₁H₁₆O₄: C, 75.89; H, 4.85. Found: C, 75.17; H, 5.01.

4-(Ferrocenylmethyl)phenyl propiolate (2): It was synthesized by a procedure similar to that of **1**. Red solid; yield 75.8%. IR (thin film), ν (cm⁻¹): 3254, 3090, 3042, 2944, 2922, 2846, 2118, 1722, 1504, 1432, 1292, 1208, 1106, 1058, 1018. ¹H NMR (300 MHz, DMSO-*d*₆), δ (TMS, ppm): 7.36 (d, 2H), 7.22 (d, 2H), 4.95 (s, 1H), 4.25 (s, 7H), 4.17 (s, 2H), 3.76 (s, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆), δ (TMS, ppm): 150.9, 147.5, 140.4, 129.4, 121.2, 87.7, 81.4, 74.3, 68.5, 68.3, 67.3, 34.7. Anal. Calcd for C₂₀H₁₇O₂Fe: C, 69.79; H, 4.69. Found: C, 69.34; H, 4.80.

10.2.4 Polymer Synthesis

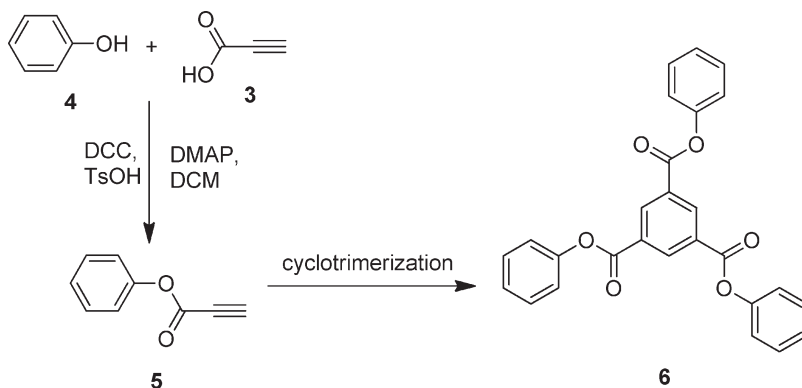
All the polymerization reactions were carried out under dry nitrogen using a standard Schlenk technique, unless otherwise specified. A typical procedure for the polymerization of **1** is given below as an example. In a 15 mL Schlenk tube with a three-way stopcock on the sidearm was placed 88.7 mg of **1** (0.267 mmol) under nitrogen in a glovebox. Distilled DMF (1.5 mL) was added to dissolve the monomer using a hypodermic syringe. After stirring under reflux for 24 h, the mixture was added dropwise to ~300 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The isolated polymer (*hb-P1*) was washed with methanol and dried under vacuum at room temperature to a constant weight.

Characterization Data for *hb-P1*: Brown powder; yield 68.4% (Table 10.2, run 2). $M_{w,r}$ 15 600; M_w/M_n 2.4 (GPC, polystyrene calibration); $M_{w,a}$ 832000 (LLS). IR (thin film), ν (cm^{-1}): 2966, 2922, 2872, 1743, 1603, 1504. ^1H NMR (300 MHz, $\text{DCM}-d_2$), δ (TMS, ppm): 9.16, 7.91, 7.26, 7.17, 7.03, 6.69, 1.70, 1.67. ^{13}C NMR (75 MHz, $\text{DCM}-d_2$), δ (TMS, ppm): 157.2, 154.9, 149.3, 136.5, 132.0, 128.7, 121.8, 115.5, 43.2, 31.4.

Characterization data of *hb-P1/2*: Brown powder; yield 46.0%. M_w 39 400; M_w/M_n 6.1 (GPC, polystyrene calibration). IR (thin film), ν (cm^{-1}): 3086, 3038, 2966, 2932, 2870, 2378, 1742, 1646, 1602, 1506, 1466, 1408, 1394, 1334, 1294, 1218, 1200, 1170, 1104, 1080, 1016. ^1H NMR (300 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 9.31, 9.07, 7.37, 7.35, 7.11, 6.76, 4.26, 4.20, 3.77, 3.46, 1.77, 1.71. ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 171.6, 171.3, 171.0, 170.8, 170.7, 170.5, 170.2, 169.9, 163.0, 155.1, 148.1, 140.2, 136.2, 130.8, 129.3, 127.7, 121.3, 114.7, 68.5, 67.3, 34.7, 30.4.

10.2.5 Model Reaction

Triphenyl benzene-1,3,5-tricarboxylate (**6**) was prepared as a model compound by cyclotrimerization of phenyl propiolate **5** (Scheme 10.3). The experimental



Scheme 10.3 [Copyright (2009) American Chemical Society]

procedures for the synthesis of **5** and its cycloaddition are similar to those described above for the synthesis of **1** and *hb*-**P1**.

Characterization data for 5: Colorless oil; yield 68.3%. IR (thin film), ν (cm^{-1}): 2931, 2854, 2117, 1732. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.42 (t, 2H), 7.27 (t, 2H), 7.13 (d, 1H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 151.3, 121.6, 129.1, 125.5, 140.0, 76.8, 73.4.

Characterization data for 6: White solid; yield 34.2% (Table 2.1, run 4). IR (thin film), ν (cm^{-1}): 1748, 1589, 1487. ^1H NMR (300 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 9.04 (s, 1H), 7.52 (t, 2H), 7.38 (m, 3H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 163.0, 150.4, 135.1, 130.9, 129.7, 126.4, 121.9.

10.3 Results and Discussion

10.3.1 Monoyne Model Reaction

Before studying the polycyclotrimerization of bipropiolates, we synthesized a monopropiolate carrying one triple bond (**5**) and utilized it as starting material for a model reaction (Scheme 10.3). According to our previous study, aroylacetylenes can be cyclotrimerized when refluxed in 1,4-dioxane using piperidine as a catalyst.^{9b} We thus tried to cyclotrimerize **5** under the same conditions (Table 10.1, run 1). After 24 h the solvent was evaporated and the crude product was purified by silica gel column chromatography using chloroform/hexane (1:1 v/v) as eluent. Product isolation and structural characterization reveal that **6** is the sole product, confirming that **5** can undergo cyclotrimerization in the presence of the base in a regioselective fashion, although the conversion is not so efficient because the reaction conditions have not been optimized. Changing the solvent to toluene slightly lowered the yield, whereas when the reaction is carried out in a toluene/DMF mixture no product is isolated. The reaction conducted in DMF gives the best result (Table 10.1, run 4). Furthermore, triethylamine fails to initiate the cycloaddition reaction, probably due to its reaction with the acidic ethynyl proton of **5**.

Table 10.1 Cyclotrimerization of phenyl propiolate (**5**).

<i>run</i>	<i>solvent</i>	<i>catalyst</i>	<i>yield (%)</i>
1	1,4-dioxane	piperidine	25.0
2	toluene	piperidine	21.2
3	toluene/DMF ^b		00.0
4	DMF		34.2
5	triethylamine ^c		

^aRefluxed under nitrogen for 24 h; [**5**] = 0.178 M; [piperidine] = 5.7 mM. ^bVolume ratio = 1:1.

^cReaction mixture turned black with heat dissipation immediately after triethylamine was added. Copyright (2009) American Chemical Society.

10.3.2 Diyne Polycyclotrimerization

After confirming that monopropiolate **5** can undergo regioselective cyclotrimerization, we utilized the reaction to synthesize new hyperbranched polymers. We prepared arylene bipropiolates **1** and **2** by esterification reactions of their corresponding phenol derivatives with propiolic acid in the presence of DCC, DMAP and TsOH (cf., Scheme 10.2). All of the monomers were fully characterized spectroscopically from which satisfactory analysis data corresponding to their molecular structures were obtained (see Experimental Section for details).

We attempted to cyclotrimerize **1** by piperidine in 1,4-dioxane but isolated no polymeric product. We tried the reaction in refluxed DMF and succeeded in the transformation of the diyne monomer into its polymer *hb*-P1 (Table 10.2, run 1). The active catalytic species for the reaction is believed to be the trace amount of dimethylamine generated from the *in situ* decomposition of DMF at the high temperature.¹² We increased the monomer concentration by ~1.5-fold and obtained a soluble polymer in a higher yield (~68%). Further increasing the monomer concentration, however, promoted the formation of crosslinking product and hence decreased the yield of soluble polymer.

We followed the time course of the polymerization of monomer **1** in DMF. The yield was generally increased with time and reached its maximum value of ~72% at 24 h (Table 2.3). After polymerization for 18 h, the $M_{w,r}$ of the resultant polymer is high enough (14 200) for general-purpose applications. It should be pointed out that this relative value is probably considerably underestimated because of the hyperbranched nature of the polymer.¹³ Our previous investigations reveal that the underestimation can be very large.¹⁴ The absolute molecular weight ($M_{w,a}$) of *hb*-P1 may be much higher than the relative value estimated from the GPC analysis ($M_{w,r}$). Indeed, analysis of *hb*-P1 by a LLS spectrometer gives an $M_{w,a}$ value of 8.32×10^5 (cf., Table 10.2, no. 2), which is 53-fold higher than its $M_{w,r}$ value.

Temperature exerts a strong influence on the polymerization reaction. Both the yield and molecular weight of the polymer are increased when the temperature is raised from 110 to 130 °C (Table 10.4). When the temperature is

Table 10.2 Effect of monomer concentration on the polymerization of monomer **1**.

run	[I] (M)	yield (%)	$M_{n,r}^b$	$M_{w,r}^b$	$M_{w,r}/M_{n,r}^b$	$M_{w,a}^c$
1	0.120	51.7	5700	14 200	2.5	
2	0.178	68.4	6500	15 600	2.4	832 000
3	0.267	44.8	5800	15 200	2.6	
4	0.534	37.5	5600	15 800	2.8	

^aCarried out in refluxed DMF for 24 h under nitrogen. ^bDetermined by GPC in THF on the basis of a linear polystyrene calibration. ^cAbsolute value measured by LLS technique in THF. Copyright (2009) American Chemical Society.

Table 10.3 Time course for polymerization of monomer **1**.

run	time (h)	yield (%)	$M_{n,r}^b$	$M_{w,r}^b$	$M_{w,r}/M_{n,r}^b$
1	6	19.7	4200	5400	1.3
2	12	22.1	4500	7200	1.6
3	18	55.8	6200	14 200	2.3
4	24	71.3	4800	13 800	2.9
5	36	71.2	4100	10 200	2.5

^aCarried out in refluxed DMF under nitrogen; $[I] = 0.178$ M. ^bDetermined by GPC in THF on the basis of a linear polystyrene calibration. Copyright (2009) American Chemical Society.

Table 10.4 Effect of temperature on polymerization of monomer **1**.

run	temp (°C)	yield (%)	$M_{n,r}^b$	$M_{w,r}^b$	$M_{w,r}/M_{n,r}^b$
1	110	7.1	3600	5400	1.5
2	130	17.5	4200	6300	1.5
3	153 ^c	68.4	4600	11 100	2.4

^aCarried out in DMF for 24 h under nitrogen; $[I] = 0.178$ M. ^bDetermined by GPC in THF on the basis of a linear polystyrene calibration. ^cBoiling point of DMF. Copyright (2009) American Chemical Society.

further increased to the boiling point of DMF, the polymerization results are improved significantly, with the polymer yield being ~4 times higher than that obtained at 130 °C.

The above investigations enable us to polymerize **1** and copolymerize **1** with **2** under optimal conditions. Table 10.5 summarizes the polymerization results. All the polycyclotrimerizations proceeded smoothly, giving *hb*-P1 and *hb*-P1/2 in satisfactory yields. Comparing the polymerization results of **1** obtained under nitrogen and in air, it is clear that oxygen and moisture exert little effect on the polymerization reaction (cf., Table 10.5, runs 1 and 2). This helps simplify the reaction procedures. As no transition-metal catalyst is used in the process, this metal-free polycyclotrimerization has the advantages of being less toxic, environmentally friendlier, and economically sounder.

Table 10.5 Polymerizations of bipropiolate monomers.

run	monomer	yield (%)	$M_{n,r}^b$	$M_{w,r}^b$	$M_{w,r}/M_{n,r}^b$	$M_{w,a}^c$
1 ^d	1	68.4	6500	15 600	2.4	832 000
2 ^e	1	72.3	4200	13 000	3.1	
3	1 + 2	46.0	6600	39 400	6.0	

^aCarried out in refluxed DMF for 24 h under nitrogen; $[I] = [2] = 0.178$ M. ^bDetermined by GPC in THF on the basis of a linear polystyrene calibration. ^cAbsolute value measured by LLS technique in THF. ^dData taken from Table 2.2, run 2. ^eConducted in air.

10.3.3 Structural Characterization

In the model reaction, the cyclotrimerization of monoyne **5** gives **6** as the sole product. Diyne **1** thus must have been polycyclotrimerized in a 1,3,5-regioselective manner. To collect direct structural information, we characterized the polymers by spectroscopic methods. Examples of the IR spectra of **P1** and its monomer **1** are given in Figure 10.1. Diyne **1** shows absorption bands at 3266 and 2124 cm^{-1} due to $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ stretching vibrations, respectively. All of these bands disappear in the spectrum of its polymer, indicating that the acetylene triple bonds have been converted to the benzene rings by the diyne polycyclotrimerization. Similarly, the spectrum of *hb-P1/2* shows no $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ stretching vibrations of **1** and **2** but display absorption bands characteristic of monosubstituted ferrocene moiety at 1105 and 1000 cm^{-1} , confirming that the polycyclotrimerization reaction has proceeded as expected and has been unharmed to the Fc group.

The ^1H NMR spectra of *hb-P1* and its monomer **1** as well as model compound **6** are shown in Figure 10.2. The acetylene proton of **1** resonates at δ 3.06, which completely disappears after the monomer is subjected to polycyclotrimerization reaction. By comparison with the spectra of monomer **1** and model compound **6**, the resonance peaks in the spectrum of polymer *hb-P1* can be readily assigned (*cf.*, Chart 10.1). The polymerization shifts the resonance of the phenyl protons *ortho* to the ester group in **1** at 7.05 to δ 7.17 in *hb-P1*, while the phenyl protons in the periphery of *hb-P1* resonate at δ 7.03. The new peak at δ 9.16 is assigned to the proton resonances of the benzene rings newly formed by the cyclotrimerization polymerization. End-capping of one triple bond in a terminal branch by two triple bonds in one diyne

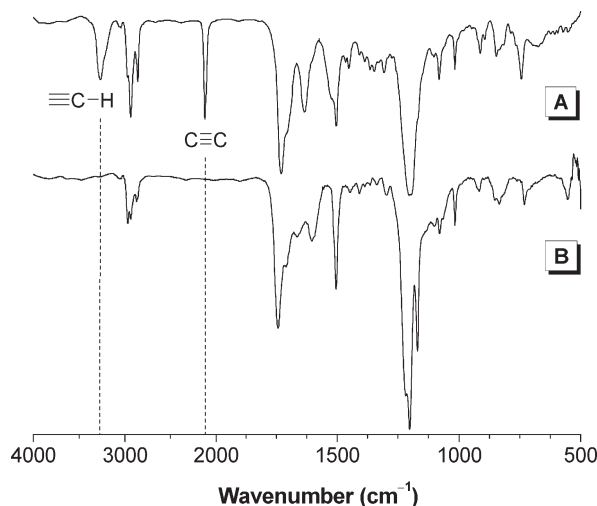


Figure 10.1 IR spectra of (A) monomer **1** and (B) its polymer *hb-P1* (sample taken from Table 10.2, run 2). Copyright (2009) American Chemical Society.

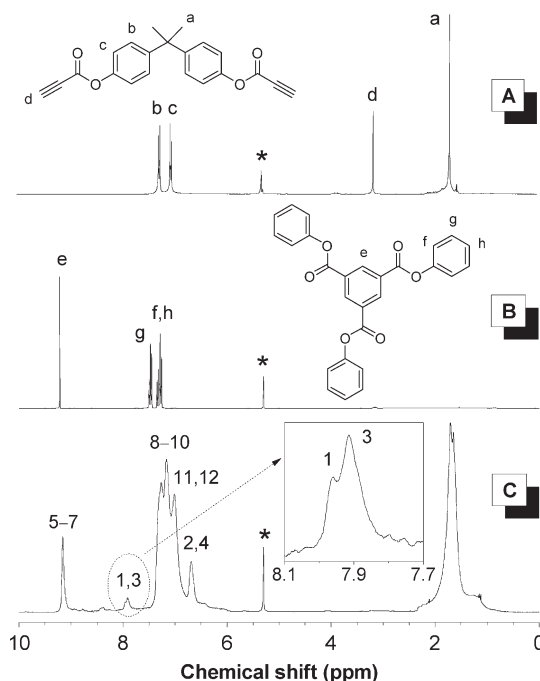


Figure 10.2 ^1H NMR spectra of (A) monomer **1**, (B) model compound **6** (sample taken from Table 10.1, run 4), and (C) polymer *hb-P1* (Table 10.2, run 2) in $\text{DCM-}d_2$. The solvent peaks are marked with asterisks. Copyright (2009) American Chemical Society.

monomer will generate a cyclophane ring, whose aromatic protons should resonate at $\delta \sim 9.3$ and ~ 8.7 . However, no such resonance peaks are observed in the spectrum of *hb-P1*. Instead, two peaks arising from the resonance of the olefinic unit formed by the alkyne hydroamination (Scheme 10.4) are detected at $\delta 7.91$ and 6.69 (Figure 10.2C, peaks 1 and 3). The spectrum of *hb-P1/2* also exhibits no acetylene proton resonances of **1** and **2**. New resonance peaks associated with the proton resonances of the benzene rings of the terminal and dendritic units are observed at $\delta 9.29$ and 9.06 . No absorption peaks associated with the linear unit are observed. Thus, it is difficult for us to calculate the DB of *hb-P1/2*. The protons of the cyclopentadienyl ring of the ferrocene moiety resonate at $\delta 4.23$. From its integral, the iron content of *hb-P1/2* is calculated to be 5.82%.

The ^{13}C spectrum of *hb-P1* shows no resonance peaks of the acetylenic carbons of **1** at $\delta 76.6$ and 74.3 (Figure 10.3). New peaks corresponding to the absorptions of the triphenoxycarbonylphenyl and olefinic carbons are observed at $\delta 136.5$, 132.0 , and 115.5 due to the conversion of the acetylene triple bonds of **1** to the benzene rings and double bonds of *hb-P1*. Similar observations are also found in *hb-P1/2*.

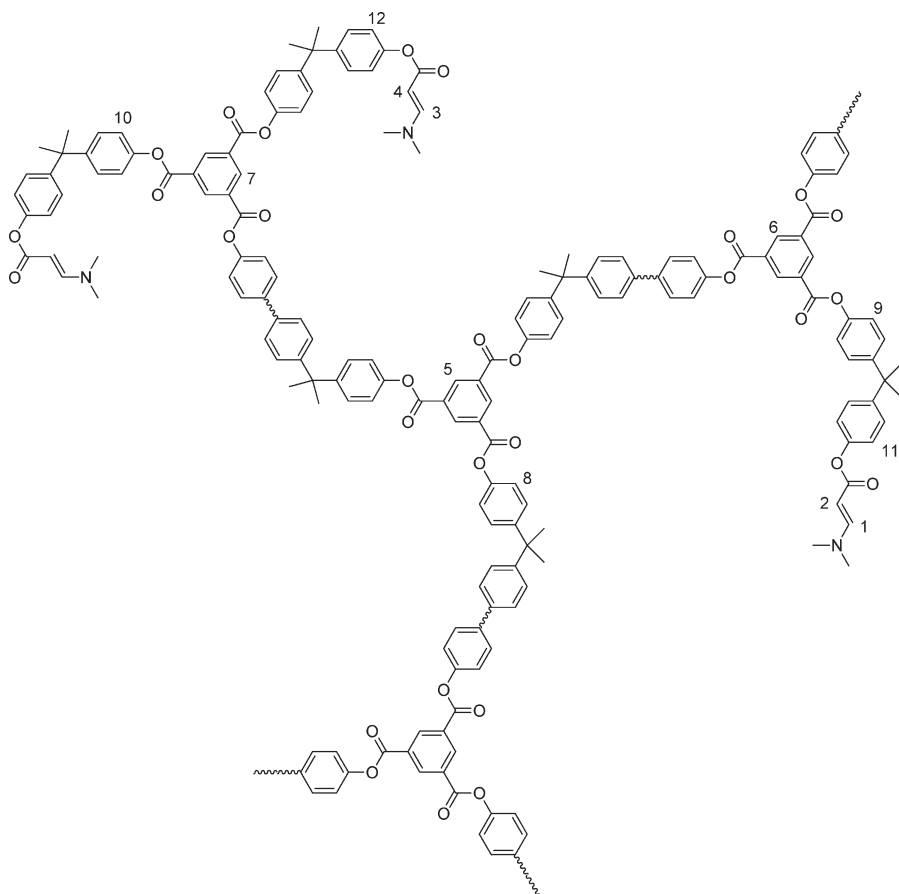
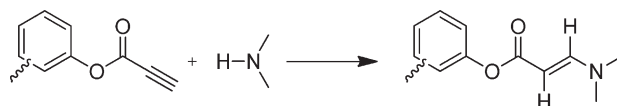


Chart 10.1 [Copyright (2009) American Chemical Society]



Scheme 10.4 [Copyright (2009) American Chemical Society]

10.3.4 Degree of Branching

As shown in Chart 10.2, there exist three structural components in *hb*-P1: dendritic (D), linear (L) and terminal (T) units. Comparing the ^1H NMR spectrum of *hb*-P1 with those of its monomer and the model compound, the following relationships between the contents or fractions (f) of the structural units can be established.

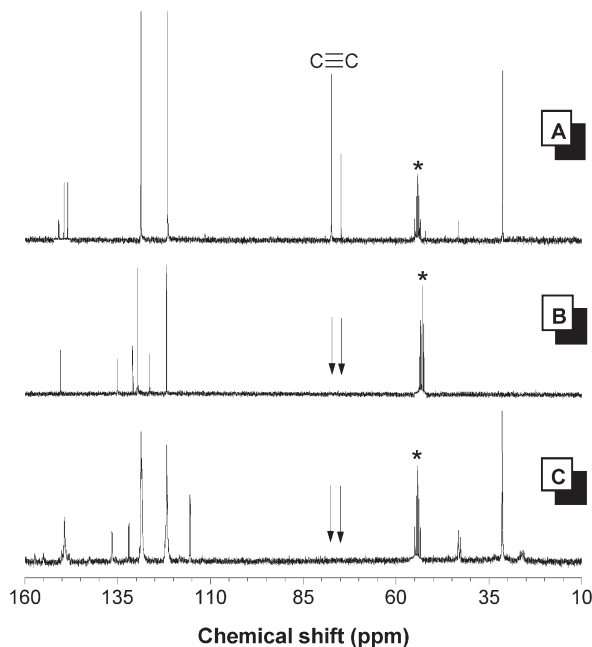


Figure 10.3 ^{13}C NMR of (A) monomer **1**, (B) model compound **6** (sample from Table 10.1, run 4), and (C) polymer *hb*-P1 (Table 10.2, run 2) in $\text{DCM-}d_2$. The solvent peaks are marked with asterisks. Copyright (2009) American Chemical Society.

$$\frac{3f_L + 3f_T + 3f_D}{f_L + 2f_T} = \frac{A_{5-7}}{A_{1,3}} \quad (10.1)$$

$$f_D + f_L + f_T = 1 \quad (10.2)$$

where A_{5-7} and $A_{1,3}$ represent the integrals of the areas of resonance peaks (5–7) and (1,3), respectively, as labeled in Chart 10.1 and panel C of Figure 10.2. The values can be determined from the ^1H NMR spectral data, from which the following equation is deduced:

$$\frac{3f_L + 3f_T + 3f_D}{f_L + 2f_T} = \frac{1}{0.362} \quad (10.3)$$

Combining eqns (10.10) and (10.3) gives eqn (10.4):

$$f_L + 2f_T = 1.086 \quad (10.4)$$

The peak at δ 7.91 corresponds to the resonance of the olefinic proton capped by the dimethylamino group. Magnification of the peak manifests that it is actually a doublet and the amount of the olefinic bond in the L unit is ~ 8 -

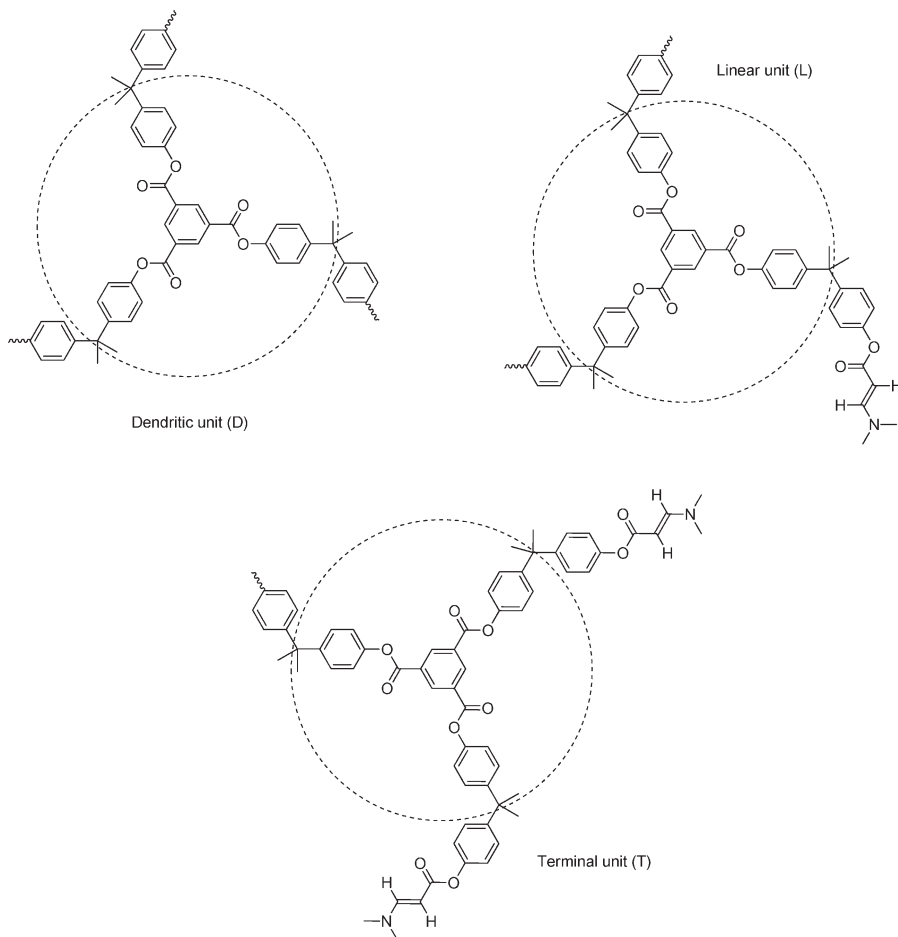


Chart 10.2 [Copyright (2009) American Chemical Society]

fold lower than that in the T unit. Because there are two such protons in the T unit, but only one in the L unit eqn (10.5) thus holds:

$$\frac{f_L}{2f_T} = \frac{1}{8} \quad (10.5)$$

From the above equations, f_L is calculated to be:

$$f_L = 0.121 \quad (6)$$

According to definition, DB is expressed as:¹⁵

$$DB = \frac{f_D + f_T}{f_D + f_L + f_T} \quad (10.7)$$

Incorporating eqns (10.2) and (10.6) into eqn (10.7) gives the DB value of *hb-P1*:

$$\text{DB} = 1 - f_L = 0.879 \quad (10.8)$$

This value is much higher than those of the “conventional” hyperbranched polymer (commonly $\text{DB} \sim 0.5$),¹ which further confirms the hyperbranched structure of the polymer.

10.3.5 Solubility and Stability

All the hyperbranched polymers are completely soluble in common organic solvents, such as toluene, dichloromethane, chloroform, THF and dioxane, and can be readily fabricated into tough solid films by spin-coating or solution-casting processes. They also exhibit high thermal stability. As can be seen from Figure 10.4, the temperatures for their 5% weight loss or the degradation temperatures (T_d) are near or higher than 300 °C under nitrogen, indicative of their strong resistance to thermolysis and oxidation at high temperatures.

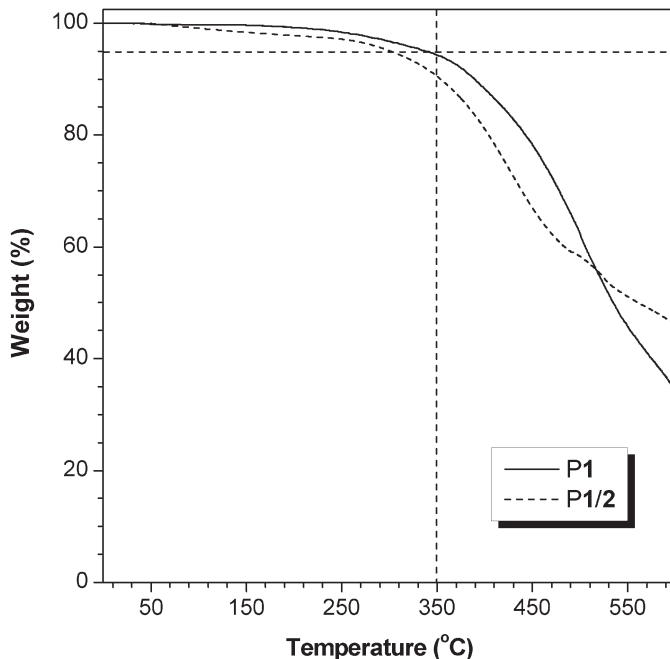


Figure 10.4 TGA thermograms of *hb-P1* and *hb-P1/2* recorded under nitrogen at a heating rate of 10 °C/min.

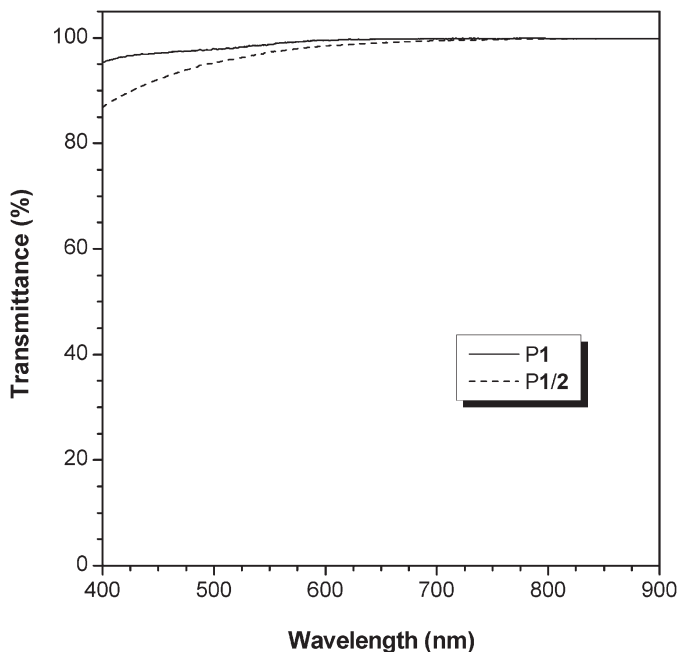


Figure 10.5 Light transmission spectra of THF solutions of *hb*-P1 and *hb*-P1/2. Polymer concentration: 6.4 $\mu\text{g mL}^{-1}$.

10.3.6 Optical Transparency

Polymers with high optical clarity are promising candidate materials for photonic applications.¹⁶ As shown in Figure 10.5, both *hb*-P1 and *hb*-P1/2 absorb little light in the visible spectral region and allow all light at wavelengths longer than 600 nm to transmit through. This excellent optical transparency is due to their molecular structures. Polyesters often show high optical clarity, with poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET) and polycarbonate (PC) being the best-known and widely used “organic glasses”. The ester groups weaken the electronic communications between the aromatic rings in the polymer structure and decrease their extents of electronic conjugations, thereby enhancing their optical transparency.

10.3.7 Light Refractivity

hb-P1 and *hb*-P1/2 are comprised of polarizable aromatic rings, ester groups, and metallic species and they may thus show high refractive indices. Indeed, as can be seen from Figure 10.6, *hb*-P1 displays high RI values ($n = 1.6255\text{--}1.6181$) in a wide wavelength region (400–1700 nm). The RI spectrum is almost flat: the RI value changes little over a wavelength span as wide as

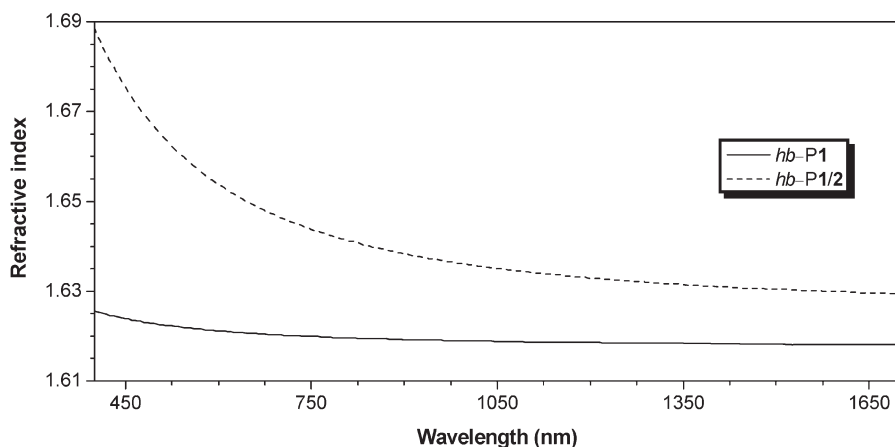


Figure 10.6 Wavelength dependence of refractive index of thin films of *hb-P1* and *hb-P1/2*.

1300 nm, which is very unusual and truly remarkable (*vide post*). Due to the presence of ferrocene units in the polymer structure, *hb-P1/2* shows even higher RI values ($n = 1.6885\text{--}1.6295$) at the same wavelength region. The RIs of the polymers are much higher than those of the commercially important optical plastics (*e.g.*, $n \sim 1.49$ for PMMA). No or little birefringence is detected, which implicative of the amorphous nature of their thin solid films.

10.3.8 Chromatic Dispersion

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

$$v_D = \frac{n_D - 1}{n_D - n_C} \quad (10.9)$$

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. A modified Abbé number (v'_D) has been proposed to evaluate the application potential of an optical material, using its RI values at the nonabsorbing wavelengths of 1064, 1319 and 1550 nm.¹⁷ The first two wavelengths are chosen in 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:

$$v'_D = \frac{n_{1319} - 1}{n_{1064} - n_{1550}} \quad (10.10)$$

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

$$D^{(c)} = \frac{1}{v_D^{(c)}} \quad (10.11)$$

The v_D and v_D' values for *hb-P1* are as high as 258.9 and 1030.7, corresponding to D and D' values as low as 3.86×10^{-3} and 0.97×10^{-3} , respectively (Table 10.6). The chromatic dispersions of the polymer are much lower than those of the commercially important “organic glasses” such as PC ($D = 29.7 \times 10^{-3}$) and PMMA ($D = 17.5 \times 10^{-3}$).¹⁸ The D' value is also much lower than those of the poly(aryltriazole)s recently synthesized by our research groups by the metal-free “click” polymerizations ($D' = 6.1 \times 10^{-3}$ – 3.66×10^{-3}).¹⁹ Although the Abbé numbers of *hb-P1/2* are larger than those of *hb-P1*, its chromatic dispersions ($D = 29 \times 10^{-3}$, $D' = 7 \times 10^{-3}$) are still comparable to those of the commercial optical plastics¹⁸ and the newly synthesized poly(aryltriazole)s.¹⁹

Table 10.6 Refractive indices and chromatic dispersions of *hb-P1* and *hb-P1/2*.

<i>polymer</i>	n_{1550}	v_D	v_D'	D	D'
<i>hb-P1</i>	1.6182	258.9	1030.7	0.0039	0.00097
<i>hb-P1/2</i>	1.6302	34.10	134.4	0.029	0.007

^aAll data taken from Figure 10.6, unless otherwise specified. Abbreviations: n = refractive index (at 1550 nm), v_D = Abbé number (calculated from equation 9), v_D' = modified Abbé number (calculated from eqn (10.10)), and $D^{(c)}$ = chromatic dispersion (calculated from eqn (10.11)).

10.4 Conclusion

In this work, we have developed a facile synthetic route to regioregular hyperbranched polymers. The homo-polycyclotrimerization of arylene bipropiolate **1** and its copolymerization with ferrocene-containing propiolate **2** proceed smoothly in refluxed DMF in the absence of externally added catalysts, furnishing soluble *hb-P1* and *hb-P1/2* with high MWs and DBs in high yields. The monomers are easy to access from commercially available starting materials and the polyaddition is strictly 1,3,5-regioselective and highly tolerant to functional groups, air and moisture. The resultant polymers are completely soluble, film-forming, thermally stable, and optically transparent. The polymers show high light refractivities with unprecedented low chromatic aberrations. These unique attributes make the polymers promising photonic materials for high-tech applications.

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