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Polycyclotrimerization of Diynes: Synthesis and Properties of Hyperbranched Polyphenylenes

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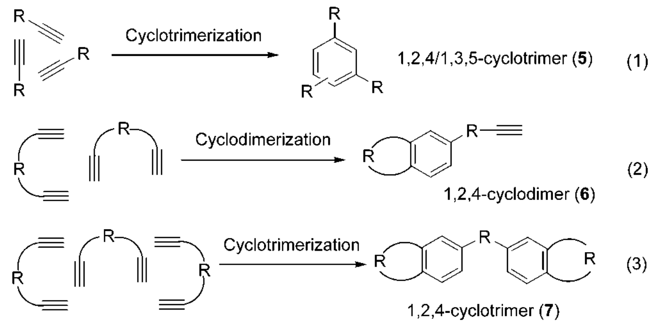
ABSTRACT: Diyne polycyclotrimerizations initiated by transition-metal catalysts afforded hyperbranched polyphenylenes, which exhibited low viscosity, outstanding thermal stability, and small optical dispersion. Under optimized reaction conditions, polycyclotrimerizations of 1,8-nonadiyne (**1**) and 1,9-decadiyne (**2**) catalyzed by $TaCl_5-Ph_4Sn$ produced hyperbranched poly(1,2,4-benzenetriyl-1,5-pentanediyl) (**3**) and poly(1,2,4-benzenetriyl-1,6-hexanediyl) (**4**),[1−5] respectively, in high yields (up to 93%). The polymers were completely soluble and film-forming, and possessed high molecular weights (M_w up to $\sim 1.4 \times 10^6$) but low intrinsic viscosities ($[\eta]$ down to 0.13 dL/g). Their structures and properties were analyzed and evaluated by IR, UV, NMR, SEC, TGA, DSC, spectrofluorometry, light scattering, and spectroellipsometry. The structural characterizations confirmed the expected hyperbranched molecular architectures of **3** and **4** (comprising of 1,2,4-benzene rings and α,ω-alkyl spacers) and revealed the regioselective feature of the diyne polycyclotrimerizations. Polymers **3** and **4** underwent glass transitions at 43 and 23 °C, respectively, and lost almost no weights when heated to ~500 °C. Polymer **3** emitted UV light upon excitation, whereas **4** was practically nonluminescent. The thin films of **3** were highly transparent (≥99.5% transmittance) and displayed an optical dispersion as low as 0.009 in the visible spectral region, much superior to those of the commercially important "organic glasses" such as poly(methyl methacrylate) and polycarbonates.

Introduction

Cyclotrimerization of alkynes to benzenes (**5**, Scheme 1) is a century-old reaction[6,7] and has now been developed into a chemo-, regio-, and stereoselective reaction for the synthesis of organic molecules of theoretical and practical interest.[8] Cycloaddition of diacetylenes (or diynes) has also been studied, but the research was mainly focused on the creation of small molecules of novel structures such as cyclodimers **6** (eq 2) and -trimers **7** (eq 3) as well as its applications in the synthesis of natural products.[8,9]

Scheme 1



Hecht and Frechet have recently elegantly utilized the alkyne cyclotrimerization to build dendritic molecules, in which the Frechet dendrons (D_n) linked by a triple bond ($D_n-C\equiv C-D_n$) are cyclized via a [2 + 2 + 2] cycloaddition process, generating benzene-cored dendrimers **8** in a convergent fashion (eq 4, Scheme 2).[10] We wish to go one step further and are interested in exploring synthetic utility of the diyne cyclotrimerization as an elementary reaction for the construction of new hyperbranched polymers.[11] This possibility is suggested by the frequent reports that insoluble polymers have often been formed in diyne cyclization reactions (eq 5), although to the synthetic chemists, the polymers are undesirable byproducts, which were thus discarded without isolation. A few research groups looked into the possibility of using diyne cyclization for polymer synthesis in the early 1970s, but as summarized by Sergeyev et al. in a symposium review article[12] at that time, the resultant polymers "are infusible and insoluble in conventional organic solvents" and "are difficult to reprocess into manufactured articles". Though the solubility problem was solved in some cases by using monoynes as comonomers to *co*polymerize with diyne monomers,[12,13] the interest in the *homo*polymerization of diynes has subsided, with almost no one revisiting the subject over the past few decades[14] because the insolubility of the homopolydiynes renders their structural characterization a difficult proposition and their nonprocessability makes them almost useless in terms of finding practical applications as plastic materials.

We rose to the challenge and tackled the intractability problem in the homopolymerization of diynes. We are intrigued by the exciting upshot: success in solving the problem will offer a powerful tool for assembling small molecules into hyperbranched polymers by aromatic rings. Development of hyperbranched polymers is a hot topic of current interest.[2−4,15,16] Many hyperbranched polymers have been synthesized by polycondensation or

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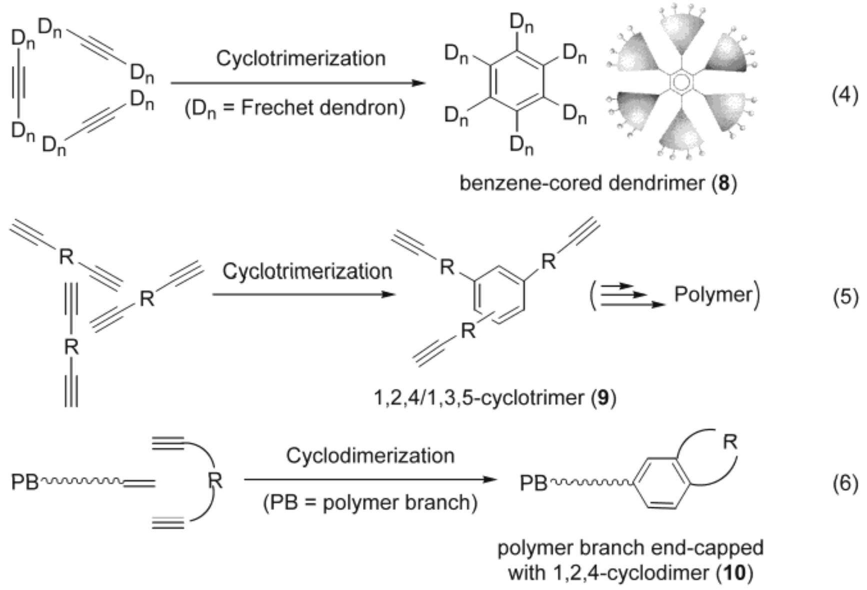
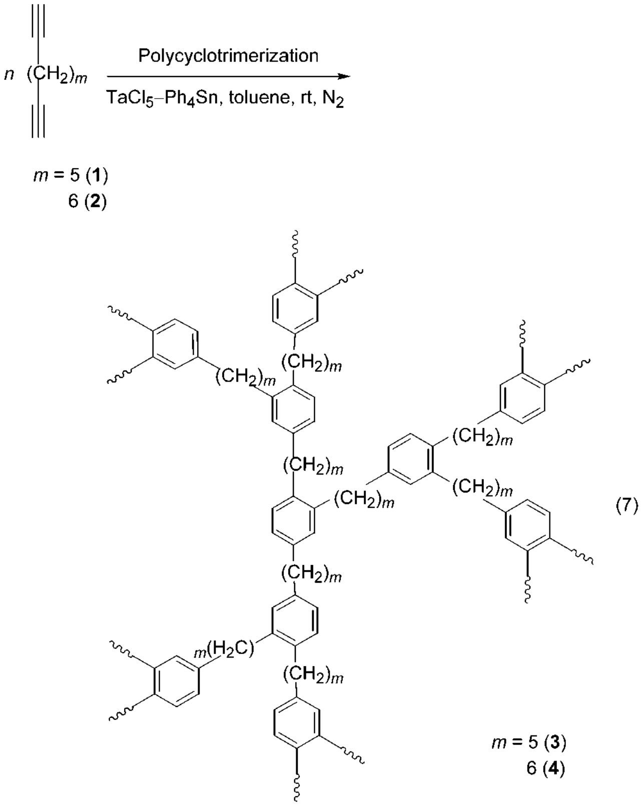
Scheme 2



polycoupling of multifunctional monomers. The stoichiometric requirement between the pairs of the functional monomers is, however, practically difficult to meet, which often limits the growth of propagating species and gives rise to oligomeric products. Incomplete condensation or coupling yields repeat units of linear structures, contributing to a decrease in the degree of branching of the resultant polymers. The decomposition of the functional linkages (e.g., hydrolysis of polyesters and polyamides)[17] is another concern, especially when the polymers are put to use for long-term applications. On the other hand, alkyne polycyclotrimerization is a unimolecular event or a polyaddition reaction involving a single monomer species, which thus suffers no stoichiometric constraints and can potentially produce polymers with very high molecular weights. The divergent growth of the polymer branches is via convergent cyclotrimerization of three single diyne monomers, and a bimolecular event of dimerization between a propagating branch and a diyne monomer will terminate the growth of the branch and give a cyclodimer periphery end (eq 6). The polymeric products formed thus should be inherently highly hyperbranched, because of the intolerance of the polycyclotrimerization mechanism with the formation of linear repeat units inside the spherical cores. The repeat units are knit together by robust benzene rings instead of labile functional bridges, and the polymers thus should be very stable. If the diyne polycyclotrimerization can be brought under control, it will pave the way to the creation of a variety of new hyperbranched polyphenylenes because the advancement in the synthetic alkyne chemistry has made many diyne monomers of different structures readily available.[18]

Scheme 3



Attracted by the unique advantages and bright prospects of diyne polycyclotrimerization, in this work, we studied homopolycyclotrimerizations of 1,8-nonadiyne (**1**) and 1,9-decadiyne (**2**) catalyzed by a binary mixture of $TaCl_5$ and Ph_4Sn (Scheme 3). Under optimal reaction conditions, the polycyclotrimerizations proceeded in a regioselective fashion and produced completely soluble hyperbranched diyne homopolymers consisting of 1,2,4-benzenetriyl cores. The polymers possessed high molecular weights but low intrinsic viscosities. Being hyperbranched derivatives of polyphenylene,[1−5] the polymers exhibited excellent thermal stability and lost little weight at ~500 °C. Polymer **3** emitted UV light of 286 nm upon photoexcitation and exhibited a high Abbé number (107.6) and a low optical dispersion (0.009).

Experimental Section

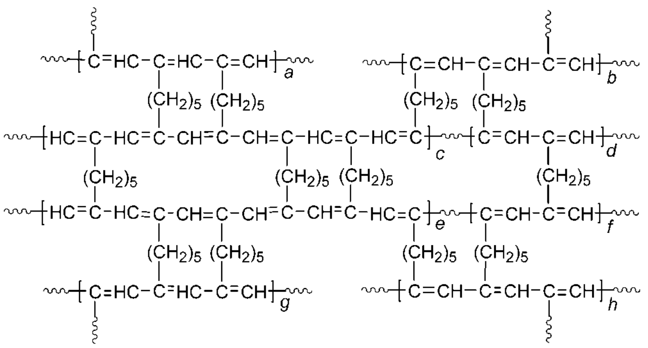
Full experimental details including materials, instrumentation, polymerization procedures, and spectroscopic analysis data are all given in the Supporting Information. Only a few explanatory notes are provided here. Because of the hyperbranched nature of the polymers, their molecular weights were evaluated by different means. Their relative molecular weights

Table 1. Polymerization of 1,8-Nonadiyne (1)[a]

no.	catalyst[b]	$[M]_o$ (M)	solvent	temp[c] (°C)	yield (wt %)	solubility[d]	M_w[e]	M_w/M_n[e]
1	$[CpMo(CO)_3]_2$	0.50	CCl_4	65	100	×		
2	$Mo(CO)_4(nbd)$	0.50	CCl_4	65	64	×		
3	$CpCo(CO)_2$	0.54	toluene	118	0			
4	$Pd/C-ClSiMe_3$	0.54	THF	65	0			
5	$TaCl_5-Ph_4Sn$	0.54	toluene	rt	nd[f]	×		
6	$TaCl_5-Ph_4Sn$	0.27	toluene	rt	77	○	34 700	4.6
7	$TaCl_5-Ph_4Sn$	0.13	toluene	rt	trace			
8	$NbCl_5-Ph_4Sn$	0.27	toluene	rt	42	△		

[a] Carried out under nitrogen for 24 h; [cat.] = ([cocat.] =) 20 mM (nos. 1, 2, and 5−8); [cat.] = 80 mM (no. 3); [cat.] = 50 mM, [cocat.] = 1 M (no. 4). [b] Abbreviations: Cp = cyclopentadiene; nbd = 2,5-norbornadiene. [c] rt = room temperature (~23 °C). [d] Tested in common organic solvents including toluene, benzene, dichloromethane, chloroform, and THF: ○ = completely soluble; △ = partially soluble; × = insoluble. [e] Estimated by SEC in THF on the basis of a polystyrene calibration. [f] Not determined.

Chart 1



were estimated by a SEC system with RI and UV detectors (polystyrenes calibration)[19] and their absolute molecular weights were determined by another SEC system equipped with RI, right-angle laser light scattering (RALLS), and differential viscometer (DV) detectors.[20,21] The static and dynamic light scattering measurements were carried out on a modified laser light scattering spectrometer.[22] The molar absorptivities (ϵ) of the polymers were calculated on the basis of their structural repeating units, one of which consists of 1.5 diyne molecules.[23]

Results and Discussion

Polymerization. We first conducted a brief survey of polymerization conditions of diyne **1**. As shown in Table 1, in the presence of $[CpMo(CO)_3]_2$, **1** was polymerized quantitatively, but the polymeric product was completely insoluble in common solvents. A similar result was obtained when $Mo(CO)_4(nbd)$ was used. The insolubility of the polymeric products suggests that the triple bonds of the diyne monomer have undergone metathesis polymerization[24] to form heavily cross-linked polyacetylene gels (Chart 1). In sharp contrast, when the reactions of **1** were catalyzed by $CpCo(CO)_2$ and $Pd/C-ClSiMe_3$, no polymeric products could be isolated (Table 1, nos. 3 and 4), probably because the diyne has been converted by the cycloaddition catalysts into di-, tri-, and oligomeric species[8] that were soluble in methanol and acetone, and the reaction products were thus dissolved into, and/or washed away by, the solvents used in the polymer isolation processes (see the detailed procedures for the polymer purification described in the Supporting Information).

While many complexes of late transition metals such as cobalt and palladium are good catalysts for alkyne cyclotrimerization,[8] few compounds of early transition metals of tantalum and niobium are known to catalyze [2 + 2 + 2] cycloadditions.[25] We checked whether a $TaCl_5-Ph_4Sn$ mixture could initiate polycyclotrimerization of **1** to give soluble polymeric products.[26] A vigorous reaction with readily recognizable heat release immediately occurred when 0.54 M of **1** was admixed with 20 mM of $TaCl_5-Ph_4Sn$ in toluene at room temperature, but the polymeric product formed was completely insoluble. This indicates that **1** has not undergone cyclodimerization (eq 2) and -trimerization (eq 3) because such reactions should give soluble products of low molecular weights. Formation of a polyene structure through a metathesis mechanism is also ruled out because it is known that Ta mixtures are incapable of initiating metathesis polymerizations of terminal alkynes.[27] The exclusion of the possibilities of the alkyne cyclooligomerization and metathesis polymerization leads to the conclusion that **1** has been polymerized by the Ta mixture via the desired cycloaddition mechanism. We thus tried to optimize the reaction conditions of the polycyclotrimerization. We decreased the monomer concentration to 0.27 M, and as a nice surprise, the polymerization product was completely soluble (Table 1, no. 6)! Further dilution in the monomer concentration made, however, the polycyclotrimerization ineffective, indicating that there is a concentration window for the polymerization of **1**. This is easy to understand, considering that the polymerization is an intermolecular reaction involving fusing of three triple bonds together. We applied the “optimal” concentration of **1** to its polymerization by $NbCl_5-Ph_4Sn$ but failed to obtain a completely soluble product (Table 1, no. 8): the optimization is clearly catalyst-dependent.

We then investigated the polymerization of 1,9-decadiyne (**2**) and found that it behaved like **1**, its structural congener. Again there was an optimal monomer concentration window in the Ta-catalyzed polycyclotrimerization and the Nb catalyst failed to give completely soluble polymeric product (Table 2). The polymerization of this monomer was attempted in the late 1980s[14] and the preliminary results were reported in a short communication. The authors described that the catalysts gave *partially* soluble polymers and found that the Ta-initiated polymerizations in toluene and benzene gave polymer gels with toluene-soluble fractions as low as 20 and 5%, respectively. Our results are thus truly exciting and encouraging: we are able to produce a *completely* soluble polymer by optimizing the polymerization conditions.

The diyne monomers **1** and **2** showed similar polymerization behaviors; the molecular weights and molecular weight distributions of their polymers **3** and **4** are, however, quite different. As can be seen from Figure 1, the SEC curve of **3** is single peaked and roughly symmetric but that of **4** is bimodal with the major peak locating in the higher molecular weight region. The higher molecular weight peak contributes to the increase in both the average molecular weight and poly-

Table 2. Polymerization of 1,9-Decadiyne (2)[a]

no.	catalyst	$[M]_0$ (M)	solvent	temp[b] (°C)	yield (wt %)	solubility[c]	M_w[e]	M_w/M_n[d]
1	$TaCl_5-Ph_4Sn$	0.50	toluene	rt	nd[e]	×		
2	$TaCl_5-Ph_4Sn$	0.25	toluene	rt	84	○	366 000	25.2
3	$TaCl_5-Ph_4Sn$	0.12	toluene	rt	0			
4	$NbCl_5-Ph_4Sn$	0.25	toluene	rt	24	△		

[a] Carried out under nitrogen for 24 h, [cat.] = [cocat.] = 10 mM. [b] rt = room temperature. [c] Tested in common organic solvents; for the solubility symbols, see footnote *d* of Table 1. [d] Estimated by SEC. [e] Not determined (gel formed in ~10 min).

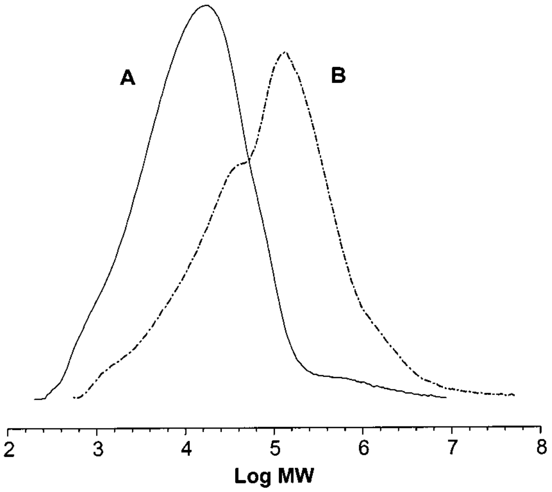


Figure 1. Typical SEC chromatograms of hyperbranched (A) poly(1,2,4-benzenetriyl-1,5-pentanediyl) (**3**; sample from Table 1, no. 6) and (B) poly(1,2,4-benzenetriyl-1,6-hexanediyl) (**4**; Table 2, no. 2).

Table 3. Effect of Catalyst Concentration on Polycyclotrimerization of 1,8-Nonadiyne (1)[a]

no.	[catalyst] (mM)	yield (wt %)	M_w[b]	M_w/M_n[b]
1	1.5	trace		
2	3.5	trace		
3	5.0	48	194 000	4.7
4	7.5	50	169 000	3.1
5	10.0	85	41 200	4.0
6	15.0	51	40 900	5.0
7	20.0	77	34 700	4.6

[a] Carried out in toluene at room temperature under nitrogen for 24 h using $TaCl_5$ as catalyst and Ph_4Sn as cocatalyst ([cat.] = [cocat.]) with $[M]_0$ = 0.27 M. All the polymer products are completely soluble in common organic solvents. [b] Estimated by SEC.

dispersity index of **4**: its M_w (366 000) and M_w/M_n (25.2) are respectively 10.5 and 5.5 times higher than those of **3** (34 700 and 4.6). Obviously, there exist some differences in the details of the polymerization processes of the two monomers.

We thus further studied the polycyclotrimerizations of **1** and **2**, with the intension of further optimizing their polymerization conditions, understanding their polymerization behaviors, and gaining insights into their polymerization mechanisms. We first examined the effect of the catalyst concentration ([cat.]) on the polymerization of **1** initiated by the Ta mixture at its "optimal" monomer concentration ($[M]_0$ = 0.27 M). When a low catalyst concentration of 1.5 mM was used, the polymerization was ineffective, and only a trace amount of polymer was isolated (Table 3, no. 1). Similar result was obtained at [cat.] = 3.5 mM. When the catalyst concentration was raised to 5 mM, the reaction became effective and produced a polymer with a high molecular weight (M_w 194 000). Further increase in the catalyst concentration led to a monotonic decrease in the molecular weight of the resultant polymer, in agreement of the general trend observed in an addition polymerization: molecular weight of an addition polymer is inversely affected by an increase in catalysis concentration.[28]

Table 4. Effect of Catalyst Concentration on Polycyclotrimerization of 1,9-Decadiyne (2)[a]

no.	[catalyst] (mM)	yield (wt %)	solubility[b]	M_w[c]	M_w/M_n[c]
1	1.5	51	○	668 000	28.5
2	3.5	88	○	750 000	25.9
3	5.0	89	○	621 000	23.0
4	7.5	84	○	582 000	35.1
5	10.0	91	○	305 000	21.4
6	15.0	nd[d]	×		

[a] Carried out in toluene at room temperature under nitrogen for 24 h (no. 1) or 30 min (nos. 2−6) using $TaCl_5$ as catalyst and Ph_4Sn as cocatalyst ([cat.] = [cocat.]) with $[M]_0$ = 0.25 M. [b] Tested in common organic solvents; for the solubility symbols, see footnote *d* of Table 1. [c] Estimated by SEC. [d] Not determined due to gel formation.

The diyne monomer **2** appeared to be more reactive than **1**, although it differs from **1** by only one methylene group in molecular structure. Even when the catalyst concentration was as low as 1.5 mM, the polymerization proceeded smoothly, giving a polymer with an M_w as high as 668 000 (Table 4, no. 1). The isolation yield of polymer **4** monotonically increased but its molecular weight generally decreased when the catalyst concentration was increased to 10 mM, while the polydispersity index remained broad. Further increase in [cat.] made the polymerization difficult to control, leading to the formation of insoluble gels (Table 4, no. 6).

We then checked the temperature (*T*) effect on the diyne polycyclotrimerizations. When the polymerization of **1** was carried out at 0 °C, insoluble gel was formed (Table 5, no. 1). The polymerization carried out at an elevated temperature of 60 °C produced an oligomer with an M_w of 4200. Similar temperature effect was observed in the polymerization of **2**. Clearly, there is also a temperature window in the polycyclotrimerization and luckily, the optimal temperature is room temperature. For an exothermic polymerization reaction ($\Delta H < 0$), a decrease in the temperature will compensate the unfavorable entropy effect ($\Delta S > 0$), making the Gibbs energy (ΔG) more negative and hence the polymerization reaction more favorable.[28] Too vigorous a reaction, however, easily induces gel formation. The increase in the reaction temperature may have activated and accelerated undesirable side reactions such as cyclodimerization (eqs 2 and 6), which actively terminates the growth of the propagating species, thus decreasing both the isolation yields and molecular weights of the polymers.

After investigating the effects of the key reaction parameters $[M]_0$, [cat.], and *T*, we looked into the time courses of the diyne polycyclotrimerizations at their "optimal" conditions. The polymerization reactions were followed by batch type and fluctuation in the experi-

Table 5. Effect of Temperature on Polycyclotrimerizations of Diynes 1 and 2[a]

no.	monomer **1** temp[b] (°C)	polymer **3** yield (wt %)	solubility[c]	M_w[d]	M_w/M_n[d]
1	0	nd[e]	×		
2	rt	85	○	82 000	5.4
3	60	60	○	4 200	2.3

no.	monomer **2** temp[b] (°C)	polymer **4** yield (wt %)	solubility[c]	M_w[d]	M_w/M_n[d]
4	0	nd[e]	×		
5	rt	89	○	621 000	23.0
6	60	13	○	32 800	8.8

[a] Carried out in toluene under nitrogen using $TaCl_5$ as catalyst and Ph_4Sn as cocatalyst; for nos. 1–3: $[M]_0 = 0.27$ M, [cat.] = [cocat.] = 10 mM, 2 h reaction; for nos. 4–6: $[M]_0 = 0.25$ M, [cat.] = [cocat.] = 5 mM, 30 min reaction. [b] rt = room temperature (~23 °C). [c] Tested in common organic solvents; for the solubility symbols, see footnote *d* of Table 1. [d] Estimated by SEC. [e] Not determined due to gel formation.

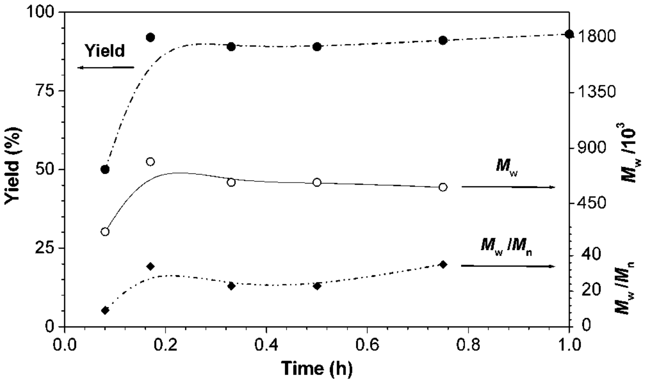


Figure 2. Time course of the polycyclotrimerization of 1,9-decadiyne (**2**) catalyzed by $TaCl_5$–Ph_4Sn in toluene at room temperature under nitrogen. $[M]_0 = 0.25$ M; [cat.] = [cocat.] = 5 mM. The polymeric product obtained at a reaction time of 1 h was partially soluble, whose M_w and M_w/M_n values were thus not determined.

mental data from batch to batch was thus unavoidable. The general trend was, however, quite clear: the diyne polycyclotrimerization was very fast. When conducted at room temperature in toluene at $[M]_0 = 0.27$ M and [cat.] = 10 mM, the polycyclotrimerization of **1** proceeded rapidly and the polymer yield reached 85% in a short time of 20 min. The M_w and M_w/M_n values of the polymers varied in the ranges of 23 800–92 300 and 4.0–5.5, respectively, over a time span of 24 h, with the polymer obtained after a 24-h reaction still being completely soluble. The polymerization of **2** was even quicker, and the polymer yield reached 92% in a reaction time as short as 10 min (Figure 2). Prolonging the polymerization time is detrimental in this system. Polymerizations over 45 min yielded partially insoluble polymers: the longer the polymerization time, the higher the insoluble fraction.

Characterization. The products of the diyne polymerizations were analyzed by different spectroscopic methods. Figure 3 shows the IR spectrum of polymer **3** along with that of its monomer **1**. While the monomer absorbed strongly at 3302 and 2118 cm^{-1} due respectively to the ≡C–H and C≡C stretching,[29,30] these alkyne absorption bands completely disappeared in the spectrum of the polymer (Figure 3B). Alternatively, two new benzenoid peaks appeared at 1892 and 1774 cm^{-1}. The disappearance of the alkyne bands and the appearance of the benzenoid peaks suggest that the triple bonds have been converted to benzene rings by the Ta-catalyzed cyclotrimerization. We carefully examined the "fingerprint" spectral region of the benzenoid absorption by comparison with the authentic spectra of some typical 1,2,4- and 1,3,5-trisubstituted alkylbenzenes in the hope of identifying the isomeric structures of the benzene rings of the polymer. The simplest trialkylbenzenes are 1,2,4- and 1,3,5-trimethylbenzenes: the former absorbs at 1889 and 1778 cm^{-1} while the latter absorbs at 1789 and 1740 cm^{-1}.[30] The similarity of the absorption pattern of **3** with those of the 1,2,4-trialkylbenzenes and its dissimilarity with those of the 1,3,5-isomers[30c] indicate that the benzene rings of the polymer are 1,2,4- but not 1,3,5-substituted. Similarly, **4** exhibited diagnostic absorption bands of 1,2,4-trialkylbenzene at 1890 and 1770 cm^{-1} (Figure 4). However, different from **3**, polymer **4** still showed weak but clearly identifiable acetylene stretching bands at 3310 and 2118 cm^{-1}, revealing that this polymer carries functional triple-bond moieties.

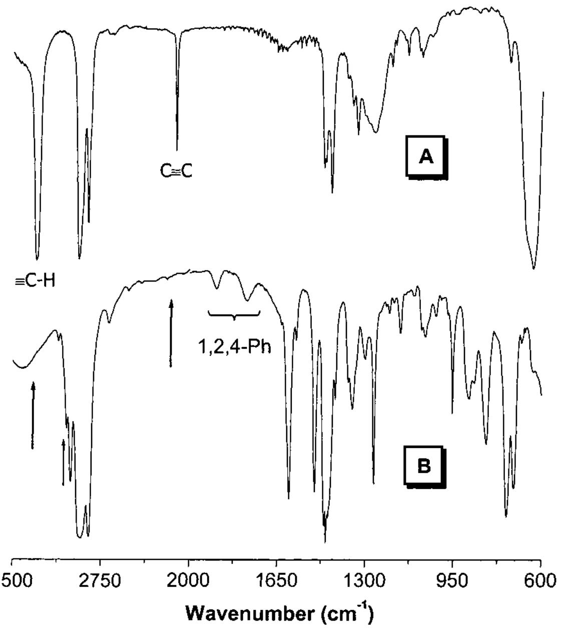


Figure 3. FT-IR spectra of (A) 1,8-nonadiyne **1** and (B) its hyperbranched polymer **3** (sample taken from Table 1, no. 6).

The excellent solubility of the polymers enabled us to further characterize their molecular structures in detail by "wet" spectroscopic methods. Figure 5 shows the ^{1}H NMR spectra of polymer **3** and its monomer **1**. The strong absorption peak of the acetylene protons of the monomer (a) at δ 1.97 was replaced by the multiple absorption peaks of the polymer (f) in the aromatic spectral region. The formation of the benzene rings changed the propargyl protons (b) to benzyl protons, whose resonance occurred accordingly in the lower field (e and d).[30a] Ring strain is kwon to downfield-shift benzyl absorption: for example, the benzyl protons of "acyclic" ethyl- and propylbenzenes absorb at δ 2.61 and 2.57, while those of "cyclic" indan and tetralin resonate at δ 2.91 and 2.85, respectively (noticing the decrease in the ring strain effect with an increase in the ring size).[31,32] The peaks of the benzyl protons of **3** thus can be further distinguished, with the major and minor peaks at δ 2.51 and 2.72 assignable to the absorptions

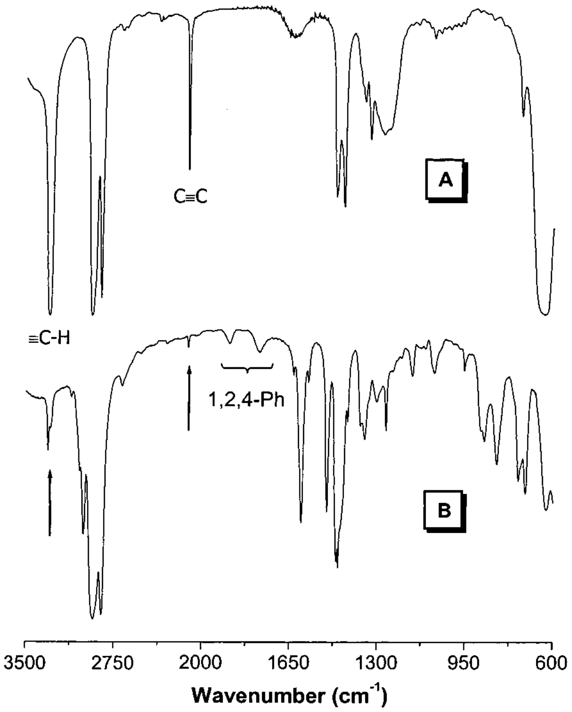


Figure 4. FT-IR spectra of (A) 1,9-decadiyne **2** and (B) its hyperbranched polymer **4** (sample taken from Table 4, no. 4).

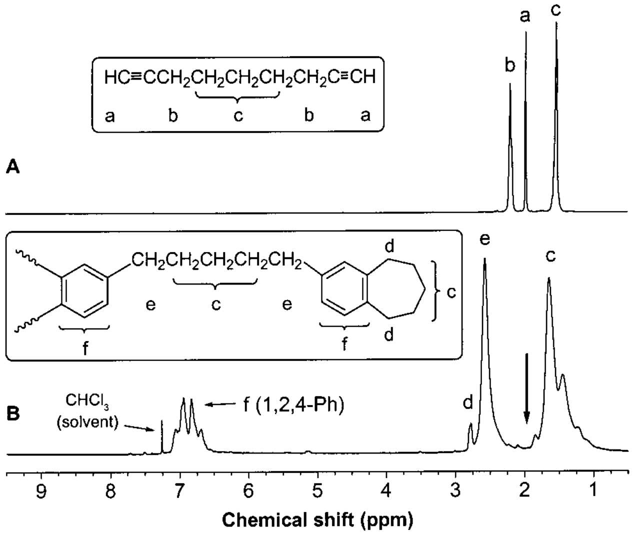


Figure 5. ^{1}H NMR spectra of (A) 1,8-nonadiyne **1** and (B) its hyperbranched polymer **3** (sample from Table 3, no. 4).

of the acyclic (e) and cyclic (d) benzyl protons in the pentamethylenebenzene and benzosuberan units, respectively. It is known that a 1,2,4-trialkylbenzene (an asymmetric molecule) exhibits multiple peaks in the vicinity of δ 6.9, but its symmetric cousin 1,3,5-trialkylbenzene shows a single upfield peak.[32] The multiple absorption peaks of polymer **3** in the aromatic spectral region thus suggest that the benzene rings in the polymer is 1,2,4-trisubstituted, in agreement with the conclusion derived from the IR analysis.

The benzosuberan rings formed by cyclodimerization are obviously the periphery ends of the hyperbranched polymer. To know how many such rings exist in the polymer periphery, we built an ideal dendritic model, in which the periphery ends of the perfect dendritic species are all capped by the benzosuberan rings, demonstrative examples of which are given in Chart 2 (for simplicity, only the dendrimers with low generation numbers are shown). While the growth of the numbers of different types of protons with the increase in the generation could all be expressed by integer sequences, we paid special attention to the sequential growth of the numbers of the protons whose absorptions are associated with the NMR peaks f (phenyl core), d (ring benzyl), and c (propyl spacer). The theoretic ratio of the proton number of phenyl ($N_{\text{Ph-H}}$) to that of ring benzyl ($N_{\text{Bz-H}}$) can be defined by eq 8, which rapidly approaches a constant (1.5) when the generation number n increases.[33] Similarly, the ratio of the proton number of propyl ($N_{\text{C3-H}}$) to $N_{\text{Bz-H}}$ can be defined by eq 9, which also converges on a constant (4.5) when $n \to \infty$.

$$\lim_{n\to\infty}\frac{N_{\text{Ph-H}}}{N_{\text{Bz-H}}} = \lim_{n\to\infty}\frac{6(3 \times 2^{n-1} - 1)}{12 \times 2^{n-1}} = \frac{3}{2} \qquad (8)$$

$$\lim_{n\to\infty}\frac{N_{\text{C3-H}}}{N_{\text{Bz-H}}} = \lim_{n\to\infty}\frac{18(3 \times 2^{n-1} - 1)}{12 \times 2^{n-1}} = \frac{9}{2} \qquad (9)$$

The degree of cyclodimerization (DC) can thus be estimated by comparison of the theoretical values given by eqs 8 and 9 with the experimental values obtained from the NMR analysis:

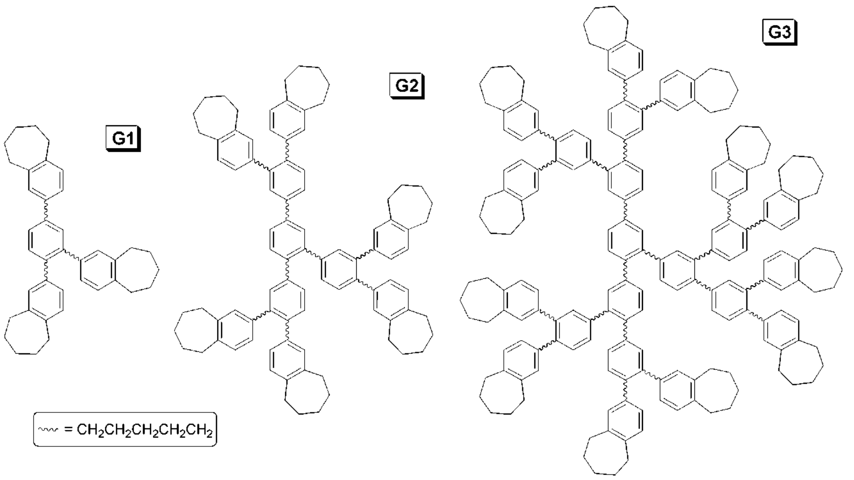
$$\text{DC} = \frac{A_{\text{Bz-H}}}{A_{\text{Ph-H}}}\lim_{n\to\infty}\frac{N_{\text{Ph-H}}}{N_{\text{Bz-H}}} = \frac{3A_{\text{Bz-H}}}{2A_{\text{Ph-H}}} \qquad (10)$$

$$\text{DC} = \frac{A_{\text{Bz-H}}}{A_{\text{C3-H}}}\lim_{n\to\infty}\frac{N_{\text{C3-H}}}{N_{\text{Bz-H}}} = \frac{9A_{\text{Bz-H}}}{2A_{\text{C3-H}}} \qquad (11)$$

where $A_{\text{Bz-H}}$, $A_{\text{Ph-H}}$, and $A_{\text{C3-H}}$ are the integrated areas of the absorption peaks of the benzyl (d), phenyl (f), and propyl (c) protons. The DC values calculated from eqs 10 and 11 are 0.150 and 0.132, respectively, in fair agreement with each other, taking into consideration the involved experimental errors. The low DC value ($\leq$15%) also agrees with the polymerization results, because a high DC value means a ready formation of cyclodimers and suggests an active termination of propagating species, which should not give high polymers. Indeed, when 1,6-heptadiyne, whose spacer length (m) between the two triple bonds is 3 (compared to 5 in diyne **1**), was reacted in the presence of $\text{TaCl}_5\text{-Ph}_4\text{Sn}$, stable cyclodimeric indan species were produced, as evidenced by a strong absorption peak of the indanyl protons at δ 2.88, whose intensity was about the same as that of the acyclic benzyl protons at δ 2.61.[11d] This led to the formation of no polymeric products but oligomeric species of low molecular weights.

Polymer **4** also exhibited absorption peaks of phenyl (f) and benzyl (e) protons (at δ ~6.95 and ~2.55, respectively; Figure 6B). The multiple peaks in the aromatic spectral region again suggest a 1,2,4-trisubstituted isomeric structure.[32] In this case, however, the absorptions of the (a)cyclic benzyl protons merged into one single peak (e), because the strain in a eight-membered benzocyclooctene ring is small.[31] Another noteworthy feature of the spectrum of this polymer is the small peaks associated with the absorptions of acetylene (a) and propargyl (b) protons. This suggests that **4** has periphery ends of "living" triple bonds. To figure out the percent coverage of the hyperbranched polymer sphere by the peripheral triple bonds, we evaluated the numbers of phenyl ($N_{\text{Ph-H}}$), acetylene ($N_{\text{Ac-H}}$), and propargyl ($N_{\text{Pr-H}}$) protons in an ideal model

Chart 2



Sequential Growth of the Numbers of Phenyl [Ph-H (*f*)], Benzyl [Bz-H (*d*)], and Propyl [C3-H (*c*)] Protons in 1,2,4-Trisubstituted Polyphenylenes with Ideal Dendritic Structures Constructed from a Diyne Monomer of 1,8-Nonadiyne (**1**)

type of proton	generation (*G*)						
	1	*2*	*3*	*4*	*5*	···	*n*
Ph-H (*f*)	12	30	66	138	282	···	$6(3 \times 2^{n-1} - 1)$
Bz-H (*d*)	12	24	48	96	192	···	$12 \times 2^{n-1}$
C3-H (*c*)	36	90	198	414	846	···	$18(3 \times 2^{n-1} - 1)$

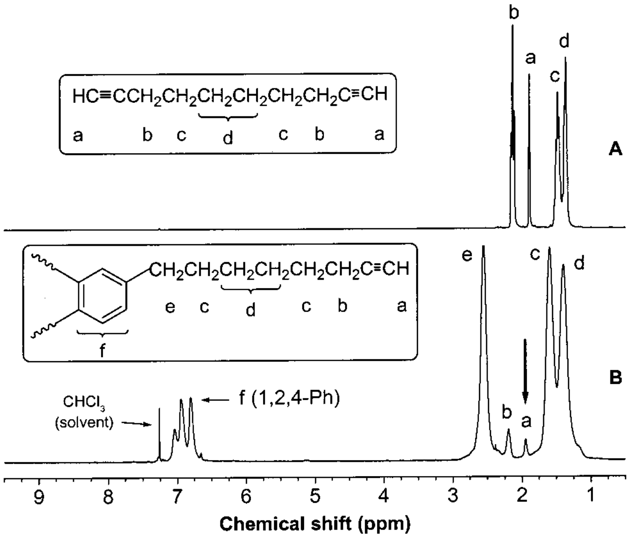


Figure 6. ^{1}H NMR spectra of (A) 1,9-decadiyne **2** and (B) its hyperbranched polymer **4** (sample from Table 4, no. 2).

of perfectly dendritic 1,2,4-trisubstituted polyphenylene. Chart 3 illustrates the demonstrative examples of the growth patterns of the proton numbers with the increase in the generation number of the dendritic species. When the dendritic generation (n) becomes large enough ($n > 10$), the theoretic ratios of $N_{\mathrm{Ph-H}}$, $N_{\mathrm{Ac-H}}$, and $N_{\mathrm{Pr-H}}$ can be calculated by the following equations:

$$\lim_{n\to\infty}\frac{N_{\mathrm{Ph-H}}}{N_{\mathrm{Ac-H}}} = \lim_{n\to\infty}\frac{3(3 \times 2^{n-1} - 2)}{3 \times 2^{n-1}} = \frac{3}{1} \tag{12}$$

$$\lim_{n\to\infty}\frac{N_{\mathrm{Ph-H}}}{N_{\mathrm{Pr-H}}} = \lim_{n\to\infty}\frac{3(3 \times 2^{n-1} - 2)}{6 \times 2^{n-1}} = \frac{3}{2} \tag{13}$$

The coverage of the sphere by the unreacted triple-bond functional groups or the degree of unsaturation (DU) can thus be estimated by the following equations using the integrated areas of the absorption peaks of acetylene ($A_{\mathrm{Ac-H}}$), propargyl ($A_{\mathrm{Pr-H}}$), and phenyl ($A_{\mathrm{Ph-H}}$) protons:

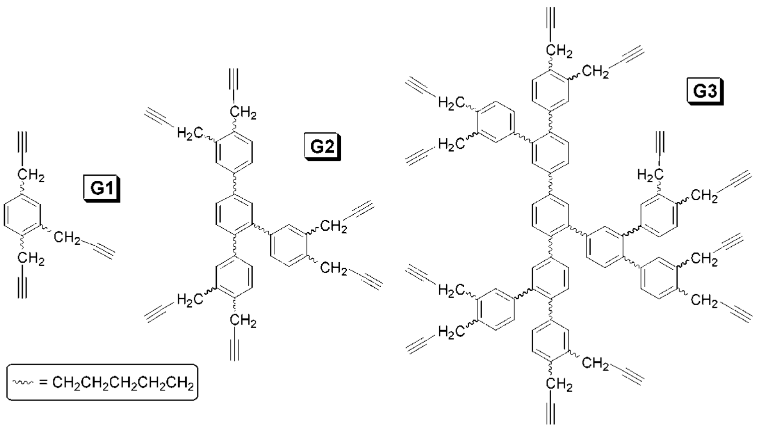
$$\mathrm{DU} = \frac{A_{\mathrm{Ac-H}}}{A_{\mathrm{Ph-H}}}\lim_{n\to\infty}\frac{N_{\mathrm{Ph-H}}}{N_{\mathrm{Ac-H}}} = \frac{3A_{\mathrm{Ac-H}}}{A_{\mathrm{Ph-H}}} \tag{14}$$

$$\mathrm{DU} = \frac{A_{\mathrm{Pr-H}}}{A_{\mathrm{Ph-H}}}\lim_{n\to\infty}\frac{N_{\mathrm{Ph-H}}}{N_{\mathrm{Pr-H}}} = \frac{3A_{\mathrm{Pr-H}}}{2A_{\mathrm{Ph-H}}} \tag{15}$$

From the spectral data of Figure 6B, the DU values calculated by the two equations are 0.249 and 0.256, respectively, agreeing with each other reasonably well. It becomes clear now that ~25% of the periphery ends of **4** are unsaturated triple bonds. The acetylenic periphery ends made the polymer active in terms of undergoing post-polymerization. Polymer **4** gradually became partially insoluble upon storage under ambient conditions. In contrast, polymer **3**, which carried no active acetylenic end groups, remained completely soluble even after storage for as long as ~3 years under the same conditions.

The ^{13}C NMR spectral data further substantiated the molecular structures of the polymers derived from their FT-IR and ^{1}H NMR spectral analyses. As can be seen from Figure 7, the resonance peaks associated with the acetylenic functionality of monomer **1** at δ 84.60, 68.95, and 18.70 all disappeared in the spectrum of its polymer **3**, and the phenylene and methylene units of **3** resonated in the appropriate aromatic and aliphatic spectral regions. We again compared the absorption patterns of our polymer with those of model compounds. 1,3,5-Triethylbenzene, for example, exhibits a simple absorption pattern, with single peaks of phenylene and methylene absorptions at δ 144.2 (quaternary carbon), 127.8 (tertiary carbon), and 28.8 (secondary carbon); on the other hand, 1,2,4-triethylbenzene displays five peaks

Chart 3



Sequential Growth of the Numbers of Phenyl [Ph-H (*f*)], Acetylene [Ac-H (*a*)], and Propargyl [Pr-H (*b*)] Protons in 1,2,4-Trisubstituted Polyphenylenes with Ideal Dendritic Structures Constructed from a Diyne Monomer of 1,9-Decadiyne (**2**)

type of proton	generation (*G*)						
	1	*2*	*3*	*4*	*5*	···	*n*
Ph-H (*f*)	3	12	30	66	138	···	$3(3 \times 2^{n-1} - 2)$
Ac-H (*a*)	3	6	12	24	48	···	$3 \times 2^{n-1}$
Pr-H (*b*)	6	12	24	48	96	···	$6 \times 2^{n-1}$

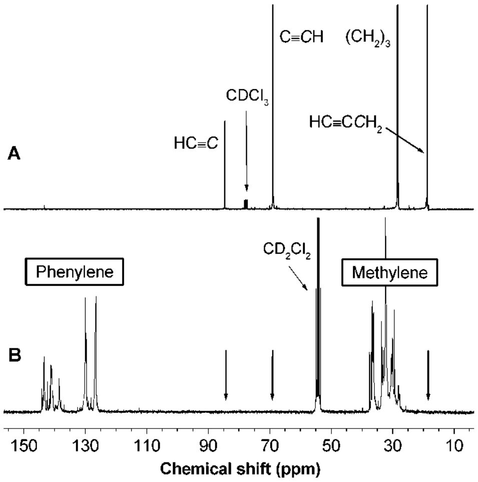


Figure 7. ^{13}C NMR spectra of (A) 1,8-nonadiyne **1** and (B) its hyperbranched polymer **3** (sample from Table 3, no. 4).

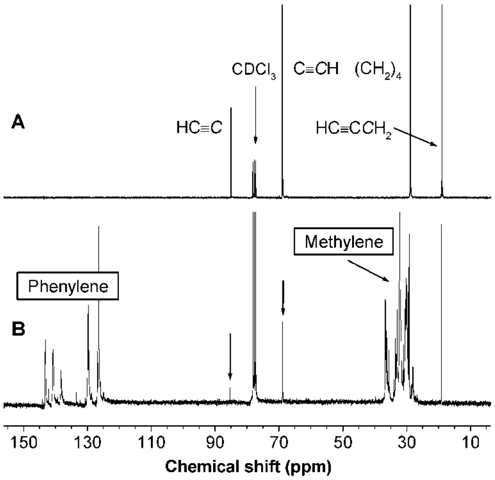


Figure 8. ^{13}C NMR spectra of (A) 1,9-decadiyne **2** and (B) its hyperbranched polymer **4** (sample from Table 4, no. 2).

in the aromatic region and three peaks in the aliphatic region.[31,32] Although it looks somewhat complicated at first glance, careful reading reveals that the basic absorption patterns of **3** resemble those of 1,2,4-triethylbenzene, which further confirms the 1,2,4-substitution of the benzene rings of the polymer. The absorption patterns of **4** in the phenylene and methylene regions were similar to those of **3**, but **4** clearly showed acetylene-related absorption peaks at δ 85.39 ($\equiv$C), 68.79 ($\equiv$CH), and 19.06 ($\equiv$C$-$$CH_2$; Figure 8B). This confirms the molecular structure of **4** derived from its ^{1}H NMR spectral data: a hyperbranched polyphenylene whose periphery shell is partially decorated by the active triple-bond functional groups.

To study the electronic structures of the polymers, we measured their UV absorption spectra. Polymer **3** exhibited B bands characteristic of isolated aromatic rings in the short wavelength region: its $\pi \rightarrow \pi^*$ transitions occurred at 267.6 and 275.8 nm with respective molar absorptivities (ϵ) of 497.8 and 437.5 mol^{-1} L cm^{-1} (Figure 9). Polymer **4** underwent similarly weak $\pi \rightarrow \pi^*$ transitions. The polymers resemble mesitylene, a trimethylbenzene, in terms of short-wavelength absorption and low molar absorptivity. Other isolated aromatic rings such as benzene, toluene, and xylenes all absorb in the vicinity of 260 nm with ϵ values of a few hundred, irrespective of whether and how the rings are substituted.[30a,34] Conjugated aromatic rings such as biphenyl and stilbene and conjugated (a)cyclic olefins such as 1,3-butadiene, 1,3,5-hexatriene, and 1,3-cyclohexadiene show much higher ϵ values [8000$-$52 500 (typically $\sim$20 000$-$35 000) mol^{-1} L cm^{-1}].[30a] Polyacetylenes with polyene backbones absorb in the visible spectral region with high absorptivities.[27f,29,35,36] The UV data of **3** and **4** thus rule out the likelihood of (a)cyclic polyene structures and verify their hyperbranched molecular architectures constructed with isolated benzene rings.

Properties. Linear polyphenylenes are notoriously intractable: an oligo(*p*-phenylene) is already insoluble in any organic solvents.[37] With the aid of the flexible methylene spacers in separating the benzene rings in

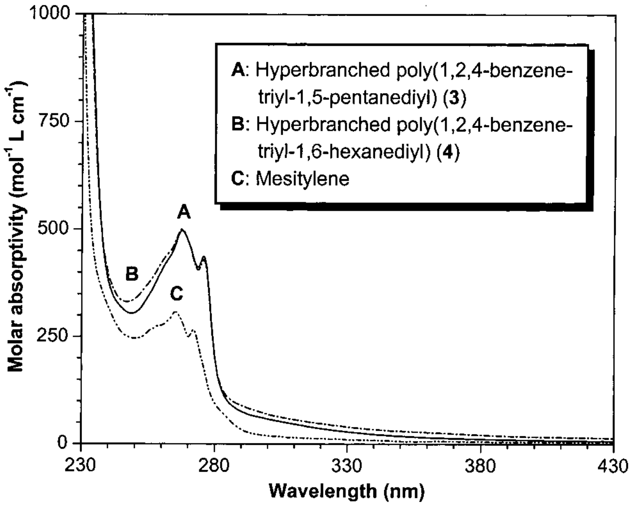


Figure 9. UV absorption spectra of hyperbranched polyphenylenes (A) **3** (sample from Table 3, no. 4) and (B) **4** (Table 4, no. 2), with the spectrum of (C) mesitylene shown for comparison. Solvent: dichloromethane.

the divergent three-dimensional space, the hyperbranched polyphenylenes **3** and **4** became soluble in common solvents. Dissolution of the as-purified polymers[38] was almost instant; for example, when a drop of toluene was added into a test tube containing a sample of **3**, the powdery solid immediately disappeared into the solvent "ocean".

Because of their spherical topology, hyperbranched polymers normally give lower-than-real average molecular weights when measured by an SEC system calibrated with linear polymer standards such as polystyrene.[2b,15,39] Grayson and Frechet, for example, found that the polystyrene-relative M_n of their dendronized poly(*p*-hydroxystyrene) of the fourth generation were more than 4-fold underestimeated.[39a] Deffieux's group used a "normal" SEC with a RI detector (SEC/RI; linear polystyrene standards) and an "advanced" SEC with RI and laser light scattering (LLS) dual detectors (SEC/RI/LLS) to measure the average molecular weights of their hyperbranched polystyrenes and found that the relative M_n's estimated by SEC/RI were normally ~7-fold lower than the absolute M_n's determined by SEC/RI/LLS.[39b] In some cases, the difference went up to ~30-folds.[39b] Our polyphenylenes, being hyperbranched, also displayed such difference, though not to the extent of Deffieux's system. We measured the average molecular weights of our polymers by an SEC system equipped with light scattering and differential viscometry detectors (SEC/RI/RALLS/DV)[21] and found that the absolute M_w's were much higher than the relative M_w's estimated by SEC/RI/UV, the difference being in the range of ~2−7 (Table 6). The highest M_w of our polymers reached 1.388 × 10^6 Da. These results prove that the diyne polycyclotrimerization is a powerful tool for the synthesis of hyperbranched polyphenylenes with high molecular weights and excellent solubility.

Table 6. Molecular Weights and Intrinsic Viscosities of Hyperbranched Polyphenylenes 3 and 4[a]

no.	polymer	M_w (by SEC/RI/UV)[b]	M_w (by SEC/RI/RALLS/DV)[c]	$[\eta]$[d] (dL/g)
1	**3**	194 000	1 388 000	0.16
2	**3**	169 000	1 042 000	0.17
3	**4**	220 000	1 088 000	0.19
4	**4**	85 000	195 000	0.13

[a] Measured in THF at room temperature. [b] Estimated by an SEC system equipped with a set of refractive index (RI) and ultraviolet photometer (UV) detectors using polystyrenes as calibration standards. [c] Measured by an SEC system equipped with a set of RI, right-angle laser light scattering (RALLS), and differential viscometer (DV) detectors.[20−22] [d] Intrinsic viscosity.

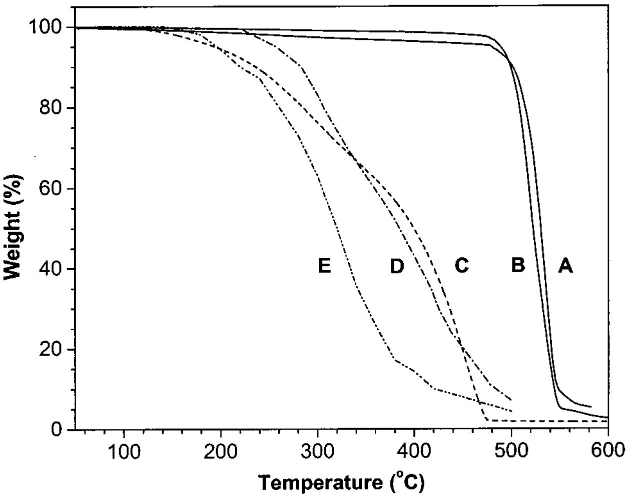


Figure 10. TGA thermograms of hyperbranched polyphenylenes (A) **3** (sample from Table 3, no. 2) and (B) **4** (Table 4, no. 2) prepared by $TaCl_5-Ph_4Sn$ catalyst. The thermograms of (C) cross-linked poly(1,8-nonadiyne) network prepared by $Mo(CO)_4(nbd)$ catalyst (Table 1, no. 2),[24] (D) poly(phenylacetylene) prepared by $W(CO)_6-CCl_4$-*hν* catalyst,[42a] and (E) poly(1-hexyne) prepared by $Fe(acac)_3-3Et_3Al$ catalyst[42a] are shown for comparison. The thermal analyses were carried out under nitrogen at a heating rate of 20 °C/min.

The high molecular weight polymers exhibited, however, very low solution viscosities. The intrinsic viscosities of the polymer solutions were <0.2 dL/g and changed little with a change in the molecular weight of the polymers (Table 6). This is similar to Deffieux's system: their hyperbranched polystyrenes also exhibited very low viscosities (0.1−0.2 dL/g) and the change in $[\eta]$ with M_w was small and irregular.[39b] The low solution viscosity is actually another characteristic feature of hyperbranched polymers, due partly to the lack of chain entanglements between the spherical macromolecules.[15,39,40] We determined the average radius of gyration ($\langle R_g \rangle$) and hydrodynamic radius ($\langle R_h \rangle$) of a sample of **3** by static and dynamic light scattering and found that they were 52 and 60 nm, respectively. It is known that solid sphere, hyperbranched polymer, and random coil give respective $\langle R_g \rangle/\langle R_h \rangle$ ratios of ~0.77, ~1.0, and ~1.5−1.8.[40c,41] The $\langle R_g \rangle/\langle R_h \rangle$ ratio of 0.87 of **3** thus further verifies its hyperbranched topology.

The hyperbranched polyphenylenes exhibited outstanding thermal stability, losing little weight at ~500 °C (Figure 10). In contrast, the polyene network gel (cf., Chart 1) prepared by the metathesis polymerization of **1** catalyzed by $Mo(CO)_4(nbd)$[24] was labile, starting to lose its weight at ~125 °C. This is not surprising, because monosubstituted polyacetylenes such as poly(1-hexyne) and poly(phenylacetylene) all start to decompose in this low-temperature region.[42] Linear polyphenylenes are, however, thermally much more robust (stable at ~450−550 °C).[37] The comparison of the thermal stabilities of polymers **3** and **4** with those of polyacetylenes and polyphenylenes further validates the basic polyphenylene structures of our hyperbranched polymers.

The hyperbranched polyphenylene **3** underwent glass transition at 43 °C (Figure 11). This glass transition

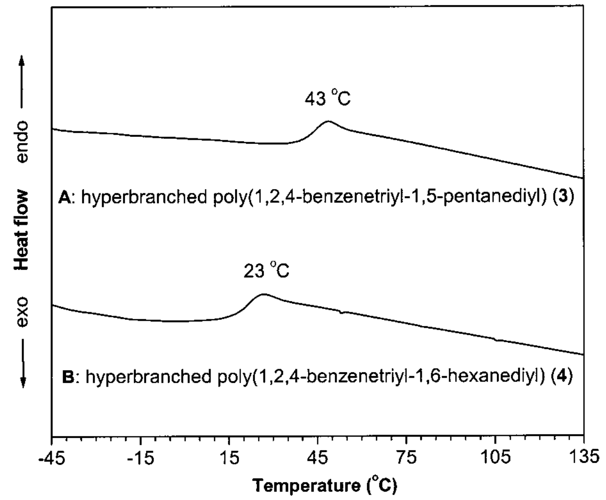


Figure 11. DSC thermograms of hyperbranched polyphenylenes (A) **3** (sample from Table 3, no. 4) and (B) **4** (Table 4, no. 2) measured under nitrogen at a heating rate of 10 °C/min (recorded during the second heating scan).

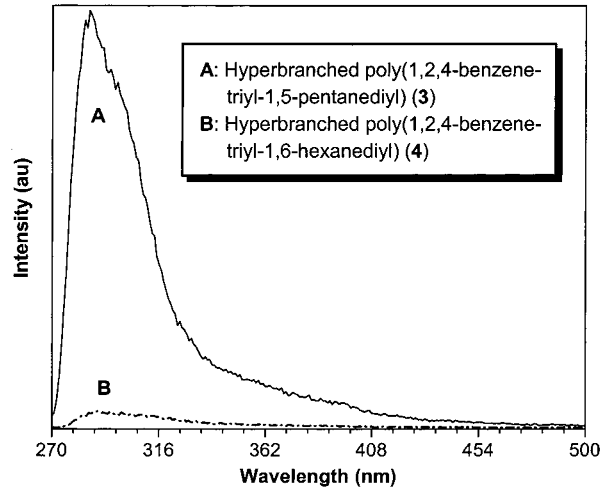


Figure 12. Photoluminescence spectra of hyperbranched polyphenylenes (A) **3** (sample from Table 3, no. 3) and (B) **4** (Table 4, no. 2). Solvent: dichloromethane. Concentration: 0.5 mg/mL. Excitation wavelength: 265 nm.

temperature (T_{g}) is lower than that (80 °C) of poly(1,4-phenyleneethylene) (PPE),[43] a linear polyphenylene whose benzene rings are separated by ethylene spacers. The lower T_{g} of **3** is probably due to the internal plasticization effect[44] of the long pentamethylene spacers between the benzene rings. In **4**, the length of the flexible spacer is increased to hexamethylene, and as a result of the enhanced internal plasticization, its T_{g} was further decreased to 23 °C.

Polymers **3** and **4** are comprised of nonconjugated or isolated trisubstituted benzene rings and it is of interest to check the optical properties of such aromatic systems. Upon excitation, **3** fluoresced at a wavelength as short as 286 nm (Figure 12), due to the radiative delay of the excited isolated benzene rings to their ground state. Although **4** differed from **3** only by one methylene spacer in molecular structure, it emitted a UV light whose peak intensity was only one twenty-third ($^1/_{23}$) of that of **3**. It is remarkable that the light-emitting property of the polymer can be tuned to such a great extent by varying one methylene spacer. We do not know the exact cause for the big difference at present time but suspect that the aggregation quenching[45,46] may have played a role in the photoluminescence process of **4**: the aromatic rings separated by the even-numbered hexamethylene spacer in **4** may have experienced stronger electronic interactions and hence have higher possibilities of forming less emissive excimer species than those separated by the odd-numbered pentamethylene spacers in **3**.[46]

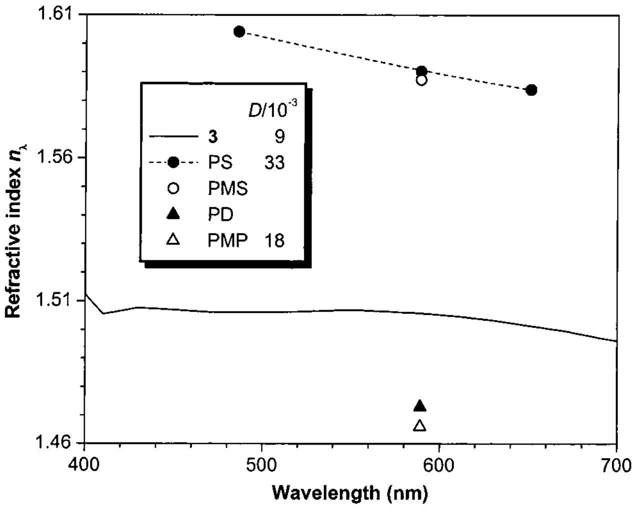


Figure 13. Wavelength dependence of refractive index (n_λ) for a thin film of hyperbranched polyphenylene **3** (sample taken from Table 3, no. 3) in the visible spectral region. The n_λ data for polystyrene (PS), poly(*o*-methylstyrene) (PMS), poly(1-decene) (PD), and poly(4-methyl-1-pentene) (PMP) are shown for comparison (data taken from ref 49). Inset: optical dispersion (D) values of **3**, PS, and PMP.[49]

As described above, the hyperbranched polyphenylenes underwent electronic transitions in the deep UV region and absorbed practically no visible light. Casting toluene solutions of the freshly prepared polymers on flat substrates afforded colorless, isotropic, and transparent films of optical quality:[47] for example, spin coating a 1% toluene solution of **3** onto quartz disks or silicon wafers gave films with thicknesses of ~400−850 Å and transmissibilities of ~99.5−99.8% in the wavelength region of 350−1190 nm. Such highly transparent films may find photonic applications and we thus measured their wavelength-dependent refractive indices (n_λ) using spectroellipsometry. From the n_λ data, the Abbé number (ν_{D}) and optical dispersion (D) of the polymer were calculated by the following equations:[48,49]

$$\nu_{\mathrm{D}} = \frac{n_{\mathrm{D}} - 1}{n_{\mathrm{F}} - n_{\mathrm{C}}} \tag{16}$$

$$D = \frac{1}{\nu_{\mathrm{D}}} \tag{17}$$

where n_{D}, n_{F}, and n_{C} are the refractive indices at λ = 589, 486, and 656 nm, respectively. The D value is a parameter indicative of the bandwidth over which a material is optically useful.[48−50] Compared with inorganic glasses, organic polymers suffer a thorny disadvantage of having high optical dispersions: their n_λ values vary appreciably over the visible spectral region.[51]

The spectroellipsometry measurement of a thin film of **3** with a thickness of 403 Å gave a rather flat refractive index spectrum, with its n_λ value varying in a small range (Δn_λ = 0.0163) over the whole visible spectral region (400−700 nm; Figure 13). Little difference in n_λ was recognized when the same measurement was conducted using a "thicker" film (836 Å). The n_λ values of **3** are lower than those of "aromatic" vinyl polymers such as polystyrene and poly(*o*-methylstyrene) but higher than those of "aliphatic" vinyl polymers such as poly(1-decene) and poly(4-methyl-1-pentene). It is known that a benzene ring exhibits higher refraction than an alkyl chain.[49b] The fact that the n_λ values of **3** fell between those of the aromatic and aliphatic vinyl polymers indicates that a hyperbranched polymer also observes Denbigh-Stein "additive rule": the molar refractivity of a molecule is the sum of the individual refractions from all the chemical bonds or group units that make up the molecule.[52]

From the wavelength-dependent n_λ data of **3**, a ν_D value of 107.6 was obtained. The high Abbé number gave a low optical dispersion ($D = 0.009$), which is about a one-quarter ($\sim^1/_4$) and one-half ($\sim^1/_2$) of those of polystyrene and poly(4-methyl-1-pentene), respectively. The optical dispersion of **3** is also lower than those of commercially important optical plastics such as polycarbonate ($D = 0.0297$), poly(methyl methacrylate) (0.0175), and CR-39 (0.0173).[49b] The low optical dispersion of **3**, coupled with its excellent optical clarity and outstanding thermal stability, endows the polymer with a high potential of finding photonic applications.

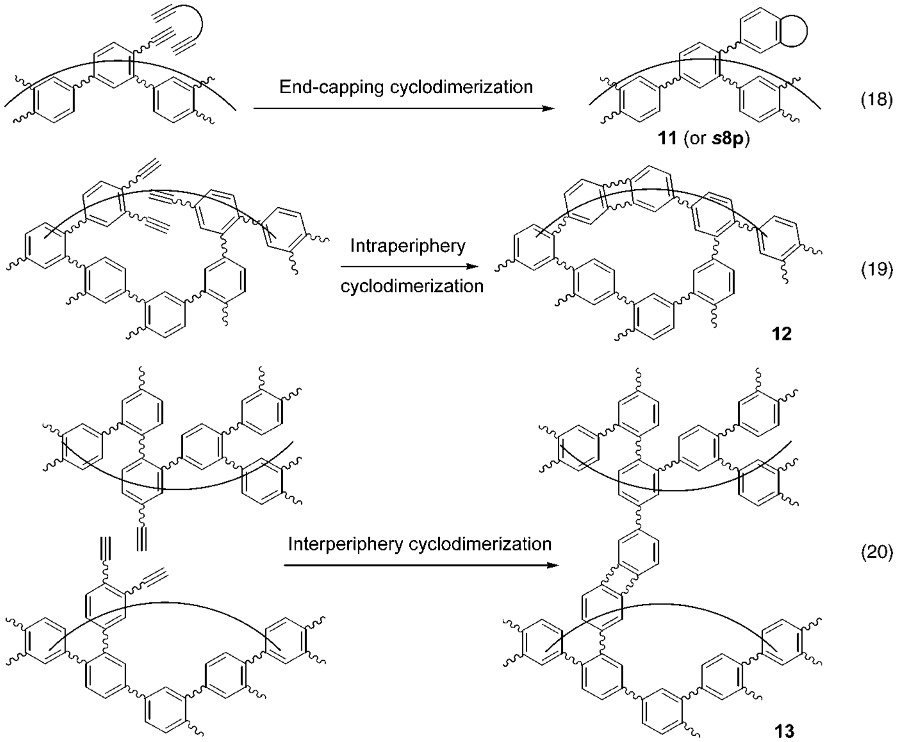
Mechanism. The alkyne cyclotrimerizations catalyzed by late transition-metal complexes have been extensively investigated and the involved reaction mechanisms have been well established.[8,53] Many complexes of late transition metals (Ni, Zn, Rh, Pd, Ru, Co, Ir, etc.) catalyze regioselective cyclotrimerizations of monoynes and diynes.[8,53,54] Although the alkyne cyclotrimerizations catalyzed by early transition-metal compounds have been less studied, highly regioselective systems have been developed.[55] For example, some titanium complexes effectively catalyzed regioselective cyclotrimerizations of terminal alkynes, producing 1,2,4-trisubstituted benzenes in excellent regioselectivities (≥97%) and isolation yields (≥95%).[55a] Phenylacetylene cyclizations catalyzed by $TaCl_5$ and $NbCl_5$ proceeded in a regioselective way, yielding 1,2,4-trisubstituted benzenes in up to 94% selectivity.[25d]

It has been proposed that a Ta-catalyzed alkyne cyclotrimerization involves tantallacyclic intermediates.[25c,25f,27b,56] Our polycyclotrimerization system may have followed the similar reaction pathways with the matallacyclic intermediates acting as initiating and propagating species. An in situ generated Ta(III) species[57,58] may undergo oxidative addition to a diyne monomer (***s*1d**) to form a tantallacyclopropene intermediate ***s*2** (Supporting Information, Scheme *s*1). Insertion of a triple bond of another diyne monomer to ***s*2** gives three possible regioisomers of tantallacyclopentadienes ***s*3**−***s*5**, among which ***s*3** experiences the least steric repulsion from the metal ligands and may be preferentially formed. Addition of a third diyne to ***s*3** can potentially generate two tantallacycloheptatriene isomers and two Diels−Alder adducts of tantallanorbornadienes, each possessing different steric properties but all giving the same product of 1,2,4-trisubstituted benzene ***s*6** through reductive elimination of the metal species. The arene ***s*6** formed during the initiation step will serve as propagating species ***s*1p** to follow the same reaction path of monomer ***s*1d** to grow to a higher generation by forming new 1,2,4-arenes. Iterative repeats of the oxidative addition and reductive elimination cycles in the propagation step will lead to the formation of hyperbranched polyphenylenes.

In Scheme *s*1, only the possibility for one triple bond of a diyne monomer to react with a metal center is considered. As outlined in Scheme *s*2 (Supporting Information), it is possible that through a "backbiting" reaction path, two triple bonds of a same diyne molecule add to a same metal center to form a tantallacyclopentadiene intermediate ***s*7**, further reaction of which with another triple bond would produce benzocycloalkene ***s*8**. When R in ***s*1** is a propagating branch (i.e., ***s*1p**), this reaction will terminate the growth of the branch by endcapping it with a benzocycloalkene ring, as illustrated in eq 18 of Scheme 4. Fortunately, however, this endcapping termination was not so active in our diyne polycyclotrimerization systems, as evidenced by the formation of only a small fraction of the benzocycloalkene structures in the final products. The DC value for polymer **3** was ≤15% (cf., Figure 5). Judging from its higher molecular weights, **4** may have an even lower DC value although it could not be quantitatively evaluated because of the overlapping of the absorption peaks of its cyclic and acyclic benzyl protons (cf., Figure 6). This is probably due to the size effect: the benzocycloalkene in **4**, if formed, is an eight-membered ring, which is less stable and thus more difficult to form, in comparison to the seven-membered ring formed in **3**. When the size of the benzocycloalkene ring was further reduced to five, the formation of high molecular weight polymers became impossible[11d] because of the active termination of the propagating species by the ready formation of stable indan rings.

When a hyperbranched polyphenylene divergently grows to a high generation (or when its degree of polymerization becomes high), the triple-bond functional groups at the propagating front on the outer shell of the dendritic sphere will come to close proximity. As illustrated in Scheme 4, three triple bonds in immediate vicinity on the same periphery shell may form one benzene ring (eq 19), provided that they possess the right configurations and are located in the accessible positions. Such intraperiphery cyclodimerization would terminate the growth of multiple propagation branches, although NMR analyses cannot differentiate the benzene rings formed on the periphery shells by this termination mechanism from those in the spherical cores formed by the propagation reactions. It is possible that the triple bonds on the outer shells of different polymer spheres also come to close contact and cyclodimerize. Such interperiphery cyclodimerization will link two polymer spheres together and generate a new polymer adduct (**13**; eq 20). In the bimodal SEC chromatogram of polymer **4** (cf., Figure 1B), the peak in the higher molecular weight region is probably due to the partial formation of such polymer adducts, which significantly broadens the molecular weight distribution of the polymer, in addition to greatly boosting its average molecular weights. At high monomer concentrations, the chances for the triple bonds on different shells to meet and react will be increased, and network gels would be formed as a result of active interperiphery dimerization. This is indeed the case: we obtained insoluble polymers at high monomer concentrations ($[M]_0 \geq 0.5$ M) for both diynes **1** and **2** (cf., Tables 1 and 2). To reduce the possibility of the undesired interperiphery cyclodimerization, the polycyclotrimerization should be carried out in dilute solutions. The dilution

Scheme 4



should, however, be appropriate, for too low concentrations would, on the other hand, make the polycyclotrimerization reactions ineffective. This thus explains why there exist optimal concentration windows in the diyne polycyclotrimerizations.

Concluding Remarks

In this work, we investigated homopolycyclotrimerizations of two commercially available diynes, 1,8-nonadiyne (**1**) and 1,9-decadiyne (**2**). Our results and findings can be summarized as follows.

(1) $TaCl_5-Ph_4Sn$ was a better catalyst than its counterpart $NbCl_5-Ph_4Sn$. Under similar reaction conditions, the Ta catalyst polymerized the diyne monomers into completely soluble polymers with high molecular weights in high isolation yields, whereas the Nb catalyst gave only partially soluble polymers in rather low yields.

(2) Reaction conditions had profound effects on the diyne polymerizations. (a) For $[M]_0$ and [cat.], too low concentrations made the polymerization ineffective, whereas too high concentrations induced undesirable cross-linking. (b) Room temperature was found to be the best: decreasing the reaction temperature induced cross-linking, but increasing the temperature decreased the molecular weights and isolation yields of the polymers. (c) The polymerization of **2** proceeded rapidly; a long reaction time (>1 h) resulted in the formation of partially soluble polymers, though such implication was not observed in the polymerization of **1**.

(3) Diyne **2** was more reactive than its congener **1**. Under comparable conditions, the polymerizations of **2** consistently gave polymers with higher molecular weights in higher yields. The polymerizations of **2** were very fast and finished in ~10 min. Its polymerization could be initiated at extremely low catalyst concentrations, so low that the polymerization of **1** could not be effectively initiated.

(4) The diyne polymerizations propagated via a polycyclotrimerization mechanism and produced hyperbranched polyphenylenes, as verified by the structural characterizations of the polymeric products. The spectroscopic analyses further identified the benzene rings in the polymers to be 1,2,4-substituted isomers and revealed the regioselective feature of the Ta-catalyzed diyne polymerization reactions.

(5) The hyperbranched polyphenylenes exhibited properties originating from their unique molecular structures. (a) The polymers possessed very high molecular weights but very low intrinsic viscosities, due to their hyperbranched molecular architectures. (b) The polymers showed outstanding thermal stability, thanks to their benzene-based constitutional repeat units. (c) Owing to post-polymerization of its acetylenic periphery ends, **4** cross-linked during storage, which may find uses as thermally curable coating materials.[59] (d) The polymers emitted UV light from the isolated benzene cores, with their photoluminescence behaviors tunable by the change in their molecular structure. (e) The films of the polymers were highly transparent and absorbed almost no visible light. The thin films of **3** displayed an optical dispersion much lower than those of commercially important organic glasses, which may find useful applications as photonic materials in high-tech industries.

The encouraging results of the polycyclotrimerizations of diynes **1** and **2** described above have prompted us to extend our research efforts to the studies on the polycyclotrimerizations of other diyne monomers of different molecular structures with variations in, e.g., spacer lengths (nonconjugated) and functional bridges (conjugated).[60] We are also working on the polycyclotrimerizations of internal diynes.[61] Through the development of functionality-tolerant new catalyst systems,[62] we are further expanding our work and have succeeded in the synthesis of conjugated functional hyperbranched polyarylenes with excellent light-emitting (fluorescence quantum yield up to 98%) and optical-limiting properties (low nonlinear optical limiting thresholds).[63] All these results[60−63] prove that the alkyne polycyclotrimerization is a powerful tool for the design and synthesis of hyperbranched macromolecules with novel architectural structures and unique materials properties. The hyperbranched polymers have nanodimensional molecular sizes and may potentially be used as active nanocomponents in the construction of molecular nanodevices.

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Supporting Information Available: Text giving experimental details and Schemes s1 and s2 showing polymerization mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) According to the source-based nomenclature system, the polymers prepared from the diyne monomers 1,8-nonadiyne (**1**) and 1,9-decadiyne (**2**) may be named as “hyperbranched poly(1,8-nonadiyne)” (**3**) and “hyperbranched poly(1,9-decadiyne)” (**4**), respectively. The polymers may also be regarded as hyperbranched derivatives of polyphenylenes.[2−4] Systematically, however, the polymers may be called as “hyperbranched poly(1,2,4-benzenetriyl-1,5-pentanediyl)” (**3**) and “hyperbranched poly(1,2,4-benzenetriyl-1,6-hexanediyl)” (**4**), following the nomenclature system proposed for the constitutional repeating units of hyperbranched polymers by the Nomenclature Committee of the Division of Polymer Chemistry of the American Chemical Society.[5.]

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