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Controlled Synthesis of Hyperbranched Polymers by Slow Monomer Addition to a Core

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ABSTRACT: Continuous, slow addition of AB_2 monomer (3,5-diiodophenylacetylene) to a solution of a multifunctional core results in high molecular weight hyperbranched phenylacetylene polymers with narrow polydispersites. Control over the molecular weight ($M_w = 8-90$ kDa) was achieved by varying the monomer:core ratio from 17.5 to 560. At low ratios (<140, $M_w = 49$ kDa), monomodal molecular weight distributions were observed by SEC. A bimodal distribution was observed at higher ratios. Using an azobenzene functionalized core, in combination with SEC photodiode array detection, it was found that the core was not uniformly distributed over the entire bimodal distribution but rather predominantly found in the high molecular weight part of the distribution. The polydispersities of the hyperbranched polymers were found to decrease with increasing degree of polymerization and with increasing core functionality. Our experimental results are in good qualitative agreement with computer simulations reported by Frey et al. and the theoretical work of Müller.

Introduction

Hyperbranched polymers (HBPs) and dendrimers are highly branched macromolecules that have received considerable attention.[1−5] Though these two macromolecules share many architectural similarities such as multiple terminal groups and globular shape, they differ in their method of preparation. Perfectly branched dendrimers are synthesized by multistep reactions requiring time-consuming purification, whereas hyperbranched polymers are prepared by one-step polymerization resulting in less regular structures. An undesirable feature of the one-step polymerization is the loss of control in molecular weight, accompanied by broad molecular weight distributions[6] and possible intramolecular cyclization.[7,8]

A challenging goal is the development of general AB_2 polymerization methods that achieve control over molecular weight and narrow molecular weight distributions. Recently, Frey et al.,[9] in their computer simulation work, and Müller,[10] by theoretical calculations, have shown that the introduction of multifunctional B_f core molecules in the hyperbranched polymerization process narrows polydispersites. Experimental efforts have also been made in an attempt to narrow molecular weight distributions. Fréchet et al.[11] reported that slow monomer addition (without core molecules) did not produce any change in molecular weights of polyether HBPs. Very recently, Frey et al.[12] reported a slow monomer addition technique in the preparation of hyperbranched polyglycerols by ring-opening polymerization using a core initiator. The degree of polymerization was reported in the range 15−85, leading to molecular weights (M_n) of 1.25−6.5 kDa with polydispersities of 1.13−1.47. Fréchet et al. also prepared hyperbranched poly(siloxysilane)s in a controlled fashion using various monomer addition strategies.[8] Molecular weights (M_w) of 6−86 kDa were obtained with polydispersities of 2−15 in the slow addition process, and both the narrowness of the distribution and the average molecular weight could be controlled by changing the rate of addition and the amount of AB_2 monomer added. A similar trend was observed in seeded polymerization whereas the single-batch bulk polymerization resulted in low molecular weight polymers ($M_w = 5$ kDa, PDI = 2.2), presumably because of the intramolecular hydrosilylation.

We recently reported the solid-supported hyperbranched polymerization of phenylacetylene HBPs by slow monomer addition.[13] Narrow polydispersities and control over the molecular weight were obtained from the support grown polymerization. We also found that the polymers not bound to the support had a bimodal distribution consisting of a narrow, high molecular weight peak and a broad, long tail on the lower molecular end. The growth of the polymer bound to the support was limited by the nature of the support (e.g., cross-link density, loading). We speculated that these limitations could be overcome by carrying out the polymerization on nonsupported core molecules in solution. Therefore, to achieve high molecular weight hyperbranched polymers with molecular weight control and narrow polydispersities, systematic studies were performed in solution using slow monomer addition in the presence of core molecules. The results of these studies are detailed here.[14] These HBPs have interesting properties as precursors to amorphous carbon materials and as a dry release layers for MEMS fabrication.[15]

Experimental Section

Size exclusion chromatography (SEC) was performed in THF at 25 °C with a Waters 515 pump together with a Viscotek HR 40 refractive index detector and a Viscotek T60A dual light scattering and differential pressure viscometer. Three Viscogel 7.8 × 300 mm columns (one of GM HXL X2 and two of G3000HXL) were connected in series, calibrated with narrow molecular weight polystyrene standards over the range $(1.1-4.5) \times 10^3$ kDa with a column exclusion limit of 1×10^6 kDa. Data analyses were performed using Viscotek TriSEC software. MALDI-TOF spectra were obtained using a PerSeptive Biosystems Voyager-DE STR mass spectrometer

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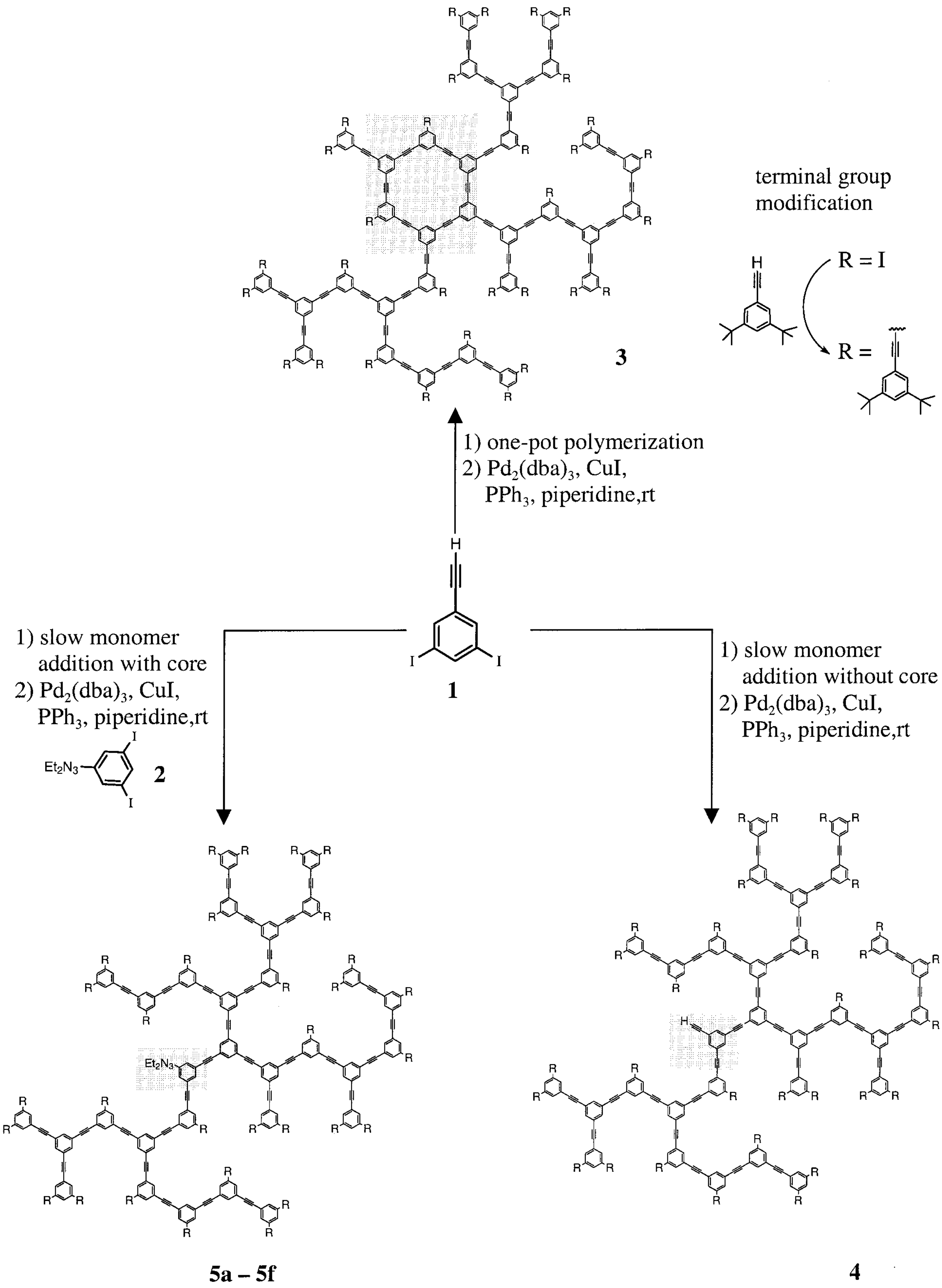

Figure 1. Schematic representation of hyperbranched phenylacetylene polymers prepared by three different methods.

using a dithernol/silver adduct as the matrix.[16] ^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity 400 MHz spectrometer using residual proton from the solvent as reference. All starting materials were obtained from commercial suppliers and were used without further purification. 1-(3,5-Diiodophenyl)-3,3-diethyltriazene (**2**) was prepared according to a literature procedure[17] from 3,5-diiodoaniline and diethylamine. 3,5-Di-*tert*-butylphenylacetylene,[17] 4,4′-diiodoazobenzene[18] (**6**), and 4-iodoazobenzene[19] (**8**) were prepared following the reported procedures. The B$_2$ (**9**) and B$_4$ (**10**) core molecules were prepared following the etherification procedure reported[20] by Fréchet et al. by refluxing the corresponding benzyl bromides with 4-hydroxyazobenzene in acetone and K_2CO_3.

3,5-Diiodophenylacetylene (1). A heavy-walled flask was charged with 1,3,5-triiodobenzene[21] (17.54 mmol, 8.0 g), $Pd_2(dba)_3$ (0.01 equiv, 80.3 mg), copper(I) iodide (0.01 equiv, 33.4 mg), and triphenylphosphine (0.05 equiv, 230 mg). The flask was degassed and back-filled with nitrogen three times. Next, degassed piperidine (60 mL) and 2-methyl-3-butyn-2-ol (15.0 mmol, 1.45 mL) were added. After stirring the mixture at room temperature for 1 h, water (300 mL) was added, and the resulting mixture was extracted with dichloromethane (3 × 50 mL). The solvent was evaporated, and the crude mixture was purified by column chromatography (4% EtOAc−hexane) to afford 1-(3-hydroxy-3-methyl-1-butynyl)-3,5-diiodobenzene (**7**) as a white solid (4.4 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (t, 1H, J = 1.4 Hz), 7.70 (d, 2H, J = 1.4 Hz), 1.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.80, 139.35, 126.23, 96.28, 93.98, 65.50, 31.24. This 1-(3-hydroxy-3-methyl-1-butynyl)-3,5-diiodobenzene (2.4 mmol, 1 g) was dissolved in toluene (50 mL) containing KOH (2.4 mmol, 130 mg) and methanol (40 mL) in a round-bottom flask equipped with a Dean−Stark trap fitted with a reflux condenser. The mixture was heated at 110 °C for 1.5 h, cooled to room temperature, washed with water, dried ($MgSO_4$), filtered, and concentrated. The resulting solution was passed through a short silica gel column eluting with hexane to give 3,5-diiodophenylacetylene (**1**) as a white powder in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (t, J = 1.7 Hz, 1H), 7.76 (d, J = 1.5 Hz, 2H), 3.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.48, 139.84, 125.59, 94.02, 80.19, 79.78. Anal. Calcd for $C_8H_4I_2$: C, 27.15; H, 1.14. Found: C, 27.17; H, 1.12.

General Procedure for the Hyperbranched Polymerization. A heavy-walled flask was charged with corresponding core molecule, $Pd_2(dba)_3$ (0.2 equiv), copper(I) iodide (0.2 equiv), and triphenylphosphine (0.1 equiv). The flask was degassed and back-filled with nitrogen three times. Degassed piperidine (2 mL) was added, and the resulting mixture was stirred for 10 min at room temperature. A solution of 3,5-diiodophenylacetylene (**1**) in degassed piperidine (155 mM) was added by syringe pump at a rate of addition 1.7 mL/h. After the addition, stirring was continued for another 5 h, and 3,5-di-*tert*-butylphenylacetylene (2 equiv based on **1**) was added under nitrogen. After stirring for 12 h at room temperature, piperidine was removed in vacuo. The semisolid was dissolved in methylene chloride and precipitated in a 20-fold volume of methanol. The white polymer precipitate was collected by vacuum filtration on 45 μm filter paper.

Results and Discussion

Three different routes to phenylacetylene HBPs are shown in Figure 1. The first is the one-pot polymerization process where 3,5-diiodophenylacetylene, **1** (AB_2 monomer), is added all at once to the catalyst solution ($Pd_2(dba)_3$), in piperidine at room temperature. The second and third approaches both involve slow monomer addition, differing by the absence or presence of **2**, a multifunctional core (B_f).

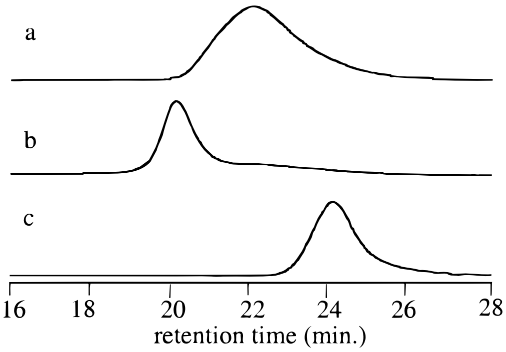

Figure 2. SEC traces of HBPs: (a) one-pot polymerization having M_w = 35.3 kDa, PDI = 2.4; (b) slow monomer addition without core M_w = 490 kDa, PDI = 33.3; (c) slow monomer addition in the presence of core (monomer:core ratio = 17.5) M_w = 8.2 kDa and PDI = 1.28.

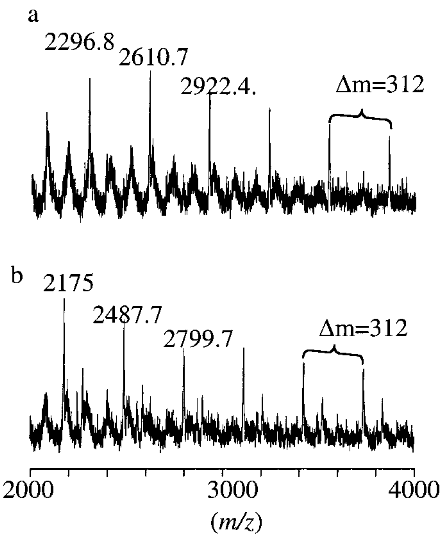

Figure 3. MALDI-TOF mass spectra of the hyperbranched phenylacetylene polymers. Mass spectra of the polymer obtained (a) one-pot polymerization of AB_2 monomer, HBP **3**, and (b) via core with slow monomer addition at monomer:core ratio of 17.5: 1 (**5a**). See Table 1 for detailed analysis.

Table 1. MALDI-TOF *m/z* Data of Hyperbranched Phenylacetylene Polymer

	calculated[a]			observed	
	acyclic				
n	no core	core	cyclic	one-pot[b]	slow addition[c]
5	2089	2164	1875	1978	2175
6	2401	2476	2187	2297	2488
7	2714	2789	2499	2611	2800
8	3026	3101	2812	2922	3112
9	3339	3414	3124	3235	3426
10	3651	3726	3437	3548	3737

[a] Molecular mass calculated according to eq 1. [b] *m/z* data of HBPs by one-pot synthesis. The *m/z* were observed as their silver cations. [c] *m/z* data of HBP **5a**, monomer:core ratio of 17.5 equiv by slow monomer addition method.

The one-pot approach results in an insoluble material with aryl iodides as the terminal group. From our earlier findings[22] terminal group modification is necessary to solublize the resulting HBP. Therefore, a large excess of 3,5-di-*tert*-butylphenylacetylene (capping monomer) is added in the same reaction flask once all the monomer is consumed. After the capping reaction is complete, piperidine is removed and the product recovered by precipitation into methanol, yielding soluble hyperbranched polymer **3**. From SEC the weight-average molecular weight (M_w) of the polymer prepared by the one-pot method is typically around 35 kDa with a polydispersity near 2 (Figure 2a).[23] An important side reaction is likely to be intramolecular cyclization which would thus terminate the polymerization by eliminating the focal point functional group. Evidence for cyclization was obtained by MALDI-TOF mass spectrometry as shown in Figure 3a and Table 1. The *m/z* values were compared to possible products, and they most closely matched that of the cyclic. It should be noted that the most intense peaks for polymer **3** (cyclized) appear as silver adducts. Given that the cyclization reaction is occurring, a reasonable approach to sustain the growth would be to add the AB_2 monomer slowly to the catalyst solution.

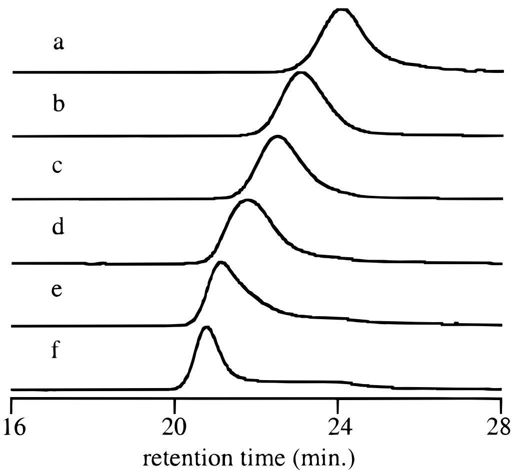

Figure 4. Size exclusion chromatograms of hyperbranched phenylacetylene polymers via core with slow monomer addition. The traces are from refractive index detector. The monomer:core ratios are (a) 17.5:1 (**5a**), (b) 35:1 (**5b**), (c) 70:1 (**5c**), (d) 140:1 (**5d**), (e) 280:1 (**5e**), and (f) 560:1 (**5f**).

Table 2. Molecular Weight and Polydispersity Data of HBPs; Effect of Monomer:Core Ratio

		SEC[b]		calibration against monodendrons[c]	
monomer:core (molar ratio) (HBP)	calcd mol wt[a] (kDa)	M_w (kDa)	PDI	M_w (kDa)	PDI
17.5 (**5a**)	6.08	8.22	1.3	10.1	1.1
35 (**5b**)	11.5	16.9	1.3	20.7	1.2
70 (**5c**)	22.5	28.9	1.3	35.5	1.2
140 (**5d**)	44.4	49.1	1.7	60.5	1.4
280 (**5e**)	88.1	72.4	2.9	89.5	2.2
560 (**5f**)	175.5	90.6	8.5 (1.2)[d]	115.9	3.4

[a] Calculated according to eq 1. [b] Calibration of SEC with narrow molecular weight polystyrene standards. [c] Calibrated against phenylacetylene monodendron prepared by the convergent method. The monodendron of molecular weight 2.5 kDa was used and the other monodendrons 0.6–10 kDa were measured for verification. [d] Polydispersity of narrow high molecular weight peak (Figure 4, trace f).

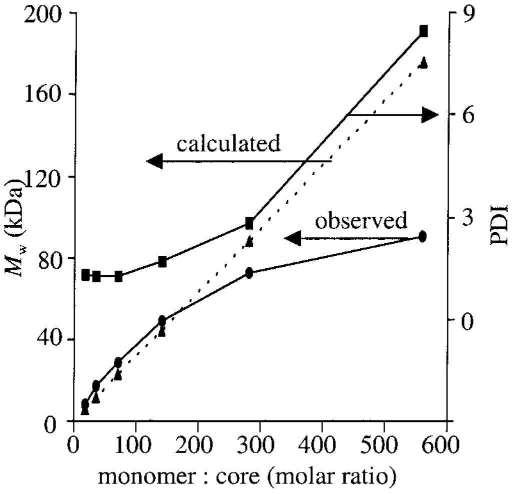

Figure 5. Plots showing the observed and calculated molecular weights and PDI of the hyperbranched polymers versus monomer:core ratio: (●) observed M_w of HBPs; (▲) calculated molecular weight of HBPs using eq 1; (■) observed PDI of HBPs.

Continuous, dropwise addition of 3,5-diiodophenylacetylene, **1** (AB_2 monomer), in piperidine to the catalyst solution without core, followed by the capping reaction, resulted in soluble HBP **4**. This polymer had a bimodal SEC profile consisting of a narrow high molecular weight peak and a broad tail on the low molecular side of the distribution $M_w = 490$ kDa and PDI = 33 (Figure 2b). Thus, slow addition of AB_2 monomer leads to high molecular weight polymers with large polydispersities. Theoretical work[9] as well as computer simulations[10] has shown that the introduction of B_f core molecules in the synthesis of hyperbranched polymers considerably lowers polydispersities. Accordingly, when the slow monomer addition was carried out in the presence of a B_2 core molecules (1-(3,5-diiodophenyl)-3,3-diethyltriazene, **2**, monomer:core ratio 17.5) in piperidine, a soluble hyperbranched polymer **5a** was obtained after the capping reaction. The SEC profile of this HBP was monomodal with $M_w = 8.2$ kDa and PDI = 1.28 (Figure 2c). Thus, the presence of B_f core molecules considerably lowers the polydispersity of a slow addition process.

To characterize the structure of the resulting HBPs (i.e., the incorporation of the core molecule, the terminal group modification, and the extent of cyclization), MALDI-TOF mass spectrometry was performed. Figure 3b shows the MALDI spectrum of the hyperbranched polymer **5a** obtained by the core/slow addition method. The peak molecular weight of the polymer can be calculated according to eq 1

$$[M_f + nM_b + (n + 2)M_c] \qquad (1)$$

where f, b, and c represent the focal point, branching, and capping monomers, respectively, and *n* is degree of polymerization or monomer:core ratio. As seen from the spectrum, the mass difference between peaks (312 amu) is the sum of mass of repeating branching and capping monomer. The observed and the calculated peaks differ by about 11 amu (Table 1) which we are unable to account for at this time. Attempts were made to fit the observed molecular weights to different possible side reactions including protonation, unreacted iodo groups, and cyclization with and without silver attached. None of these side products had masses that agreed with those observed by MALDI. The presence of only one main type of MALDI peak suggests, in close agreement with the expected mass, that polymerization is taking place on the core molecules; i.e., core is incorporated, and terminal group modification is complete. In great contrast to the products from the slow addition process, polymer **3** obtained from one-pot polymerization revealed the presence of cyclized products (Figure 3a).

By varying the monomer:core ratio, it was possible to systematically obtain HBPs of different molecular weight (**5a**–**5f**). Figure 4 shows SEC profiles of **5a**–**5f** obtained with increasing monomer:core ratios. The SEC data were calibrated by polystyrene standards and also with phenylacetylene monodendrons prepared by a convergent synthesis method (Table 2). Surprisingly, the observed molecular weights are much closer to calculated values using the polystyrene calibration method than using monodendron for calibration. Polymers of molecular weight 8–90 kDa were obtained with monomer:core ratios of 17.5–560. As seen from the SEC profiles (a–f, Figure 4), monomodal distributions were observed at low monomer:core ratios. As this ratio increases, a bimodal molecular weight distribution was observed consisting of a sharp peak at high molecular

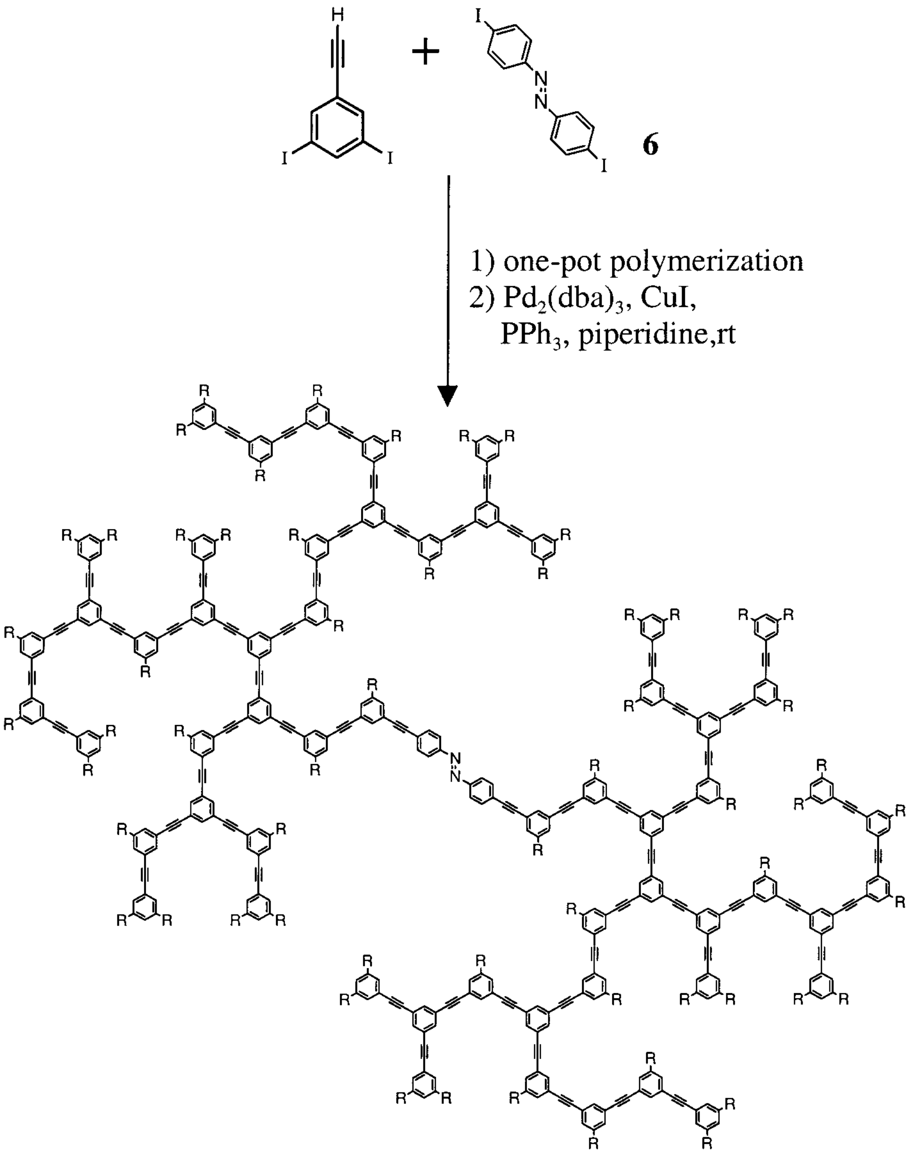

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Figure 6. Hyperbranched polymer obtained with azo chromophore as the core molecule.

weight and a broad tail at low molecular weights. The bimodal molecular weight distribution is most prominent in trace f. Thus, integrating over the entire chromatogram, the polydispersity of (a)–(c) were nearly constant but increased thereafter with increasing degree of polymerization. However, the polydispersity of the (deconvoluted) narrow high molecular weight peak alone was found to be ca. 1.2 for sample **5f**. No efforts were made to minimize the broad tail of the molecular weight distribution at high monomer:core ratio. Further optimization by variation of the rate of monomer addition or monomer concentration may be possible.

Plots of observed and calculated molecular weights versus monomer:core ratios are shown in Figure 5. At low ratios the observed molecular weight is slightly higher than the calculated values. A slight negative deviation from calculated value was observed at 140 monomer equiv, and this deviation increases at higher monomer:core ratios. The deviation might be due to deactivation of the terminal acetylene (e.g., oxidative dimerization) during the course of the polymerization, thus enabling growth of new polymers from freshly added monomer (vide infra).

At higher monomer:core ratios, a bimodal distribution was observed. It is thought that the low molecular weight distribution comes from the self-polymerization of added AB_2 monomer. To examine whether the core molecule is bound to both peaks of the bimodal distribution, the polymerization was carried out with a core molecule having a 4,4′-diiodoazobenzene chromophore (**6**) as shown in Figure 6. This chromophore has an absorption maximum at 384 nm.[24] Polymerization using a monomer:core ratio of 560 resulted in hyperbranched polymer **7** having a bimodal distribution similar to the one obtained before. The SEC trace of this HBP is shown in Figure 7a. Since the azo groups have UV absorption, the different segments of the chromatogram were examined using a photodiode array detector coupled to the SEC. The normalized UV absorption spectra of high molecular weight (region I) and low molecular weight (region II) are shown in the inset (Figure 7b,c). The absorption maxima at 293 and 307 nm are characteristic of phenylacetylene moieties, which are present in both high and low molecular weight fractions. Only the high molecular weight part of the distribution (region I) showed an absorption maximum at 384 nm. This

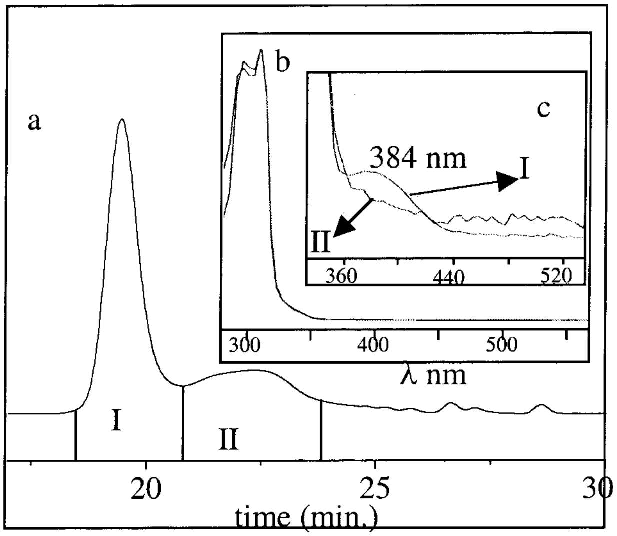

Figure 7. (a) SEC trace of the hyperbranched polymer **7** with monomer:core ratio of 560:1, using 4,4′-diiodoazobenzene as the core. The chromatogram shown was obtained using a UV detector. (b) Normalized UV spectra of regions I and II of the chromatogram using photodiode array detector. The spectra are normalized to a constant absorbance at the wavelength 307 nm. (c) Expanded UV spectra to show the presence of azo chromophore as indicated by absorption at 384 nm in region I.

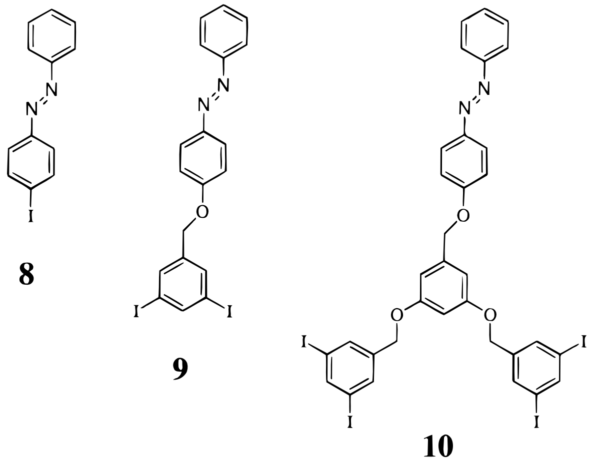

Figure 8. Core molecules with core multiplicity of 1, 2, and 4.

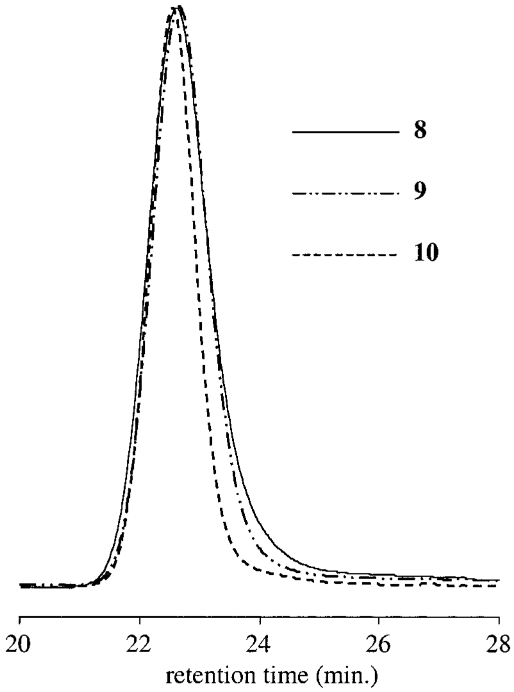

Figure 9. Size exclusion chromatograms of the hyperbranched polymers obtained using core molecules **8**, **9**, and **10** with a monomer:core ratio of 70 (refractive index detector). As the core functionality increases, the molecular distribution becomes narrower and the peaks are more symmetrical.

Table 3. SEC Analysis of Molecular Weights; Effect of Core Functionality[a]

core functionality (f)[b]	calcd PDI[c]	SEC[d] M_w (kDa)	SEC[d] PDI
1 (**8**)	2.0	23.5	1.5
2 (**9**)	1.5	21.9	1.3
4 (**10**)	1.3	24.7	1.2

[a] Polymers obtained from monomer:core ratio of 70. [b] Representative core molecules are shown in Figure 8. [c] Calculated using eq 2. [d] Calibration of SEC with narrow molecular weight polystyrene standards.

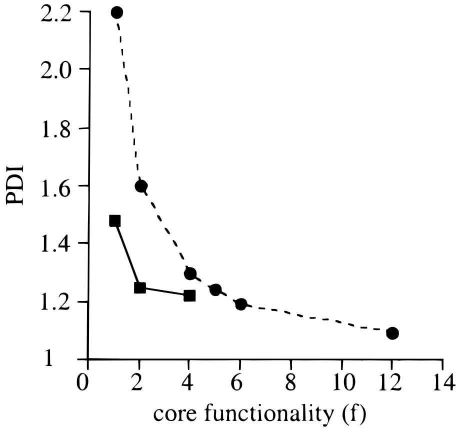

Figure 10. Plots showing a comparison of experimental and theoretical polydispersities as a function of core multiplicity. The dashed curve is generated from eq 2, and the solid line is the experimental results.

absorption was absent in the low molecular weight distribution (region II) as seen in Figure 7c. From this experiment, it is clear that the core molecule is not uniformly distributed over the entire molecular weight distribution. Attempts to separate low and high molecular weight polymers (using analytical and preparative SEC) were not successful.

These experimental results are in good qualitative agreement with the computer simulation results reported by Frey et al.[9b] According to their findings, in an ideal case where all "A" functional groups react equally and no cyclization takes place, the HBP molecular weight increases with increasing degree of polymerization. The polydispersity initially increases, reaches a maximum, and then decreases with increasing degree of polymerization to a limiting value. The polydispersity also decreases with increasing core functionality. In nonideal cases where the focal point is deactivated by a side reaction, new polymer molecules start growing, leading to a bimodal distribution at the higher degree of polymerization. Our experimental results imply that low monomer:core ratios (i.e., up to 70 equiv) represent a near ideal case whereas higher ratios (280, 560 equiv) represent the nonideal case. It should be noted that we have not performed extensive optimization studies on addition rate and concentration in an effort to improve this process.

According to the computer simulations reported by Frey et al., the polydispersity of the hyperbranched polymer decreases with increasing core functionality. To demonstrate this effect, core molecules **8**−**10** with iodide functionality 1, 2, and 4 were chosen as shown in Figure 8. The polymerization of the AB_2 monomer with these core molecules was performed by the slow monomer addition method. A monomer:core ratio of 70 was employed as it resulted in monomodal distribution of molecular weight as discussed earlier. The SEC profiles of these hyperbranched polymers are shown in Figure 9, and the data of the polymers are collected in Table 3. As seen from the chromatograms, the low molecular weight tail decreases, making the chromatogram more symmetrical at higher core functionalities. As a result, the polydispersity decreases from 1.5 to 1.2 as the core functionality increases from 1 to 4. Figure 10 shows plots of the polydispersities with increasing core functionality. The decrease in polydispersity is in qualitative agreement with the expression[25]

$$\mathrm{PDI} = 1 + 1/f \qquad (2)$$

reached by Frey et al. in their computer simulations.

Conclusions

Control over molecular weight of hyperbranched phenylacetylene polymers was obtained by slowly adding the AB_2 monomer to a multifunctional core molecule and by varying the monomer:core ratio. Narrow polydispersities as low as 1.2 were achieved by this method. MALDI analysis showed that terminal group modification was complete and that cyclization was only significant for the one-pot method. The molecular weight distribution was observed to change from monomodal to bimodal by increasing the monomer:core ratio. We were able to demonstrate that the core molecule is not uniformly distributed over the entire bimodal molecular distribution, consistent with competing self-polymerization of AB_2 monomers. The polydispersity of the HBP was found to decrease with increasing core functionality. The experimental results obtained by slow monomer addition method are in good qualitative agreement with predictions from theoretical analysis and computer simulations.

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