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Control of Molecular Weight and Polydispersity of Hyperbranched Polymers Using a Reactive B_3 Core: A Single-Step Route to Orthogonally Functionalizable Hyperbranched Polymers

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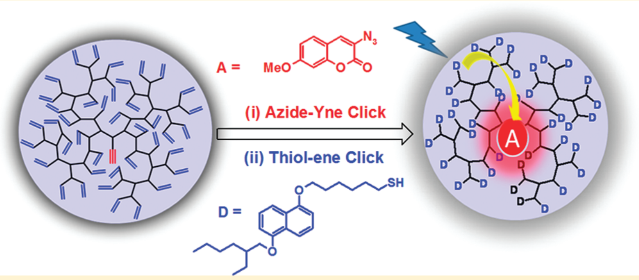
Supporting Information



ABSTRACT: Molecular weight and polydispersity are two structural features of hyperbranched polymers that are difficult to control because of the statistical nature of the step-growth polycondensation of AB_2 type monomers; the statistical growth also causes the polydispersity index to increase with percent conversion (or molecular weight). We demonstrate that using controlled amounts of a specifically designed B_3 core, containing B-type functionality that are more reactive than those present in the AB_2 monomer, both the molecular weight and the polydispersity can be readily controlled; the PDI was shown to improve with increasing mole-fraction of the B_3 core while the polymer molecular weight showed an expected decrease. Incorporation of a "clickable" propargyl group in the B_3 core unit permitted the generation of a core-functionalizable hyperbranched polymer. Importantly, this clickable core, in combination with a recently developed AB_2 monomer, wherein the B-type groups are allyl ethers and A is an hydroxyl group, led to the generation of a *hyperbranched polymer carrying orthogonally functionalizable core and peripheral groups, via a single-step melt polycondensation*. Selective functionalization of the core and periphery using two different types of chromophores was achieved, and the occurrence of fluorescence resonance energy transfer (FRET) between the donor and acceptor chromophores was demonstrated.

INTRODUCTION

Hyperbranched polymers are often prepared by the self-condensation polymerization of a suitably designed AB_2 monomer. Despite the ease of its synthesis, several structural features of hyperbranched polymers cannot be readily controlled, unlike in the case of its main rival, namely dendrimers. Among the structural imperfections present in hyperbranched polymers, the important ones are as follows: imprecise control over molecular weight, high polydispersity, absence of a well-defined core, and finally the presence of a large number of linear defects.[1] While the functional ramifications of these structural imperfections on the properties and utility of hyperbranched polymers may not be as severe as was initially perceived, it would still be desirable to develop simple approaches to minimize these imperfections. Some years ago, Frey and others demonstrated that use of a polyfunctional core, in conjunction with slow monomer-addition, can generate hyperbranched polymers with good control over both the molecular weight and defect levels.[2] This approach works best when the polymerization rate is reasonably fast, such that most of the monomer is rapidly consumed as the slow addition is in progress. An alternate approach was developed by Fossum and co-workers for the preparation of poly(arylene ether phosphine oxide)s, wherein a B_3 core that bears more reactive B groups was condensed with an AB_2 monomer in a single step to yield polymers with significantly improved molecular weight and polydispersity;[3] the theoretical basis for the use of such reactive polyfunctional cores in regulating the molecular weight and polydispersity of hyperbranched polymers was described a few years earlier.[4] Bharathi and Moore, on the other hand, developed a solid-phase supported synthesis to regulate the molecular weight and PDI of hyperbranched polymers.[5] Very recently, Yokozawa and co-workers extended their interesting pseudochain growth condensation polymerization approach for the preparation of hyperbranched polymers with very good control over both molecular weight and PDI; this approach, however, may be applicable only to certain classes of polymers.[6]

Over a decade ago, we developed a novel melt-condensation technique for the preparation of linear[7] and hyperbranched polyethers[8] that proceeds via a trans-etherification process. This process occurs via the condensation of a benzyl methyl ether moiety with a hydroxyl group, in the presence of an acid catalyst, with the liberation of methanol. The equilibrium is driven to polymer formation by continuous removal of low-boiling methanol, which in turn makes this process a completely reversible one. Thus, the AB_2 monomer (**I**) (see Figure 1), which is prepared from Mesitol in three steps,[9] self-condenses to generate hyperbranched

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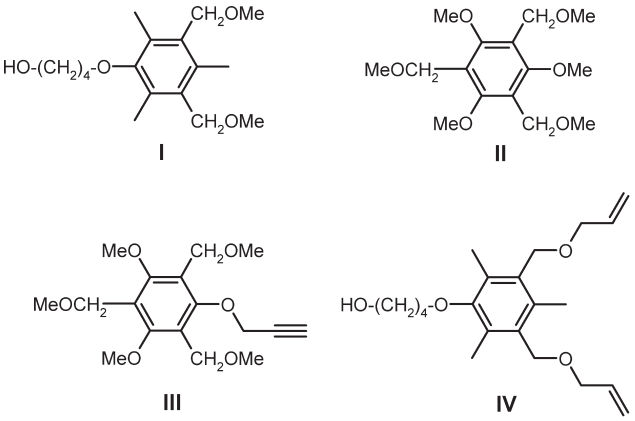


Figure 1. Structures of monomers and core molecules.

polyethers of moderately high molecular weights, although with high polydispersity. In an effort to regulate the polymerization process, we have designed a B_3 core (**II**) starting from 1,3,5-trimethoxybenzene; the presence of the three methoxy groups on the aromatic ring should render it more susceptible to the acid-catalyzed trans-etherification process than the AB_2 monomer.

In this report, we explore the utility of this specifically designed B_3 core (**II**) to regulate the molecular weight and polydispersity of hyperbranched polyethers prepared using monomer **I**. Furthermore, we designed an alternate core (**III**), wherein one of the methoxy groups on the aromatic ring was replaced by a propargyloxy group; this permitted us to incorporate a single "clickable" unit at the core of the hyperbranched structure. A similar idea of functionalizing the core of hyperbranched polymers using a comonomer carrying a labile functionality that could be later transformed as desired was demonstrated by Twyman and co-workers.[10] Finally,

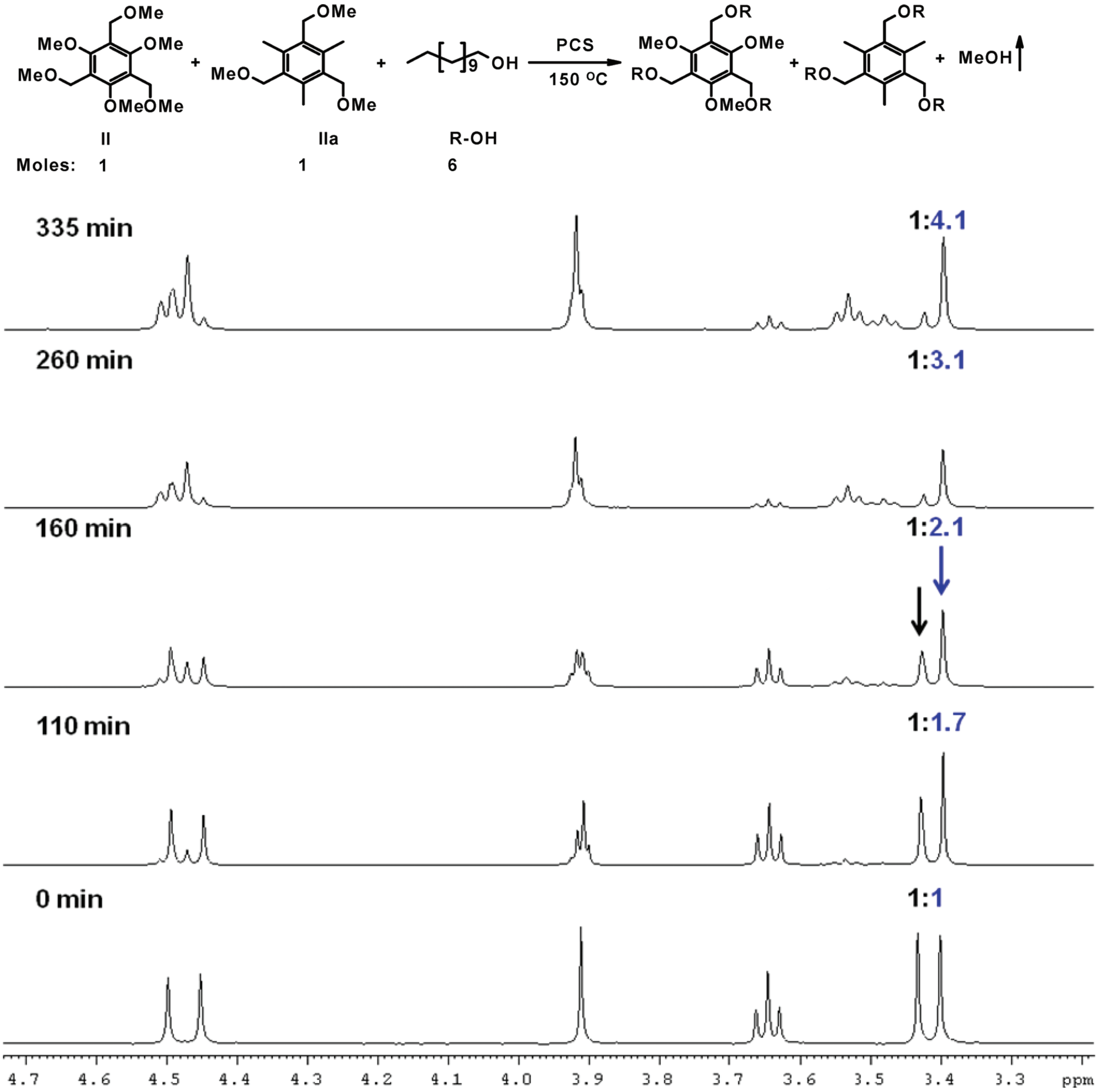


Figure 2. Variation of ^{1}H NMR spectra of the reaction mixture (only the relevant region is shown) as a function of time, during the competitive trans-etherification of the two cores **II** and **IIa** with dodecanol. The peaks marked by arrows are due to the methoxy protons ($\mathbf{CH_3}OCH_2Ph$) belonging to the two cores, and the numbers above reflect their intensity ratios.

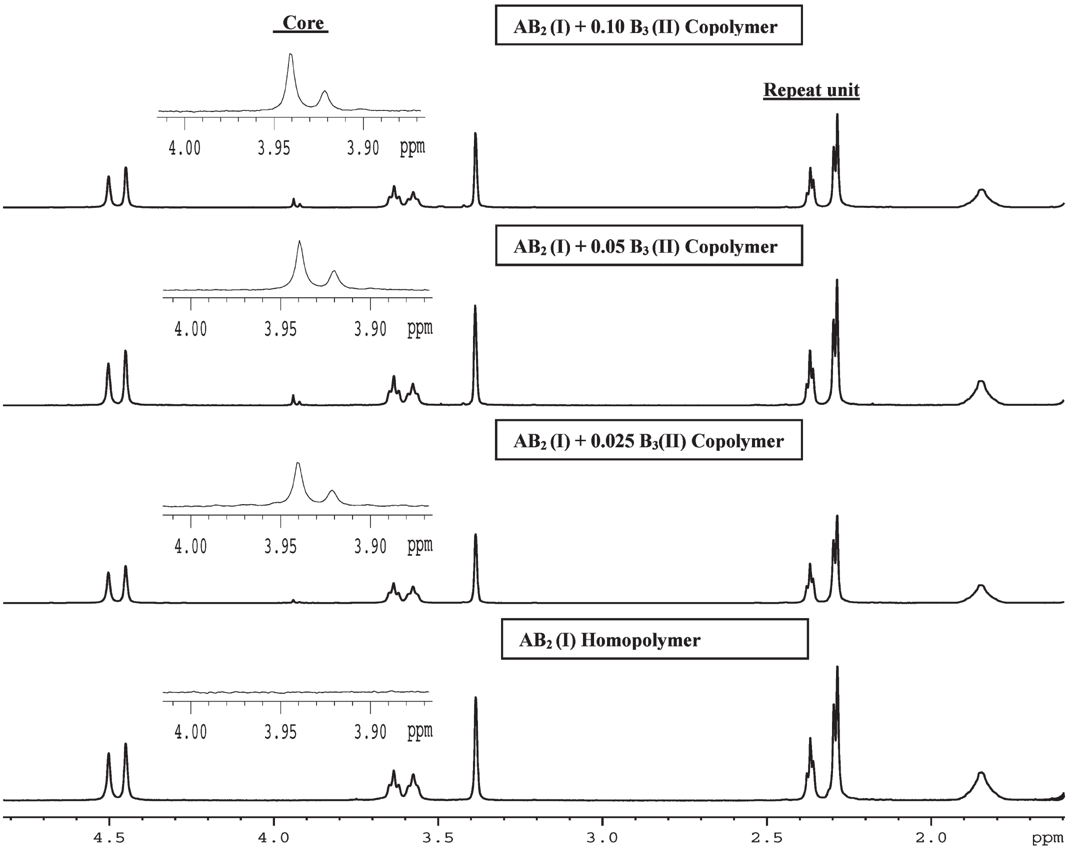


Figure 3. ^{1}H NMR spectra of the hyperbranched homopolymer, along with those of the copolymers using various mole-fractions of the B_3 core **II**. The expanded region shows the peaks corresponding to the methoxy protons (CH_3OPh) linked directly to the aromatic core.

Table 1. Synthesis, Composition, and Molecular Weights of Core-Containing HBPs

polymer	mol % of core in the feed	mol % of core incorporated	yield (%)	M_n(NMR)	M_n(GPC)	PDI	DP$_n$(GPC)
A	0.0	0.0	89	-	9300	2.78	35
B	2.5	2.0	86	13700	10100	2.58	38
C	5.0	4.1	78	6800	8100	2.22	30
D	10.0	6.0	65	4900	5400	1.46	20

using the core molecule **III**, along with a recently reported AB_2 monomer (**IV**),[11] we synthesized hyperbranched polyethers that carry a single propargyl group at the core and numerous peripheral allyl groups; this permitted the orthogonal functionalization of the core and periphery using the azide−yne and thiol−ene click reactions, respectively.

■ RESULTS AND DISCUSSION

Design and Reactivity of the Core. The B_3 core was prepared in two steps starting from 1,3,5-trimethoxybenzene; exhaustive bromomethylation followed by treatment of the tris-bromomethyl product with sodium methoxide in refluxing methanol yielded the desired product in good yields. The AB_2 monomer (**I**), bearing a C4 spacer, was selected for this study; this was prepared using a procedure that was reported earlier.[12] On the basis of the structures of the core molecule **II** and the monomer **I**, it may be expected that the acid-catalyzed trans-etherification process would occur more rapidly with the methoxymethyl groups in core **II**, when compared to those in monomer **I**; this is because the incipient positive charge that develops at the benzylic position during the acid-catalyzed polymerization would be significantly more stabilized by the three methoxy substitutents on the aromatic ring of the core. In order to compare the relative ease of displacement of the methoxy groups in the core **II** versus the AB_2 monomer, a model B_3 core, namely trimethoxymethyl mesitylene, (**IIa**; see Figure 2) with roughly similar electronic effects as those present in the monomer was prepared from mesitylene. In a control experiment, equal moles of both these cores, **II** and **IIa**, were reacted with the required amount of dodecanol (a high boiling alcohol) at 150 °C, in the presence of pyridinium camphor sulfonate (PCS) as the catalyst; the conditions were chosen to be identical to those during a typical melt polymerization. A stack plot of the variation of the ^{1}H NMR spectra of the reaction mixture as a function of reaction time is shown in Figure 2. Since the two cores exhibit distinct peaks corresponding to the methoxy (CH_3OCH_2Ph) protons (at 3.40 and 3.43 ppm) and the benzylic (CH_3OCH_2Ph) protons (4.45

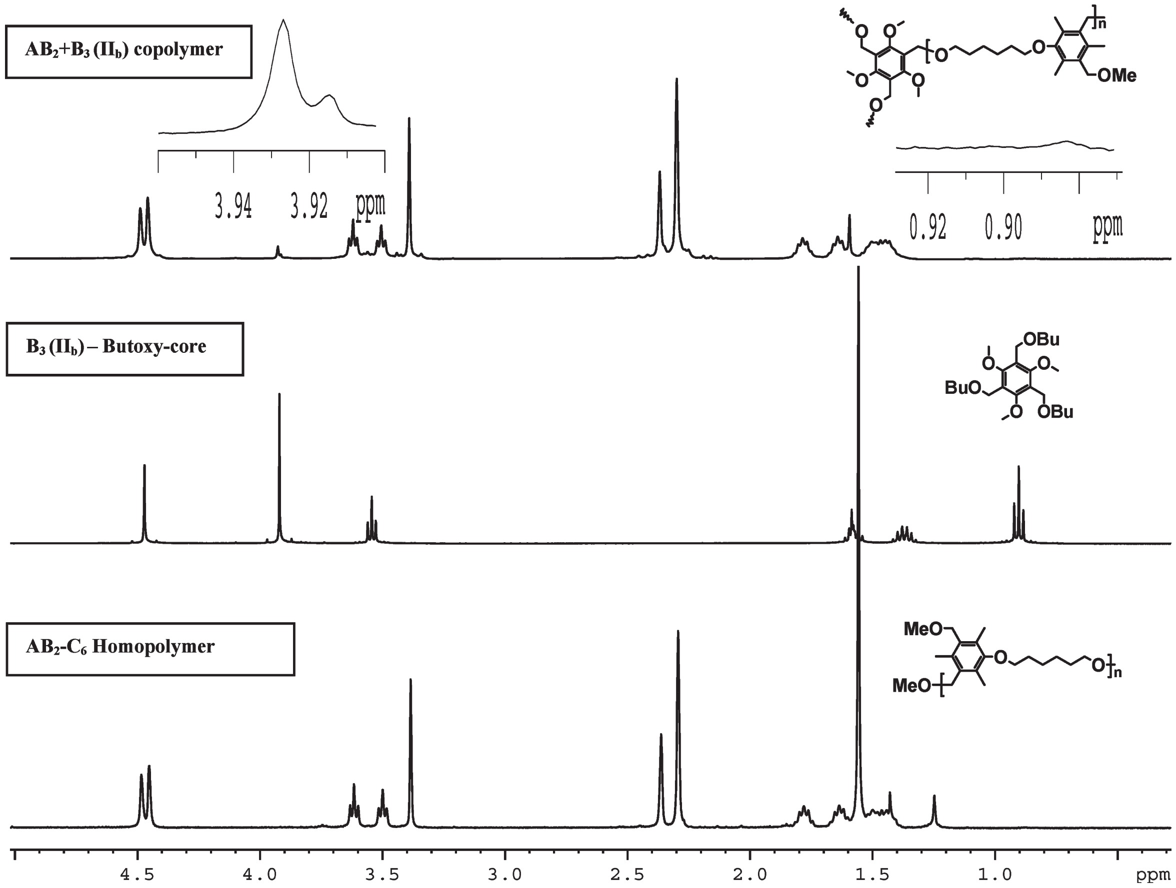


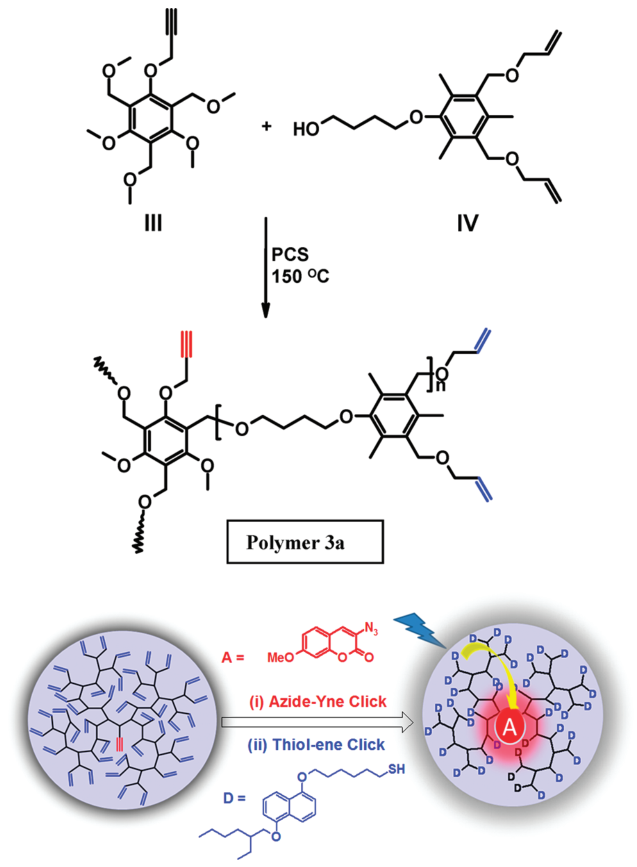
Figure 4. ^{1}H NMR spectra of the hyperbranched homopolymer, along with those of the butoxymethyl core (**IIb**) core and the copolymer. The expanded region of the copolymer spectra (top) shows the nearly complete set of the terminal methyl protons (~0.9 ppm) of the butoxy group of the core.

and 4.50 ppm), either of these peaks could be used to follow the relative rates of trans-etherification; in the present study, the former was the preferred as their intensities decrease due to loss of the methoxyl group during the reaction. From the variation in their relative intensities, it is evident that the peak at 3.43 ppm belonging to core **II** vanishes at a significantly faster rate compared to that belonging to **IIa**, at 3.4 ppm. As the reaction progresses, the benzylic region of the spectra begins to exhibit two additional peaks (one each from **II** and **IIa**), which correspond to those benzylic protons after displacement of methoxy group by a dodecyloxy one; the presence of multiple peaks in this region makes it clearly less conducive for following the kinetics. A plot of the variation of the methoxy proton peak intensities as a function of time (see Figure S1, Supporting Information) permitted us to retrieve the relative rate constants for trans-etherification; a roughly 3-fold enhancement in the rate constant was observed for core **II** (as evident from the differences in the slopes), confirming that the electron-rich core can indeed serve effectively to regulate the condensation process.

Copolymerization and Molecular Weight Regulation. The copolymerization of the AB_2 monomer **I** was carried out using three different amounts of the B_3 core **II**: 2.5, 5, and 10 mol %. The proton NMR spectra of the homopolymer and those of the three copolymers are presented in Figure 3; although the benzylic protons due to the core are not clearly discernible due to overlap, the presence of the aromatic methoxy protons confirms the incorporation of the core. The extent of incorporation of the core was estimated from the relative intensities of the core methoxy protons ($\mathbf{CH_3}O{-}Ar \sim 3.95$ ppm) compared to those of aromatic methyl protons ($Ar{-}\mathbf{CH_3} \sim 2.3{-}2.4$ ppm) belonging to the polymer repeat unit, and the values thus obtained are listed in Table 1.

The core incorporation level is seen to vary in accordance with the feed composition, although the incorporation levels estimated by NMR were consistently slightly lower. Use of a B_3 core leads to a stoichiometric imbalance and, therefore, would also lead to a lowering of the molecular weight. Since the B_3 core has the potential to anchor three directions for growth, it can be easily shown that the effect of the B_3 core on the molecular weight will be identical to that of a monofunctional impurity during a simple A—B type polymerization, and the degree of polymerization will vary as follows: $DP = (1 + r)/(1 + r - p)$, where r is the mole ratio of the B_3 core to the AB_2 monomer and p is the percent conversion.[4] Since, all the polymer samples were purified by reprecipitation, the measured DP cannot be compared directly with those calculated based on the above formula; instead, we compared the Mn values obtained by two different approaches, one by NMR end-group analysis and the other by GPC. The Mn values determined by GPC and those estimated by proton NMR (by direct comparison of the peak intensities of the $Ar{-}OCH_3$ belonging to the core with those of the $Ar{-}CH_3$ peaks belonging to the repeat unit) are listed in Table 1; in the case of the highest M_n sample the GPC value is a bit lower, while in the other two cases the GPC value is slightly higher. The may

Scheme 1. Orthogonally Clickable Hyperbranched Polymer[a]



[a] The core carries an azide-clickable unit while the periphery carries numerous thiol-clickable units.

be due to the fact that the GPC slightly underestimates the M_n value at higher molecular weights but the effect is negligible at low molecular weights.[13] The polydispersity index (PDI) of the sample is also seen to be influenced by the incorporation of the core; it is seen to decrease from 2.78 in the homopolymer to about 1.46 at the highest level of core incorporation.[14] This lowering of the PDI is most likely due to the lower molecular weights of the resulting polymers; this is an expected behavior during the polycondensation of AB_2 type monomers during which the PDI increases with percent conversion (DP_n). The yields of the polymer are also seen to decrease with increase in core mole fraction; this is possibly due to the loss of low molecular weight oligomers during reprecipitation, which expectedly will affect the lower molecular weight samples more severely. Thus, it is evident that a suitably designed $\mathbf{B_3}$ core bearing more reactive B-groups works effectively to regulate both the molecular weight as well as the PDI of hyperbranched polymers; unfortunately, however, the lowering of PDI is always accompanied by a reduction in DP, which is an intrinsic limitation of this process.

One intriguing feature of the spectra of the core-containing copolymers is the appearance of two peaks corresponding to the methoxy protons ($\mathbf{CH_3}$O–Ar) attached to the core unit; one possible reason for this could be the incomplete trans-etherification which would cause a differentiation between the three aryl-methoxy protons on the core. Unfortunately, the methoxymethyl protons ($\mathbf{CH_3}$OCH$_2$–) belonging to the monomer and the core could not be differentiated in the NMR spectra (the δ values are almost the same; see Figure S2, Supporting Information) making it difficult to confirm the completeness of the trans-etherification of the core. To confirm that all the three locations of the core have reacted during the copolymerization, we designed an alternate core (**IIb**) where the displaceable methoxy groups were replaced by butoxy ones. The NMR spectra of **IIb**, along with those of the homopolymer and the copolymer (using 5 mol % of this core) are shown in Figure 4. The nearly complete disappearance of the peak due to the terminal methyl protons of the butoxy group (at ~0.9 ppm) in the copolymer confirms that complete trans-etherification of the core unit had indeed occurred. Despite this, the aromatic methoxy protons of the core unit (at ~4.0 ppm) appear as two peaks suggesting that the origin of this could be due to some other reason. As the hyperbranched polymeric segments (could be called *hyperons* akin to dendrons) linked to the core are fairly bulky, they are likely to be located on either side of the aromatic plane; in other words, two of the hyperons could be pointing downward while one could be upward; this in turn would force the aryl methoxy groups to be disposed similarly. A rough intensity ratio of 1:2 of the two peaks, in all the three copolymers (see Figure 3), suggests that this could be a possible reason for the splitting.[15] Search of the literature revealed that a similar conformational effect on the NMR spectra has been observed in a mesitylene derivative carrying bulky substitutents on the remaining three locations of the benzene core.[16]

The use of the butoxylated core **IIb** also permitted the direct examination of the relative rates of the trans-etherification of the B-groups belonging to the core and the monomer **I** during the copolymerization, since the terminal methyl protons of the butoxy group (0.9 ppm) and the methoxy protons (3.4 ppm) of the monomer could be independently followed. The variation of the NMR spectra and the relevant peak intensities during the copolymerization (Figures S3 and S4, Supporting Information) helped reconfirm the rapid and complete trans-etherification of the core during the copolymerization; this further validates the efficacy of the new reactive core to function as an efficient regulator of the condensation process.

Orthogonal Functionalization of the Core and Periphery. Having demonstrated that the trialkoxybenzene core works efficiently to regulate the molecular weight, and consequently is incorporated within the apparent core of the hyperbranched polymer, we decided to examine the possibility of incorporating a functionalizable core unit by suitably modifying the core structure. In order to do so, we designed a reactive B_3 core where one of the methoxy groups is replaced by a propargyloxy unit; this when incorporated in the hyperbranched polymer would provide a clickable unit at the core. Thus, an alternate core, namely **III** (see Scheme 1), was prepared by selective demethylation of 1,3,5-trimethoxybenzene[17] followed by alkylation with propargyl bromide; subsequent steps to prepare the core were done as in case of **II**. Further, in an effort to generate orthogonally clickable hyperbranched polymers where the core and the periphery could be clicked independently, we prepared copolymers using the azide-yne clickable core **III** and a recently developed AB_2 monomer **IV** that carries allyloxymethyl groups instead of the methoxylmethyl groups, as depicted in Scheme 1. We had recently showed that the monomer **IV** readily undergoes polymerization to yield a clickable hyperbranched polymer, which can further be clicked quantitatively using a variety of thiols.[11] In the present study, we chose to click the core first with an azido-chromphore based on coumarin and subsequently the peripheral allyl groups were

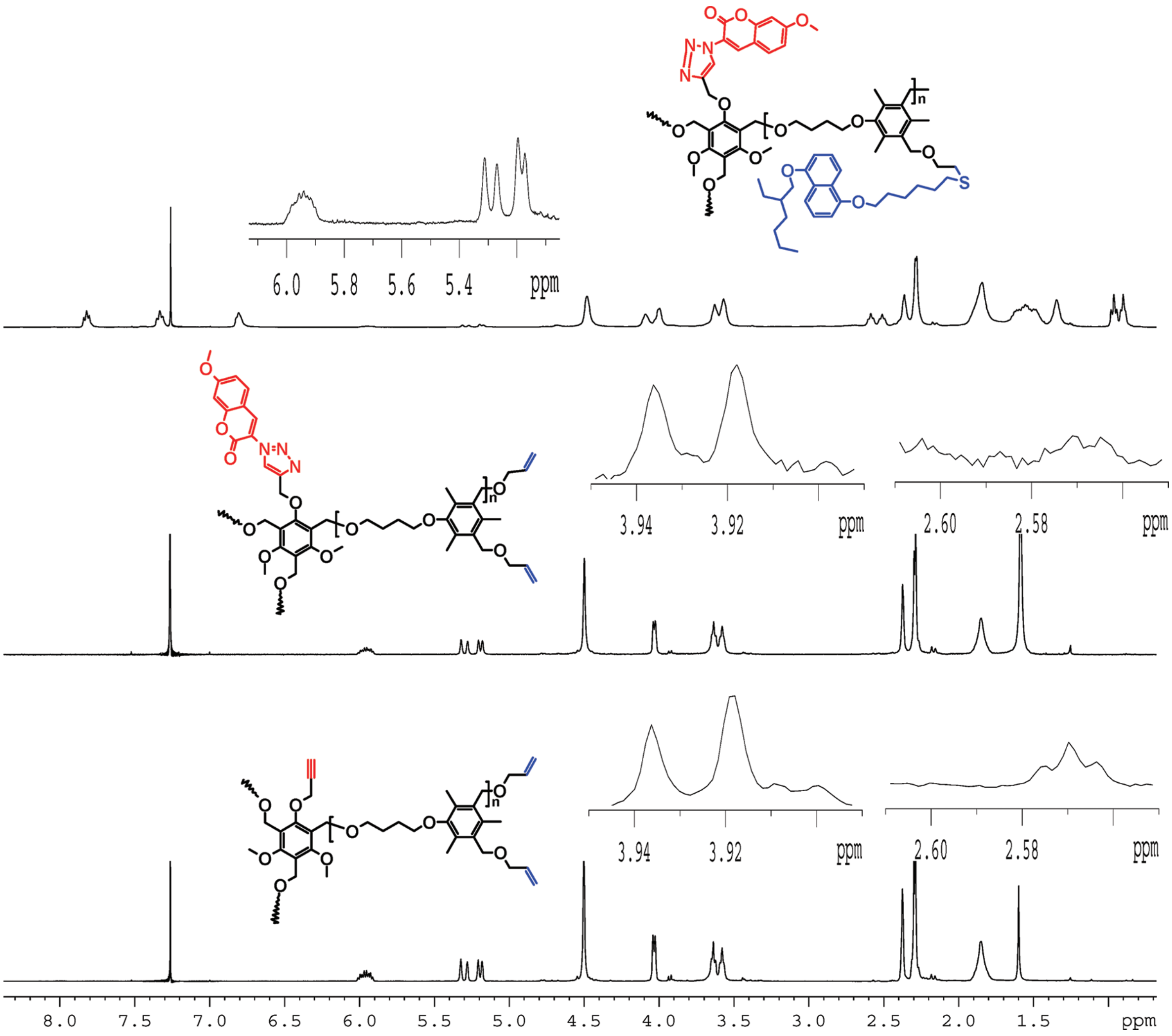


Figure 5. ^{1}H NMR spectra of the hyperbranched copolymer carrying an azide-yne clickable core and numerous thiol−ene clickable periphery, along with those of core-clicked and core and peripherally clicked polymers.

clicked with a dialkoxynaphthalene chromophore carrying a pendant thiol unit; this pair of chromophores was chosen to facilitate FRET from the periphery to the core in an effort to mimic the light-harvesting dendrimers that have been reported earlier.[18] The 2-ethylhexyl groups on the naphthalene chromophore was required to ensure the solubility of the polymer after complete clicking with the naphthalene units; our first attempt with the simple methoxynaphthalene units rendered insoluble polymers after clicking, possibly due to strong tendency of the naphthalene units to form dimers leading to physical cross-linking. In Figure 5, the proton NMR spectra of the core containing peripherally clickable hyperbranched polymer, along with those that have been clicked with the FRET pair of chromophores, are shown. The spectrum of the parent polymer clearly showed the presence of a large number of allyl groups, while the y-expanded region shows a weak peak due to the incorporation of the propargyl core. After clicking the core using the Coumarin azide, there is near complete disappearance of the terminal propargyl triplet. On the other hand, the thiol−ene click reaction with the dialkoxynaphthalene-bearing thiol resulted in the transformation of nearly 80% of the allyl groups leaving behind small residual peaks in the NMR spectrum, as evident from the expanded depiction of the allyl region.

The fluorescence spectra of the core-clicked and core and periphery clicked HBPs are shown in Figure 6. Comparison of the core-clicked HBP with a suitable model chromophore prepared using the monomer and the coumarin azide showed that the spectral position matched well, although the spectral shape of the model was devoid of any fine structure.[19] On the other hand, the fluorescence spectra of the naphthalene clicked HBP and that of a model matched perfectly, suggesting that anchoring them on the HBP did not influence their fluorescence spectra. The fluorescence spectrum of the HBP containing both the Donor and Acceptor chromophores exhibited peaks both due to the naphthalene donors and the coumarin acceptor, although the excitation was done at 295 nm, where the absorption is primarily due to the naphthalene chromophore. This suggests that FRET has indeed occurred although it is incomplete; this may be expected as a very large number of Donors are present in the HBPs while only a single acceptor is present.[20] In an effort to improve the FRET efficiency, the average distance between the donor and acceptor could be decreased. One way to achieve this is to desolvate the polymer chain by adding a suitable nonsolvent; this would cause the chain to collapse and in turn bring the peripheral donors closer to the core acceptor unit. To test this hypothesis, a solution

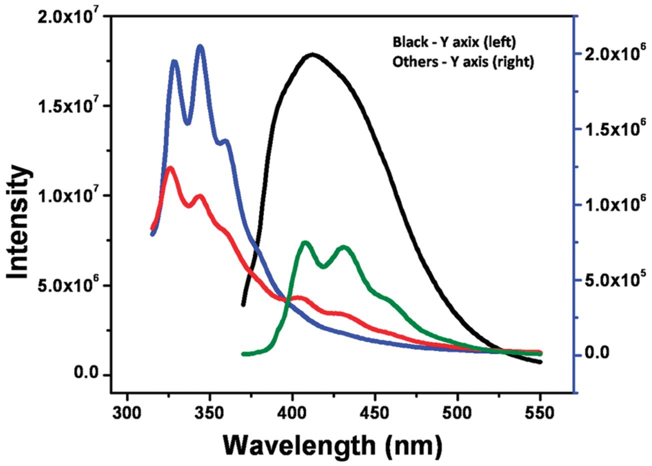


Figure 6. Fluorescence spectra of coumarine azide clicked model compound (black, 0.11 μM excited at 335 nm); naphthalene thiol clicked model compound (blue, 0.08 μM, excited at 295 nm); coumarin azide clicked HBP 3a (green, 0.035 μM, excited at 335 nm) and coumarin and naphthalene clicked HBP 3b (red, 0.035 μM, excited at 295 nm).

of the doubly clicked HBP was taken in THF and water was added to it. From the normalized spectra (Figure S5, Supporting Information), it was evident that the efficiency of the FRET does go up substantially in the presence of water although complete disappearance of the donor fluorescence was still not observed.

In conclusion, we have demonstrated that the molecular weight and PDI of hyperbranched polyethers, prepared via the trans-etherification process, can be controlled by the use of a more reactive B_3 core along with the AB_2 monomer. The DP of the HBP decreased with increase in the relative mole-fraction of the B_3 core; this is in general accordance with earlier theoretical predications.[4] As the design of the core was based on 1,3,5-trimethoxybenzene, replacement of one of the methoxy groups with a propargyloxy one, provided an easy access to a clickable core; this modified core molecule was also shown to function just as efficiently in regulating the DP, while at the same time it provided a single functionalizable unit at the core of the HBP. By using this core in conjunction with a recently developed AB_2 monomer, which provided direct access to HBPs carrying thiol—ene clickable peripheral units, we have been able to develop a single-step approach for the preparation of orthogonally clickable HBPs; this represents the first demonstration of the direct synthesis of such orthogonally clickable HBPs. In a test study, we have also shown that two different chromophores, one bearing an azide group and the other carrying a thiol unit could be clicked at the core and periphery, respectively; FRET from the periphery to the core was shown to occur, the extent of which could be modulated by varying the solvent composition. This single-step approach to access orthogonally clickable HBPs could find several interesting applications wherein selective and differential functionalization of the core and periphery may be needed, such as in light harvesting, drug delivery etc.

■ EXPERIMENTAL SECTION

Materials and Methods. 2,4,6-Trimethylphenol, 1,3,5-trimethoxybenzene, trioxane, camphor sulfonic acid, propargyl alcohol, 1,5-dihydroxy naphthalene, and mesitylene were purchased from Sigma-Aldrich chemical company and used directly. Metallic sodium, 33% acetic acid solution of HBr, 49% aqueous solution of HBr were purchased from Spectrochem Ltd. and used directly. Common organic solvents were purified and/or distilled prior to use. AB_2 monomers **I** and **IV** and the catalyst PCS were synthesized using previously reported procedures.[12] The clickable reactive core **III** was prepared by selective deprotection of 1,3,5-trimethoxybenzene followed by alkylation with propargybromide; subsequent steps were similar to that used for core **II**. The coumarin azide was prepared using a reported procedure[21] while the naphthalene thiol derivative was prepared in four steps from 1,5-naphthalene diol using some standard methodologies.[22]

^{1}H NMR spectra was recorded in 400 MHz Bruker spectrometer using $CDCl_3$ as solvent unless otherwise mentioned. Gel permeation chromatography (GPC) was carried out using a Viscotek TDA model 300 system, coupled to refractive-index, differential viscometer, and light scattering detectors, in series. The separation was achieved with two mixed-bed PLgel columns (5 μm, mixed C) maintained at 35 °C, with tetrahydrofuran (THF) as the eluent. The molecular weights were determined using a universal calibration curve based on polystyrene standards. Fluorescence measurements were carried out using a Jobin Yvon Fluorolog spectrometer; all measurements were done using μM concentration solutions of the model compound or polymer.

1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene (1).[23] To a mixture of 1,3,5-trimethoxybenzene (10 g, 60 mmol) and paraformaldehyde (6.42 g, 214 mmol) in a pressure tube, glacial acetic acid was added (30 mL) and the resulting suspension was allowed to stir for 1 h. HBr (33% in HOAc, 63 mL) was then added and the reaction mixture was heated to 70 °C for additional 3 h under a tight sealed. After cooling to room temperature, the reaction mixture was poured into water (250 mL) and precipitated solids were dissolved in chloroform. The organic layer was separated and the aqueous solution was extracted with chloroform. All organics were combined and washed with saturated aqueous $NaHCO_3$, water, brine; the solution was concentrated to yield orange oil. The crude products were purified by column chromatography using hexanes/ethyl acetate (19:1) as eluting solvent to get the desired product (7.98 g, 30%, MP = 125 °C) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.147 (s, 9H, $ArOCH_3$); 4.605 (s, 6H, $ArCH_2Br$).

1,3,5-Tris(methoxymethyl)-2,4,6-trimethoxybenzene (Core II). Sodium metal (1.85 g, 80.5 mmol) was added to 20 mL of dry methanol in portions. The solution of **1** (6 g, 13.4 mmol) in dry methanol was added dropwise to the sodium methoxide solution. The reaction mixture was refluxed for 18 h. After completion, the reaction mixture was cooled to room temperature and methanol was removed under reduced pressure. Then, 10 mL of water was added to the concentrated reaction mixture and it was extracted in ethyl acetate (2 × 20 mL). All organics were combined and washed with brine, passed over sodium sulfate, concentrated and distilled in Kugelrohr at 200 °C/6 Torr to get desired product (3 g, 75%, MP = 50 °C) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.43 (s, 9H, $ArCH_2O\mathbf{CH_3}$); 3.91 (s, 9H, $ArO\mathbf{CH_3}$); 4.38 (s, 6H, $Ar\mathbf{CH_2}OCH_3$).

1,3,5-Tris(butoxymethyl)-2,4,6-trimethoxybenzene (Core IIb). Sodium metal (1.85 g, 80.5 mmol) was added to 20 mL of dry butanol in portions. The solution of **1** (6 g, 13.4 mmol) in dry butanol was added dropwise to the sodium butoxide solution. The reaction mixture was refluxed for 18 h. After completion, the reaction mixture was cooled to room temperature and butanol was removed by using a rotary evaporator. Then 10 mL of water was added to the concentrated reaction mixture, and it was extracted in ethyl acetate (2 × 20 mL). All organics were combined and washed with brine, passed over sodium sulfate, concentrated, and distilled in Kugelrohr at 200 °C/6 Torr to get the desired product (4 g, 70%) as a colorless viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.9 (t, 9H, $ArCH_2OCH_2CH_2CH_2\mathbf{CH_3}$); 1.38 (m, 6H, $ArCH_2OCH_2CH_2\mathbf{CH_2}CH_3$); 1.57 (m, 6H, $ArCH_2OCH_2\mathbf{CH_2}CH_2CH_3$); 3.54 (t, 6H, $ArCH_2O\mathbf{CH_2}CH_2CH_2CH_3$); 3.92 (s, 9H, $ArO\mathbf{CH_3}$); 4.47 (s, 6H, $Ar\mathbf{CH_2}OCH_2CH_2CH_2CH_3$).

Typical Copolymerization Procedure. Monomer **I** (1.5 g, 4.31 mmol) along with required amount of B_3 core (**II** or **II**$_b$ or **III**) and 2 mol % of pyridinium camphorsulfonate (PCS) was taken in a test tube shaped polymerization vessel. The mixture was degassed for 10 min and maintained at a temperature of 110 °C under continuous N_2 purge, to ensure homogeneous mixing of catalyst and monomers. The polymerization was then carried out at 150 °C under N_2 for 1 h with constant stirring. Subsequently, using a Kugelröhr apparatus, the polymerization was continued for an additional period of 45 min at 150 °C under reduced pressure (2 Torr), with continuous mixing of the melt by rotation. The resultant polymer was dissolved in 2 mL of THF, the acid-catalyst was neutralized with solid $NaHCO_3$ and then the solution was filtered. The filtrate was concentrated under reduced pressure to a 1 mL of viscous solution and precipitated in 10 mL methanol. The polymer was purified once more by dissolution in 1 mL of THF and reprecipitation into 10 mL of methanol.

Polymer **3a** (**Poly-3a**) (Scheme 1) was prepared similarly using monomer **IV** and the required amount of core **III**.

Typical Azide–Yne Click Reaction (Poly-3b). A mixture of the **Poly-3a** (200 mg, 0.034 mmol; with respect to propergyl group) and coumarin azide (22 mg, 0.102 mmol) were taken in 5 mL of THF. To the reaction mixture, 30 μL aqueous sodium ascorbate (2 mg, 0.01 mmol) and $CuSO_4 \cdot 5H_2O$ (1.27 mg, 0.005 mmol) was added under N_2 atmosphere. N_2 purging was continued for another 10 min to remove dissolved oxygen from the reaction mixture. The content was heated to 50 °C for 3 days. After completion, the polymer solution was concentrated under reduced pressure to a viscous solution and precipitated in DMSO; the polymer was further purified twice by dissolution in THF and precipitated into DMSO to yield the polymer **3b**.

Typical Thiol–Ene Click Reaction (Poly 3c). A mixture of the **Poly-3b** (35 mg, 0.11 mmol) and napthalene thiol (130 mg, 0.33 mmol) were taken in 5 mL of toluene. To the reaction mixture, the photoinitiator 2,2-dimethoxy 2-phenyl acetophenone (1.12 mg, 0.004 mmol), was added. The content was irradiated with UV light for 8 h. The polymer solution was concentrated under reduced pressure to a viscous solution and precipitated in methanol; the polymer was further purified twice by dissolution in chloroform and reprecipitation into petroleum ether to yield the polymer **3c**.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed experimental schemes and procedures, kinetic plots comparing the relative reactivities of the two cores, NMR spectral variation during the polymerization and the corresponding kinetic plots, and fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a)) The ^{1}H-NMR spectra of both the parent methoxy and butoxy cores (**II** and **IIb**), however, exhibited only a single methoxy proton peak corresponding to all the three methoxy groups; this could be due to the rapid switching that occurs in the small core molecules, while this dynamics be inhibited (or considerably slowed down) when bulky substituents, such as in the case of the polymer, are present.

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