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Hyperbranched Polymers with a Degree of Branching of 100% Prepared by Catalyst Transfer Suzuki–Miyaura Polycondensation

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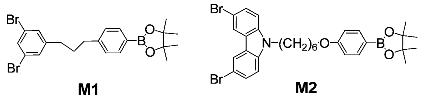
Hyperbranched polymers have attracted considerable interest because of their unique molecular structures and properties, such as good solubility, low viscosity, and large numbers of functional end groups.[1] A degree of branching (DB) of 100% is a typical feature for perfectly branched dendrimers, whereas hyperbranched polymers prepared by one-pot reaction are usually not perfectly branched and have a DB of ~50%.[1] Many attempts have been made to improve the degree of branching of hyperbranched polymers. Pioneering works have been reported by several groups. For example, Hawker and Chu[2] developed an AB_4 monomer route, which gave a hyperbranched polymer with a DB of up to 71%. Ishida et al.[3] synthesized a series of monomers (AB_2, AB_4, and AB_8) and found that the DB increases with increasingly branched monomers; AB_2 monomers gave a DB of only 32%, AB_4 monomers gave 72%, and AB_8 gave 84%. Moore, McHugh, and co-workers[4] reported a method of synthesis of hyperbranched polymers with varying degrees of branching from a single monomer. Hult and co-workers[5] developed a pseudo-one-step reaction for preparing hyperbranched macromolecules with DBs of nearly 80%. Hölter and Frey[6] reported that the maximum DB obtainable from a slow addition process is 67% for AB_2 systems. We reported that the use of an $AB_2 + AC_2$ approach could afford hyperbranched polymers with a DB of 86%.[7] These modification methods only enhance the DB, but none of them can achieve a hyperbranched polymer with a DB of 100%. Hyperbranched polymers with a DB of 100% have been recently reported by several groups but are limited to few monomers.[8]

Recently, Sinclair and Sherburn[9] reported that Suzuki–Miyaura coupling of diiodoaryls and arylboronic acid in a feed ratio of 10:1 with $Pd(PPh_3)_4$ as the catalyst precursor and Ag_2CO_3 as the base preferentially afforded the product of double coupling. Dong and Hu[10] found that Suzuki coupling of dibromobenzenes with 1 equiv of arylboronic acid using $Pd_2(dba)_3$ and $P(t\text{-Bu})_3$ as catalyst precursors formed exclusively diaryl-substituted benzenes. Later, Scherf and co-workers[11] also reported that the coupling of 2,7-dibromofluorene with 1 equiv of arylboronic acid under conditions similar to those of Dong and Hu preferentially afforded diaryl-substituted fluorenes. Yokozawa and co-workers[12] successfully demonstrated the chain-growth Suzuki–Miyaura polymerization of bromoarylboronic acid using $P(t\text{-Bu})_3Pd(Ph)Br$ as an arylpalladium halide catalyst. Herein, we report the preparation of hyperbranched polymers with a DB of up to 100% starting from AB_2-type monomers by catalyst transfer Suzuki–Miyaura coupling.

The AB_2-type monomers **M1** and **M2**, whose chemical structures are shown in Chart 1, were used to verify this concept. These two AB_2-type monomers contain one aromatic boronic pinacol ester and two aromatic bromo atoms linked by an alkyl chain spacer. The alkyl chain spacer was introduced to enhance the solubility of the hyperbranched polymers. The synthesis of **M1** was described in our previous publication.[7] **M2** was facilely synthesized in a large amount, and its synthesis is depicted in Scheme S1 in the Supporting Information. Bromination of 9-bromohexylcarbazole (**1**) with NBS afforded compound **2** in a yield of 98%. Williamson etherification of **2** and 4-hydroxybenzene boronic pinacol ester furnished **M2** in 65% yield.

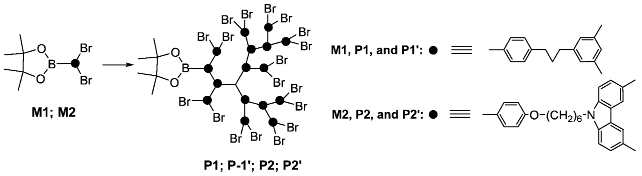
Chart 1. Chemical Structures of AB_2-Type Monomers



The synthesis of hyperbranched polymers is shown in Scheme 1. Hyperbranched polymers with a DB of 100% were first prepared by catalyst transfer Suzuki–Miyaura polymerization of AB_2 monomers **M1** and **M2**. The polymerization was carried out in a biphasic mixture of THF and aqueous $NaHCO_3$ with $P(t\text{-Bu})_3$[13] as the ligand and $Pd_2(dba)_3CHCl_3$ as the source of zero-valent palladium. The reaction was stirred and refluxed for 4 days under N_2 to afford hyperbranched polymers **P1** and **P2** in yields of 63 and 68%, respectively. During the polymerization, no polymer precipitated from the reaction mixture. The weight-average molecular weights and polydispersities of these hyperbranched polymers, as determined by GPC with THF as an eluent calibrated with polystyrene standards, were 7400 and 1.16 for **P1** and 14 900 and 1.53 for **P2**, respectively. The polymerization of **M1** and **M2** with $Pd(PPh_3)_4$ as the catalyst precursor afforded hyperbranched polymers **P1′** and **P2′** in yields of 51 and 61%, respectively, and the corresponding weight-average molecular weights were 14 100 and 2900, respectively. The weight-average molecular weights of the four hyperbranched polymers were also measured by static laser light scattering to be 1.35×10^5 for **P1**, 1.44×10^5 for **P1′**, 3.7×10^5 for **P2**, and 6.4×10^4 for **P2′**. During the polymerization, **P2′** precipitated from the reaction mixture. The lower molecular weight of **P2′** is probably caused by its poor solubility, which may be due to its more disordered topology. As studied by differential scanning calorimetry (DSC), no melting point or glass transition was observed in the range 50–200 °C for these four hyperbranched polymers.

According to the definition given by Fréchet and co-workers,[14] the DB of hyperbranched polymers was calculated as DB = (D + T)/(D + L + T), where D denotes the dendritic units, T the terminal units, and L the linear units. The content of each unit was

Scheme 1. Synthesis of Hyperbranched Polymers



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determined by NMR integration. To obtain hyperbranched polymers with a DB of 100%, the linear chain propagation should be completely suppressed.

The DB of **P1** prepared by catalyst transfer Suzuki polymerization was ~100%, which was determined by ^{13}C NMR integration methods as described in our previous paper.[7] In a control experiment, Suzuki−Miyaura polymerization of **M1** under standard conditions with a traditional catalyst, Pd(PPh$_3$)$_4$, afforded **P1′** with a DB of only ~56%.[7] The assigned peaks used for the integration are shown in Figure 1.

For **P2**, most of the signals in their alkyl regions were difficult to identify because of overlap and could not be used for integration, but the aromatic signals of the carbazole unit (as shown in Figure 1) were well-separated for the L, D, and T units. In order to assign these signals, several model compounds were synthesized (see the Supporting Information). For comparison, the ^{1}H NMR spectrum of the hyperbranched polymer prepared by using the traditional catalyst, Pd(PPh$_3$)$_4$, is also shown in Figure 1. For the hyperbranched polymers prepared by catalyst transfer Suzuki−Miyaura polymerization, only signals from dendritic and terminal units can be observed in the spectrum, whereas the signals from linear units are completely absent. The DB of **P2** is close to 100%. In contrast, for **P2′** prepared using Pd(PPh$_3$)$_4$ as the catalyst precursor, the signals from linear units could be clearly seen, and its DB was also only ~56%.

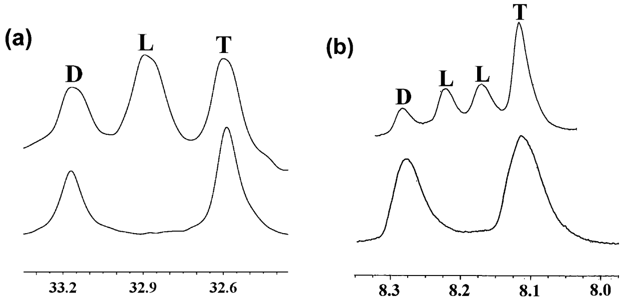
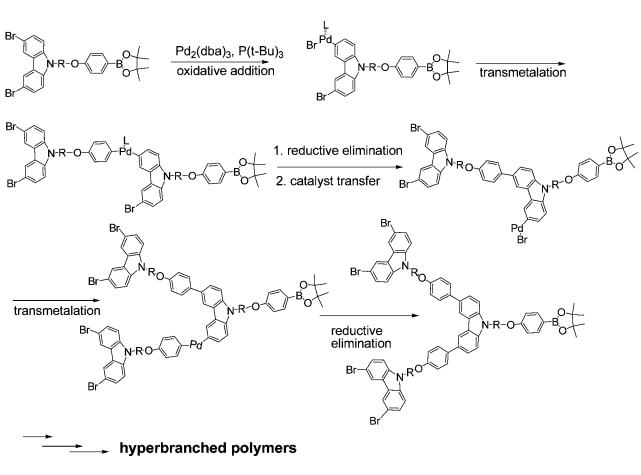


Figure 1. (a) ^{13}C NMR peak assignments for the middle alkylene carbons of (bottom) **P1** and (top) **P1′**. (b) ^{1}H NMR peak assignments for the carbazole protons of (bottom) **P2** and (top) **P2′**.

Scheme 2. Possible Mechanism for the Formation of Hyperbranched Polymers with a Branching Degree of 100%



A possible mechanism for the formation of the fully branched hyperbranched polymers can be described as follows (Scheme 2): (1) oxidative addition of the palladium atom to the aryl−bromo bond; (2) transmetalation and reductive elimination to form a carbon−carbon bond between two aryls; (3) formation of a complex between the bulk Pd(0)/P(*t*-Bu)$_3$ catalyst and the aromatic ring, which helps to prevent the palladium catalyst from diffusing to the reaction mixture; (4) oxidative addition of the catalyst to the neighboring aryl−bromo bond by catalyst transfer via the π system; (5) transmetalation, reductive elimination, and diffusion of the catalyst to the reaction mixture. Consequently, fully hyperbranched polymers are formed.

In conclusion, hyperbranched polymers with a degree of branching of 100% were prepared by catalyst transfer Suzuki−Miyaura polymerization of AB$_2$-type monomers carrying one arylboronic acid and two aryl bromides. The catalyst transfer Suzuki−Miyaura polymerization was carried out with Pd$_2$(dba)$_3$ as the zero-valent palladium source and P(*t*-Bu)$_3$ as the bulky ligand. In comparison, AB$_2$-type monomers polymerized by using the traditional Pd(PPh$_3$)$_4$ as the catalyst precursor afforded hyperbranched polymers with a DB of only ~56%. Our results clearly demonstrate that the chemical structures of hyperbranched polymers can be controlled by the choice of catalyst and also open a convenient way to prepare fully branched hyperbranched polymers from facilely achievable AB$_2$-type monomers. This is the first report of controlling the topology of hyperbranched polymers via the catalyst precursor.

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Supporting Information Available: Detailed experimental procedures, characterization of all compounds, and their spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080–1083. (b) Guan, Z. B.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059–2062. (c) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505–2525. (d) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685–1698. (e) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453–571. (f) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233–1285. (g) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183–275. (h) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2679–2699.
(2) Hawker, C. J.; Chu, F. K. *Macromolecules* **1996**, *29*, 4370–4380.
(3) Ishida, Y.; Sun, A. C. F.; Jikei, M.; Kakimoto, M. *Macromolecules* **2000**, *33*, 2832–2838.
(4) Thompson, D. S.; Markoski, L. J.; Moore, J. S.; Sendijarevic, I.; Lee, A.; McHugh, A. J. *Macromolecules* **2000**, *33*, 6412–6415.
(5) Malmström, E.; Johansson, M.; Hult, A. *Macromolecules* **1995**, *28*, 1698–1703.
(6) Holter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298–309.
(7) Bo, Z. S.; Schlüter, A. D. *Chem. Commun.* **2003**, 2354–2355.
(8) (a) Hobson, L. J.; Kenwright, A. M.; Feast, W. J. *Chem. Commun.* **1997**, 1877–1878. (b) Smet, M.; Schacht, E.; Dehaen, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4547–4550. (c) Maier, G.; Zech, C.; Voit, B.; Komber, H. *Macromol. Chem. Phys.* **1998**, *199*, 2655–2664. (d) Sinananwanich, W.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2689–2700. (e) Fu, Y.; Vandendriessche, A.; Dehaen, W.; Smet, M. *Macromolecules* **2006**, *39*, 5183–5186. (f) Fu, Y.; Van Oosterwijck, C.; Vandendriessche, A.; Kowalczuk-Bleja, A.; Zhang, X.; Dworak, A.; Dehaen, W.; Smet, M. *Macromolecules* **2008**, *41*, 2388–2393.
(9) Sinclair, D. J.; Sherburn, M. S. *J. Org. Chem.* **2005**, *70*, 3730–3733.
(10) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006–10007.
(11) Weber, S. K.; Galbrecht, F.; Scherf, U. *Org. Lett.* **2006**, *8*, 4039–4041.
(12) Yokoyama, A.; Suzuki, H.; Kubaota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.
(13) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176–4211.
(14) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4588.

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