J|A|C|S
COMMUNICATIONS

Hyperbranched Polymers with Controlled Degree of Branching from 0 to 100%

Yukari Segawa, Tomoya Higashihara, and Mitsuru Ueda*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-H120, O-okayama, Meguro-ku, Tokyo, Japan, 152-8552

Received June 15, 2010; E-mail: ueda.m.ad@m.titech.ac.jp

Abstract: A linear polymer, hyperbranched polymers with various degrees of branching, and 100% hyperbranched polymers were successfully synthesized by self-polycondensation of 2,2,2-trifluoro-1-[4-(4-phenoxyphenoxy)phenyl]ethanone by using different amounts of trifluoromethanesulfonic acid from the same AB_2 monomer.

Hyperbranched polymers (HBPs) have attracted considerable attention during the past decade[1−5] because of their intrinsic globular structures and unique properties, such as low viscosity, high solubility, and a high degree of functionality, compared to linear analogues. The majority of hyperbranched polymer syntheses involves a step-growth polycondensation reaction employing monomers of the AB_x type, where A and B represent two different functional groups. In this respect, the degree of branching (DB)[6] has been discussed as one of the key parameters for the characterization of hyperbranched polymers, which is controlled by the reactivity of the functional groups involved in the synthesis. Theoretically, for polymers derived from an AB_2 monomer, the DB is determined by statistics and only reaches around 50%, assuming it is based on equal reactivity of the two B functional groups of the AB_2 monomer.

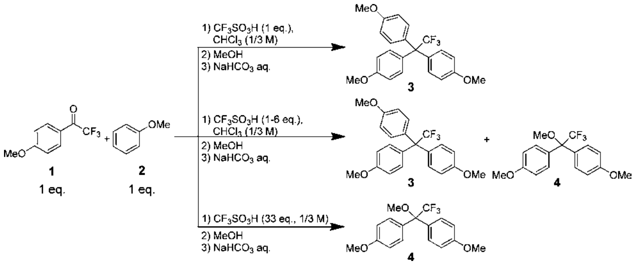
Recently, several groups have reported the synthesis of 100% HBPs.[7−14] Such 100% HBPs can be obtained when the first reaction step of an AB_2 monomer activates the second reaction. Quite recently, we briefly reported that an AB_2 monomer, 2,2,2-trifluoro-1-[4-(4-phenoxyphenoxy)phenyl]ethanone (**7**), produced a linear poly(phenylene ether) in trifluoromethanesulfonic acid (TFSA).[15] The resulting poly(phenylene ether)s with various functional groups in every single repeating unit were formed simply by pouring the polymer solutions into nucleophilic solvents. This finding prompted us to develop the synthesis of HBPs with arbitrarily controlled degrees of branching (DBs).

Herein, we report the first synthesis of HBPs with controlled DBs by one-pot polycondensation of an AB_2 monomer **7**, in various molar ratios of TFSA to monomer. We found that a 100% HBP is produced in an equimolar ratio of [TFSA]/[monomer] in chloroform. On the other hand, a linear polymer, that is, a 0% HBP, is obtained by using TFSA as a solvent. In addition, HBPs with a DB of any percent between 0 and 100% are formed by changing the ratio of [TFSA]/[monomer]. To date no other examples have been reported for the synthesis of HBPs with controlled DB from 0 to 100% derived from the same AB_2 monomer.

We investigated the model reactions of an equimolar amount of 2,2,2-trifluoro-4′-methoxyacetophenone (**1**) with anisole (**2**) by changing the ratios of [TFSA] to [**1**] at room temperature, being monitored by ^1H NMR (Scheme 1, Figure S1 in the Supporting Information (SI)). After the reaction, the solution was poured into methanol.

The products were isolated in quantitative yields, and the results are summarized in Figure S5 (see SI). Only the diarylated product, 2,2,2-trifluoro-1,1,1-tri(4-methoxyphenyl)ethane (**3**), was selectively obtained in an equimolar ratio of [TFSA]/[**1**], whereas a monoarylated product, 2,2,2-trifluoro-1,1-bis(4-methoxyphenyl)-1-methoxyethane (**4**), was formed quantitatively in molar ratios of [TFSA]/[**1**] over 7. When molar ratios of [TFSA]/[**1**] between 2 and 6 are used, a mixture of two products **3** and **4** is isolated in all cases (Scheme 1), where the product ratio of **4** to **3** increases by increasing the ratio of [TFSA]/[**1**], which means that the ratios of the rate constants, k_1/k_2, for the monoarylation (k_1) and diarylation steps (k_2) are between 0 and 100.[16]

Scheme 1. Model Reactions of 2,2,2-Trifluoro-4′-methoxyacetophenone (**1**) with Anisole (**2**) in Various Molar Ratios of [TFSA]/[**1**]

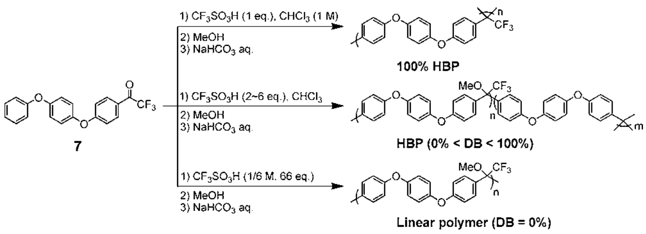


These results suggest that the condensation of **1** with **2** in an equimolar ratio of [TFSA]/[**1**] proceeds via intermediate carbocation **5** (Scheme S1 in the SI), whose reactivity is much higher than that of starting compound **1**. Therefore, when **5** is formed in a mixture, it will be readily attacked by **2** to provide diarylated product **3**, where k_2 is larger than k_1. A detailed kinetic study is presented in SI (Scheme S2, Figures S2−S4). On the other hand, in molar ratios of [TFSA]/[**1**] over 7, k_2 becomes considerably smaller than k_1. Olah et al. reported that TFSA is a highly ionizing and low-nucleophilicity medium.[17] Unexpectedly, the electrophiles primarily formed were activated by further superelectrophilic solvation, which is an interaction between the electrophile and a Lewis/Brønsted superacid. Such interaction of these cations can exist only in a superacid medium, resulting in extremely reactive dication species in the condensed state. According to Olah's report, we speculate that diprotonated carbonyl compound **6** (Scheme S3 in the SI) in the superacid condenses with **2** to give intermediate **5**, whose reactivity is lower than that of dication **6**; that is, k_2 becomes smaller than k_1.

Based on these model reactions, self-polycondensation of AB_2 monomer **7** was carried out with various molar ratios of [TFSA]/[**7**] in $CHCl_3$ at room temperature (Scheme 2). The polymerizations proceeded in a homogeneous state and were completed within several hours. The polymers were isolated by pouring the polymer

10.1021/ja105213r

Scheme 2. Synthesis of Hyperbranched Polymers with Controlled Degree of Branching from 0 to 100%



solutions into methanol. The results are summarized in Figure S6 and Table S1 (see SI). A 100% HBP is produced in an equimolar ratio of [TFSA]/[**7**], whereas a linear polymer (DB = 0%) is obtained by using TFSA as a solvent. Moreover, HBPs with a DB of any percent between 0 and 100% are formed by changing the ratio of [TFSA]/[**7**].

A linear relationship between the molar ratio of [TFSA]/[**1**] and DB of HBPs was observed when the molar ratio of [TFSA]/[**1**] was adjusted from 1 to 6. We expect that a linear polymer (DB = 0) would be obtained when the molar ratio of [TFSA]/[**1**] is over 8.6 by extrapolation of the fitted straight line. However, the polymer precipitated during the polymerization with [TFSA]/[**1**] = 8.6, because of low solubility of the linear polymer in $\mathrm{CHCl_3}$. Therefore, only TFSA, which showed better solubility than $\mathrm{CHCl_3}$, was used as a solvent.

The structures of these HBPs were characterized by FT-IR and NMR spectroscopy. The FT-IR spectra of HBPs (Figures S7 and S8 in the SI) showed characteristic absorptions at 1712 cm^{-1} due to the stretching of the C═O group of terminal units. A very weak absorption due to the C═O group of terminal units is observed for the linear polymer (Figure S9 in the SI). The ^{1}H NMR spectra of the 100% HBP and the linear polymer together with those of **7** (terminal unit), **3** (dendritic unit), and **4** (linear unit) are presented in Figure S10 (see SI). The doublet peak for the *o*-phenyl proton (7g) next to the trifluoroacetyl group is observed at 8.1 ppm for **7**, and the characteristic methoxy protons (3a and 4d) for **3** and **4** appear at 3.8 and 3.3 ppm (Figures S10c and S10b), respectively. In the 100% HBP, the *o*-phenyl protons (HBP1a) are observed at 8.1 ppm, and the signal corresponding to the methoxy protons (4d) for the linear unit cannot be found at 3.3 ppm (Figure S10d). On the other hand, a linear polymer exhibits characteristic methoxy protons (LP1d) at 3.3 ppm, and a very small peak assignable to the end trifluoroacetyl group is observed at 8.1 ppm (Figure S10e).

^{1}H NMR spectra of HBPs with various DBs were shown in Figure 1. The DB of HBPs was determined by the ratio of the *o*-phenyl proton (HBP2a) at 8.1 ppm for the terminal unit and the methoxy protons (HBP2b) at 3.3 ppm for the linear unit. The DB of HBPs decreases by increasing the molar ratio of [TFSA]/[**7**], as expected from the results of the model reactions (Figure S5 in the SI).

The observed number-average molecular weights (M_n's), weight-average molecular weights (M_w's), and polydispersities of the polymers determined by SEC using polystyrene standards were in the range of 11 000−24 000 g/mol, 26 000−189 000 g/mol, and 1.8−10.2, respectively (Table S1 and Figure S11 in the SI). The M_w and radius of gyration (R_g) of the 100% HBP were measured by static laser light scattering (SLS) to obtain values of 301 500 g/mol and 13 nm, respectively. The M_w value determined from SEC (71 400 g/mol for the 100% HBP) was much smaller than that from SLS.[18] This discrepancy is usually observed for hyperbranched polymers, due to their highly branched and compact structures compared to linear counterparts.[19] The structures of polymers obtained were confirmed by FT-IR (Figure S7−S9 in the SI) and ^{13}C NMR spectroscopy (Figure S12−S14 in the SI).

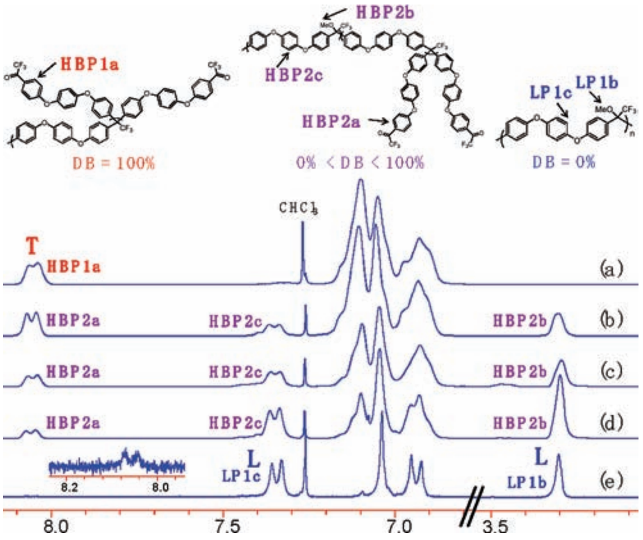


Figure 1. ^{1}H NMR spectra of HBPs with various DBs.

In conclusion, we demonstrated the first synthesis of a linear polymer, HBPs with various DBs, and 100% HBP by self-polycondensation of **7** in proper molar ratios of [TFSA]/[**7**]. These polymerizations relied on the change of the rate determination steps in the mono- and diarylation of 2,2,2-trifluoroacetophenone by changing the molar ratios of [TFSA]/[**7**]. These new findings will promote the synthesis of various series of HBPs with controlled DBs and their application to functional materials.

Acknowledgment. Y.S. thanks Yoshida Scholarship Foundation for the fundamental support.

Supporting Information Available: Full experimental details, elemental analysis, IR and NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233–1285.
(2) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685–1698.
(3) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183–275.
(4) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2679–2699.
(5) Voit, B.; Lederer, A. *Chem. Rev.* **2009**, *109*, 5924–5973.
(6) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4588.
(7) Maier, G.; Zech, C.; Voit, B.; Komber, H. *Macromol. Chem. Phys.* **1998**, *199*, 2655–2664.
(8) Smet, M.; Schacht, E. H.; Dehaen, W. *Angew. Chem., Int. Ed.* **2002**, *41*, 4547–4550.
(9) Fu, Y.; Vandendriessche, A.; Dehaen, W.; Smet, M. *Macromolecules* **2006**, *39*, 5183–5186.
(10) Fu, Y.; Oosterwijck, C. V.; Vandendriessche, A.; Kowalczuk-Bleja, A.; Zhang, X.; Dworak, A.; Dehaen, W.; Smet, M. *Macromolecules* **2008**, *41*, 2388–2393.
(11) Kono, S.; Sinananwanich, W.; Shibasaki, Y.; Ando, S.; Ueda, M. *Polym. J.* **2007**, *39*, 1150–1156.
(12) Sinananwanich, W.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2689–2700.
(13) Sinananwanich, W.; Higashihara, T.; Ueda, M. *Macromolecules* **2009**, *42*, 994–1001.
(14) Sinananwanich, W.; Segawa, Y.; Higashihara, T.; Ueda, M. *Macromolecules* **2009**, *42*, 8718–8724.
(15) Segawa, Y.; Sinananwanich, W.; Higashihara, T.; Ueda, M. *Macromolecules* **2008**, *41*, 8309–8311.
(16) Holter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298–309.
(17) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767–788.
(18) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 955–970.
(19) Peleshanko, S.; Gunawidjaja, R.; Petrash, S.; Tsukruk, V. V. *Macromolecules* **2006**, *39*, 4756–4766.

JA105213R