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"AB_2 + AC_2" approach to hyperbranched polymers with a high degree of branching†

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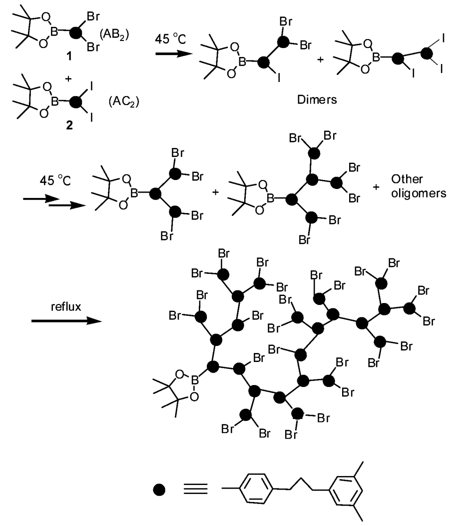
A novel one-pot "AB_2 + AC_2" approach based on palladium catalyzed Suzuki polycondensation was developed to prepare hyperbranched aryl/alkyl polymers with a high degree of branching.

Dendrimers and hyperbranched polymers have gained considerable scientific attention due to their unusual molecular structures and properties.[1] Dendrimers are mono-dispersed, well-defined, and highly branched macromolecules prepared by multistep reactions,[1] whereas hyperbranched polymers are irregularly branched and polydisperse macromolecules, which can be prepared by one-pot reaction of AB_n monomers.[2] Due to their structural similarity, dendrimers and hyperbranched macromolecules have some similar features such as good solubility, low viscosity when compared to their linear analogs, and large numbers of end groups. The main advantage of hyperbranched polymers over dendrimers is their easy preparation, which makes large-scale synthesis possible at a reasonable cost. The syntheses of many kinds of hyperbranched polymers have been well documented by excellent reviews.[2] A challenging goal in synthesis of hyperbranched polymers is control over their degree of branching (DB). Normally the DB varies from 0% for linear polymers and 100% for dendrimers, and for most hyperbranched polymers prepared from AB_2 monomers it is around 50%. In the literature some special techniques or reactions have been used to obtain high DB polymers. For example, Hawker *et al.* developed an AB_4 monomer route, which gave a hyperbranched polymer with DB up to 71%.[3] Ishida *et al.* synthesized a series of monomers AB_2, AB_4, and AB_8 and examined their polymerization results. They found that the DB increases with increasingly branched monomers. AB_2 monomers gave DB of only 32%, AB_4 ones gave 72%, and AB_8 gave 84%.[4] Another route for increasing DB was developed by Hult's[5] and Moore's groups.[6] They added a core molecule and adopted a pseudo-one-step reaction to prepare hyperbranched macromolecules with DB nearly 80%. There are only three examples reported with DBs close to 100%.[7]

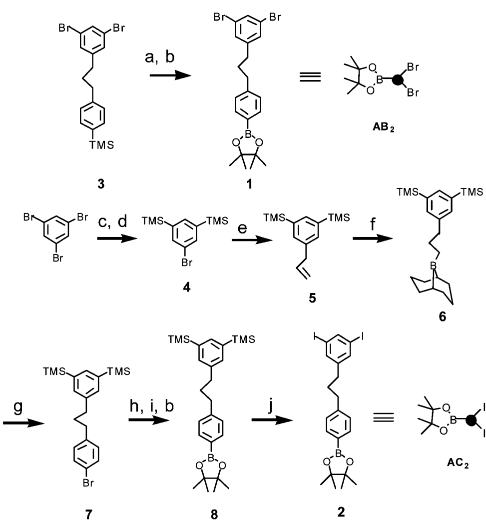
Hyperbranched polymers prepared by polymerization of AB_2 monomers are composed of dendritic (D), linear (L), and terminal (T) units. According to the definition given by Fréchet,[8] the DB is calculated by the following equation:

$$DB = (D + T)/(D + T + L)$$

Here we describe a novel "AB_2 + AC_2" approach to prepare hyperbranched polymers with a high DB (Scheme 1). The strategy was to minimize the fraction of L units and should lead to chemically relatively resistant aryl/alkyl-based structures. Monomers **1** and **2** were designed accordingly (Scheme 2). Suzuki polycondensation (SPC) was used for polymerization of the two monomers (Scheme 1).[9] It is well known that the reaction of arylboronic acid (or ester) proceeds at a higher rate with iodoaromatics than with bromoaromatics and also under especially mild conditions.[10] Ideally at 45 °C, only iodoaromatics undergo reaction. At this stage the predominant intermediates formed are oligomers, mostly composed of dendritic and terminal units as shown in Scheme 1. If the reaction temperature is further increased to reflux (about 65 °C), bromoaromatic compounds start to react and form higher molar mass polymers. Using the two monomers' rate difference, the



Scheme 1 *Reagents and conditions*: $Pd(PPh_3)_4$, aq. $NaHCO_3$, THF, 45 °C for 1 d, reflux for 1 d. (For detailed structures of the monomers see Scheme 2.)



Scheme 2 *Reagents and conditions:* a) BBr_3, CH_2Cl_2, r.t. b) Pinacol, CH_2Cl_2, reflux. c) *n*-BuLi, ether, −78 °C, 1 h. d) Trimethylsilyl chloride, −78 °C to r.t. e) $PdCl_2$, THF, allyl chloride, r.t. f) 9-BBN, THF, r.t., 2 d. g) 4-Bromoiodobenzene, $Pd(PPh_3)_4$, aq. NaOH, THF, r.t. h) *n*-BuLi, THF/ether, −78 °C to 0 °C. i) B(O-*i*-Pr)$_3$, −78 °C to r.t. j) ICl, CH_2Cl_2, r.t.

† Electronic Supplementary Information (ESI) available: experimental procedures and characterization of compounds. See http://www.rsc.org/suppdata/cc/b3/b306601k/

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whole polymerization process could be controlled, which will lead to a hyperbranched polymer with a high DB.

An alkylene spacer was introduced to make the polymer backbone more flexible and easier for determining the DB by ^{13}C NMR integration (*vide infra*). One-pot SPC of **1** and **2** was performed in a biphasic system THF/aqueous $NaHCO_3$ with $Pd(PPh_3)_4$ as catalyst precursor.[9–11] The reaction procedure was set as follows: first stirred at 45 °C for 1 d, and then refluxed for 1 d. A bromo-terminated hyperbranched polymer was obtained as a pale white solid material in 81% yield after precipitating from ether and freeze-drying from benzene. Weight-average molar mass (M_w) determined by gel permeation chromatography (GPC) calibrated with polystyrene standard was 13500 and polydispersity (PD) 2.22 (bimodal). A DB of 86 ± 10% was calculated from ^{13}C NMR integration (*vide infra*). As a contrasting reaction, SPC of monomer **1** went well and gave bromo-terminated hyperbranched polymers in a 69% yield with DB of 56 ± 10% (*vide infra*). M_w was up to 26500 and polydispersity (PD) was 1.41. The GPC shows a much smaller almost baseline separated peak at lower masses. When SPC of only the diiodo monomer was done, the polymers precipitated from the reaction mixture and could not be redissolved in any solvent. Limited solubility hampered sufficient characterization of iodo-terminated hyperbranched polymers.

^{1}H NMR spectra of polymers prepared from **1** + **2** and **1** are completely identical, and it was impossible to calculate the DB from proton integrations. In their ^{13}C NMR spectra, most signals in the aromatic region were difficult to identify due to overlapping and could not be used for integration. Fortunately the signals belonging to the middle alkylene carbons (circled in Fig. 1) were well separated for L, D, and T units. The ^{13}C NMR spectra used for integration were carefully recorded by using a longer pulse delay time (2 s) in order to account for the nuclei's different relaxation times. Some model compounds[12] were used to assign these carbons and the results are shown in Fig. 1. It is obvious that the fraction of L units decreased dramatically for polymers prepared from **1** + **2** (Fig. 1b) compared to the ones prepared from **1** only (Fig. 1a). It was also concluded from these spectra that all iodo groups had been consumed. The combustion results of both polymers also support the above conclusion.‡

The synthesis of **1** and **2** is outlined in Scheme 2. Compound **3**[13] was converted to boronic acid by treatment with BBr_3 in CH_2Cl_2, subsequent esterification with pinacol gave **1** as a white solid in a total yield of 65%. Starting from the commercially available 1,3,5-tribromobenzene, its treatment with *n*-BuLi at −78 °C and then quenching with TMSCl gave compound **4** in 99% yield.[14] **4** was converted to the corresponding Grignard reagent by treatment with Mg powder in THF,

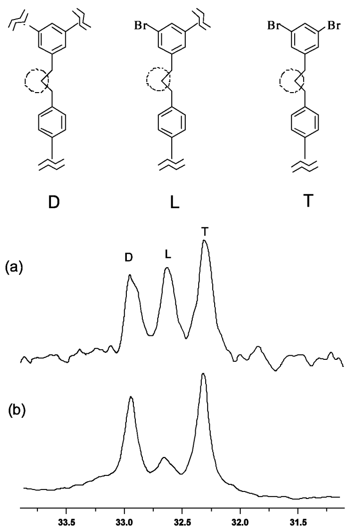

Fig. 1 ^{13}C NMR peak assignments for middle alkylene carbons of (a) polymers prepared from **1** and (b) polymers prepared from **1** + **2**.

followed by reaction with allyl bromide using $PdCl_2$ as a catalyst precursor affording **5** in 92% yield. Reaction of **5** with a 0.5 M solution of 9-BBN in THF at room temperature furnished the corresponding adduct **6**, which was used for coupling without further purification. The reaction of alkyl borane **6** with 4-bromoiodobenzene gave **7** in a 86% yield. Treatment of **7** in ether with *n*-BuLi at −78 °C and quenching with triisopropyl borate gave the corresponding boronic acid in 83% yield. Reflux of this boronic acid with pinacol in CH_2Cl_2 gave the corresponding ester **8**. Iodination of **8** with ICl in CH_2Cl_2 at room temperature afforded **2** as a white solid in 92% yield. Monomers **1** and **2** were unambiguously characterized with ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

In conclusion, hyperbranched aryl/alkyl polymers with high DB were prepared by using a novel one-pot AB_2 + AC_2 approach. The reaction temperature controlled the reaction process. At lower temperature boronic esters reacted with iodoaromatics much faster than with bromoaromatics, and formed an AB_n type hyperbranched intermediate with a high DB. After further temperature increase, bromoaromatics started to react and resulted in a higher molar mass polymer. The DB for hyperbranched polymers from **1** + **2** was 86 ± 10%, which is much higher than that for hyperbranched polymers synthesized from **1** only. For the former no iodo endgroups could be detected in their ^{13}C NMR spectra; the main difference between these two hyperbranched polymers seems to be their DB.

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Notes and references

‡ Polymers prepared from **1**: Anal. Calcd. for $(C_{15}H_{13}Br)_n$: C, 65.95; H, 4.80. Found: C, 65.70; H, 5.12. Polymers prepared from **1** + **2**: Anal. Calcd. for $(C_{15}H_{13}Br)_n$: C, 65.95; H, 4.80. Found: C, 66.08; H, 4.94%.

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