Effective Acid-Catalyzed Synthesis of 100% Hyperbranched Polyacenaphthenones

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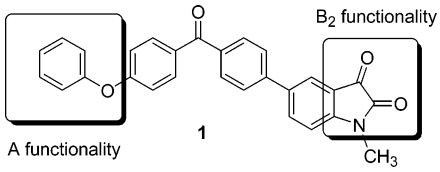
Hyperbranched polymers have attracted a lot of attention as readily available substitutes for dendrimers. Whereas the preparation of the latter requires a multistep synthesis, hyperbranched polymers can be obtained in a single step.[1] However, a degree of branching (DB) of 100%, which is a characteristic property of dendrimers, could, until recently, only be achieved by postsynthetic modification[2] or when certain requirements for the monomer are met.[3,4] Recently, we applied the acid-catalyzed condensation of isatins[5] with aromatic compounds for the synthesis of hyperbranched polymers with 100% DB.[6] The linear analogues had previously been shown to display a high T_g and excellent thermal stability.[7] We synthesized AB_2 monomer **1** (Chart 1) which could be polymerized by treatment with trifluoromethanesulfonic acid (TFSA). The resulting hyperbranched polymers were found to contain no linear units, and consequently, this strategy offers a promising one-step route toward hyperbranched polymers which are structurally more closely related to dendrimers. However, the preparation of the monomer necessitated the use of costly and highly toxic reagents and extensive chromatographic purification and was found to lack reproducibility. These serious drawbacks make the large-scale production of the AB_2 monomer **1** highly unlikely, which annihilates one of the main advantages of hyperbranched polymers over dendrimers. Besides the monomer synthesis, another hindrance to upscaling is the necessary use of the expensive and highly corrosive TFSA as solvent during the polymerization.

To provide a solution for the cited problems, a new AB_2 monomer **2** (Scheme 1), with an acenaphthenequinone and a phenoxybenzophenone residue as the B_2 and A functionality, respectively, was designed on the basis of a recent report on the synthesis of linear polymers by reactions of acenaphthenequinone with aromatic hydrocarbons.[8] The synthesis of monomer **2** started with a Friedel−Crafts acylation of diphenyl ether with *p*-anisoyl chloride, yielding 4-methoxy-4′-phenoxybenzophenone (**3**). After converting the methoxy into a hydroxyl group by treatment of **3** with BBr_3 in CH_2Cl_2, the obtained hydroxybenzophenone **4** was used to substitute 5-bromoacenaphthenequinone (**5**), formed by bromination of acenaphthenequinone,[9] yielding the desired monomer **2**. Whereas this synthesis requires four steps, identical to the route leading to monomer **1**, all the reactions are high yielding and well reproducible. The average yield of each step (88%) is much higher than for monomer **1** (70%), resulting in an ∼2.5 times increase of the total yield (60% vs 24%). Moreover, delicate chromatographic separations were not required to obtain monomer **2**, and neither toxic nor costly reagents were necessary. All the intermediates were separated by extraction and crystallization. As for the final monomer, the purification was performed by a filtration through silica followed by washing with solvent. Even more importantly, the polymerization of monomer **2** could be carried out in methanesulfonic acid (MSA), instead of the costly and highly corrosive TFSA. It is well-known that the acidity of the reaction medium plays a critical role in the superelectrophilic chemistry.[10] The change of a strong acidic medium to a weak one indicates that the superelectrophilic reactivity of the acenaphthenequinone-based monomer **2** is remarkably higher than in the case of the isatin analogues. This is probably because acenaphthenequinone, in contrast to isatin, does not contain a nitrogen atom adjacent to the carbonyl group, from which the carbonyl might delocalize the electron density and hence be deactivated.[8]

Chart 1. Our Initial Isatin-Based AB_2 Monomer Giving Rise to Fully Branched Hyperbranched Poly(arylene oxindoles)



Fully hyperbranched poly(arylene acenaphthenone) **6** could be obtained by treatment of the monomer **2** in MSA with a concentration of 100 mg/mL at room temperature for 2 days in a yield of about 85%. The resulting polymer was soluble in common solvents such as CH_2Cl_2, chloroform, and THF, and the molecular weight and polydispersity were determined by GPC in THF as $M_n = 7.0 \times 10^3$ g/mol and 1.53, respectively. The molecular weight could be increased through raising the acidity of the reaction medium by adding TFSA into the MSA solvent. For instance, a polymer with molecular weight $M_n = 9.0 \times 10^3$ g/mol could be acquired by polymerization of the monomer **2** (20 mg/mL) in a 1:1 MSA/TFSA mixture. However, precaution against gelation should be taken in this high reactivity medium. Either excessive TFSA in the solvent (as demonstrated using a MSA/TFSA 1:2 mixture) or too high monomer concentration (as demonstrated by polycondensation at 100 mg/mL) resulted in insoluble cross-linked polymers. In contrast to the behavior of monomer **1**, higher temperatures were found not to facilitate the polymerization of the monomer **2** but lead to decomposition. It is likely that the acenaphthenequinone is not stable enough in the acidic medium at high temperature.

Because both the 1- and 2-carbonyl groups of monomer **2** could take part in the superelectrophilic polymerization, three kinds of repeating units can be expected in the resulting polymer **6**, 1,1-diaryl units (D1), 2,2-diaryl units (D2), and terminal units (T), as shown in Scheme 1. To determine the abundance of these respective units in polymer **6**, model compounds **7** and **8**, corresponding to D1 and D2, respectively, were prepared by one-pot condensation of monomer **2** with 1-nitro-4-phenoxybenzene (Chart 2). By analyzing the ^1H NMR spectra of the monomer **2**, the model compounds, and polymer **6** (Figure 1), it was found that all the repeating units have well-separated characteristic proton signals which could be used to identify them. The key signals are found at 8.51, 7.57, and 8.31 ppm and correspond to the 6-H of the acenaphthenequinone moiety of the terminal units, the 8-H of the dendritic units D1, and the 6-H of the dendritic units D2, respectively. Using the integration of these signals, the percentage of the repeating units could be estimated. Half of the units are terminal units, and the

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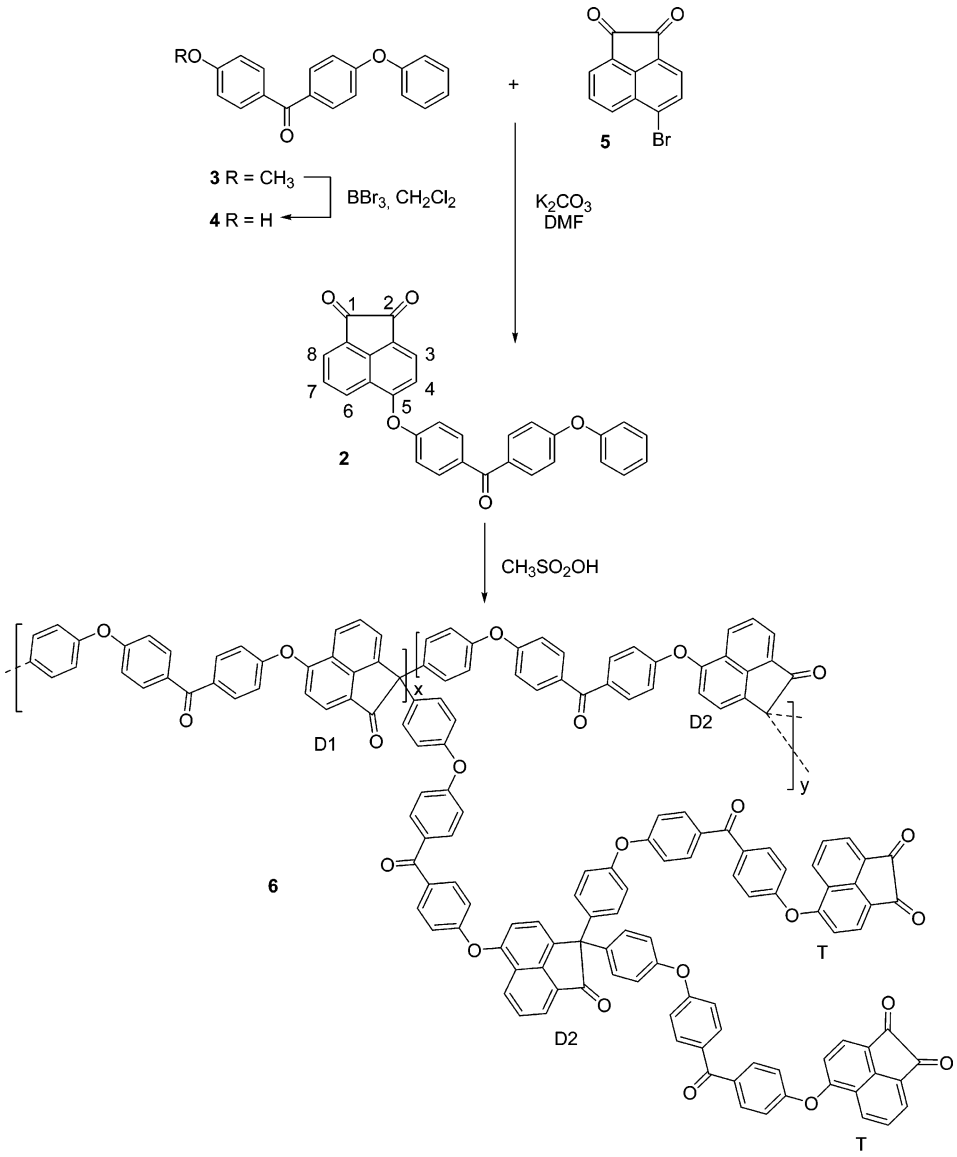
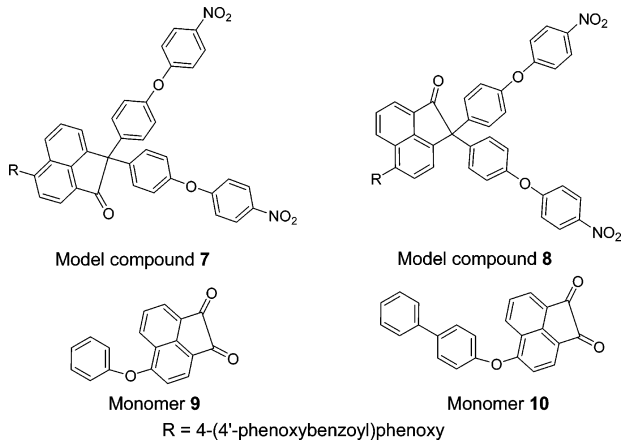
Scheme 1. Synthesis of Monomer 2 and Its Polycondensation to Hyperbranched Polymer 6



abundances of the D1 and D2 units are approximately 33% and 17%, respectively. This is consistent with the fully hyperbranched structure of polymer **6**, as only in this case the percentage of terminal groups could reach 50% due to the absence of linear units. The amount of D1 is almost twice that of D2, indicating that the 1-carbonyl group has a substantially higher reactivity than the 2-carbonyl group. This can be explained on the basis of the electron-donating effect of the oxygen in the 5-position, which predominantly decreases the reactivity of the 2-carbonyl group. Moreover, all the proton

Chart 2



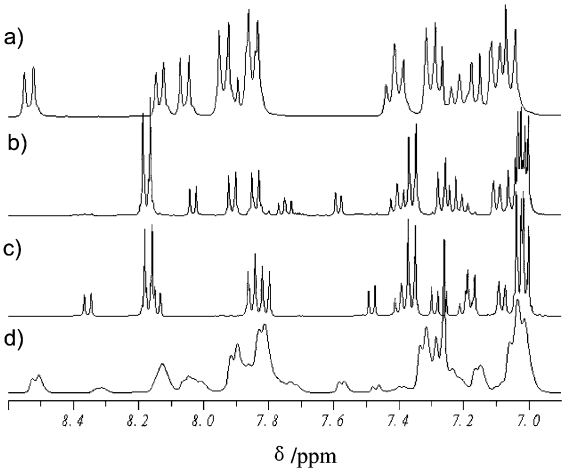
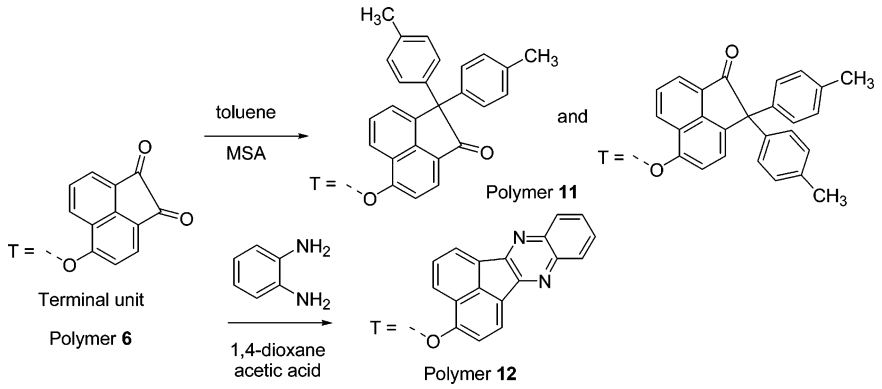


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of (a) monomer **2**, **(**b) model compound **7**, (c) model compound **8**, and (d) polymer **6**.

Scheme 2. Modification of the Terminal Groups T of Polymer 6



signals could be assigned to the above three kinds of units, confirming the DB of 100% and the high regiospecificity in the polymerization, in agreement with the observations on the linear analogues.[8]

For comparison, monomers **9** and **10** (Chart 2) were synthesized by substitution of bromoquinone **5** with the commercially available phenol and 4-phenylpenol, respectively. Whereas their synthesis necessitated only three steps instead of four in the case of monomer **2**, careful column chromatography was required to purify the monomers, and the yields were much lower compared with monomer **2**. Monomer **9** could be self-condensed in MSA, yielding the corresponding polymer with a molecular weight of 4.5×10^3 g/mol and a polydispersity of 1.3. Considering that the molar mass of monomer **9** is only little more than half that of monomer **2**, the polymerization degree of this polymer is comparable with that of polymer **6**. Furthermore, the analysis of the ^{1}H NMR spectra evidenced that the polymer presents a similarly well-defined and fully hyperbranched structure as polymer **6**. In contrast, all efforts to polymerize monomer **10** in MSA failed, as only monomer was recovered from the reaction solution. Polymerization only occurred when more acidic solvent mixtures such TFSA/MSA 1:1 were applied. However, an insoluble gel, instead of soluble hyperbranched polymers, was produced. It is likely that the phenyl group of **10** is not reactive enough against protonated acenaphthenequinone fragments in MSA and that the regioselectivity in stronger acidic media is not sufficient to avoid additional substitution, resulting in cross-linking. The above results suggest that the phenoxy group, rather than phenyl, is the eligible candidate for the A residue in AB_2 monomers for this kind of acid-catalyzed polycondensation to hyperbranched polymers with a DB of 1.

As versatile modification possibilities of the periphery of hyperbranched polymers are highly desirable in order to be able to tune their physical properties, two approaches were explored to modify the acenaphthenequinone residues at the periphery of the polymer **6**, as shown in Scheme 2. Both the superelectrophilic reaction with arenes and the condensation with aromatic 1,2-diamines were carried out, yielding polymers **11** and **12**, respectively. The preparation of polymer **11** could also be carried out in a one-pot two-step approach in which the required arene was added to the reaction mixture after the usual 2 days of polymerization. All conversions could be confirmed by ^{1}H NMR spectroscopy. In the spectrum of the polymer **11**, the characteristic signal of the terminal units, the 6-H of the acenaphthenequinone moiety at 8.51 ppm, was shifted and split into a signal at 8.22 ppm and a second one between 7.98 and 8.08 ppm overlapping with other polymer signals, which could again be assigned to 2,2-diaryl and 1,1-diaryl acenaphthenone, respectively. Their ratio is also approximately 1 to 2, analogous to that of D2 to D1. In the case of polymer **12**, the original 6-H signal of the terminal acenaphthenequinone units was shifted to 8.39 and overlapped with the signal of 6-H in D2, confirming the formation of the expected quinoxaline residue. Through the latter modification, functional fluorescent chromophores, in casu quinoxalines, could easily be incorporated onto the periphery of the hyperbranched scaffold. The resulting polymer displays a yellow-green fluorescence in both the solid phase and solution. The fluorescence spectrum in chloroform exhibits two emission bands at 455 and 485 nm, which might be ascribed to monomeric species and aggregates, respectively. The latter are likely to be formed due to the high density of the chromophores at the polymer rim. To the best of our knowledge, this is the first report of hyperbranched polymers with quinoxalines grafted at the periphery, which could have potential applications in the field of electron transport layers in light-emitting devices and sensors.[11]

In conclusion, we have significantly improved our original approach toward fully hyperbranched polymers. The monomer synthesis can be accomplished without the use of toxic and costly reagents, and all the reactions are well producible and high yielding. Moreover, MSA could be used as the solvent during polymerization instead of the expensive and highly corrosive TFSA, making the strategy more suitable for scale-up. Fluorescent polymers were easily acquired by converting the peripheral groups into quinoxalines. A further study of their photophysical properties and potential applications is underway.

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

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