Synthesis of Hyperbranched Poly(arylene ether) from Monomer Containing Nitro Group: Kinetically Controlled Growth of Polymer Chain through Dynamic Exchange of End Functional Groups

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The control of structures and functions of synthetic macromolecules in three dimensions has been a subject of intensive research during the past two decades due to the unique characteristics of three-dimensional macromolecules and their high application potential in many areas. For example, dendrimers[1] and hyperbranched polymers[2] are nanosized globular macromolecules with a highly branched structure as well as many reactive functional groups at chain ends. Hyperbranched polymers, which do not have a perfect symmetric structure but can be prepared through one-step polymerization of AB_n ($n \geq 2$) type monomers, are more readily available than comparable dendrimers that require multistep syntheses.[1−3] Highly branched polymeric structures are also attainable through the polymerization of A_2 and B_3 monomers.[4] However, the $A_2 + B_3$ polymerization requires careful control of the reaction to produce soluble hyperbranched polymers.[5] Various polymerization systems based on the unequal reactivity of functional groups have been investigated to facilitate the formation of AB_2 type intermediates which are further polymerized to a hyperbranched polymer.[6] Such attempts generally involve the formation of two different chemical bonds to produce the hyperbranched polymers with alternating linkages, such as hyperbranched poly(amide−imide)s,[6c] hyperbranched poly(amine−ester)s,[6d] and hyperbranched poly(urea−urethane)s.[6e,f] Previously, we reported the controlled nucleophilic aromatic substitution reaction (S_NAr) of BC type monomer (5-fluoro-2-nitrobenzotrifluoride; reactivity: B (fluoro group) > C (nitro group)) with A or A_2 type phenolate for the formation of two aromatic ether linkages.[7] The nitro group activated by the trifluoromethyl group at the ortho position had a strong electron-withdrawing capability, enabling the displacement of other (leaving) groups at the para position before it was displaced. In this study, unusual growth of a hyperbranched polymer was investigated with A_3 + BC (generally denotable as B_3 + A*A) and A_2C (B_2A) monomer systems containing nitro groups.

A previous report[7] on the selective and sequential displacement of the fluorine group and the nitro group of 5-fluoro-2-nitrobenzotrifluoride provides a basis for the synthesis of the hyperbranched poly(arylene ether) containing pendent trifluoromethyl groups (CF_3-HPAE1) from 1,1,1-tris(4-hydroxyphenyl)ethane (A_3) and 5-fluoro-2-nitrobenzotrifluoride (BC), as shown in Scheme 1. The polymerization was carried out via one-pot method, but in a sequential manner—the selective fluorine displacement followed by the nitro displacement. Fluorine displacement of 5-fluoro-2-nitrobenzotrifluoride with 1,1,1-tris(4-hydroxyphenyl)ethane was carried out in DMSO at 80 °C for 4 h in the presence of K_2CO_3, and then the reaction mixture was subjected to the nitro displacement reaction at 170 °C for 6 h. The polymerization proceeded homogeneously without gelation or precipitation at a concentration of 10 wt % monomers.

The analysis of the reaction mixture after the fluorine displacement reaction revealed that the specific intermediates were accumulated preferentially, but not exclusively.[8] Not only the desired intermediate (**1**) but also two other intermediates (**2** and **3**) were formed. The ratio of three intermediates, i.e., mono- (**1**, A_2C), di- (**2**, AC_2), and trisubstituted (**3**, C_3) compounds, and the remaining A_3 type monomer was about 47:23:2:28. The situation of this system became more complicated during the nitro displacement reaction because the severe transetherification occurred at the chain ends of the growing polymers, i.e., where the ether linkages were activated by the strong electron-withdrawing nitro group at the para position.[9] As shown in Scheme 2, any of the nitro-substituted benzene rings of the growing polymer chains could be transferred to another one through the transetherification until all of the nitro groups disappeared by the nitro displacement reaction, resulting in the change of the two types of growing species (from A_xC_y and A_zC_w to $A_{x-1}C_{y+1}$ and $A_{z+1}C_{w-1}$, respectively). In this system, the functional groups at the chain ends of growing species were dynamically exchanged through the transetherification, preventing the consecutive nitro displacement reaction.

In another set of experiments, the A_3 + BC polymerization mixture was taken via syringe at a certain time interval during the nitro displacement and subjected to GPC measurement after precipitation into water in order to monitor the molecular weight development of the growing hyperbranched polymer chains.[8] Despite the occurrence of the transetherification, the weight-average molecular weight (M_w) continuously increased up to 104 kDa after 6 h. Since the transetherification occurred at the chain ends, not in the main chains,[10] it did not reduce the molecular weight of the growing polymers. To our knowledge, this is the first example of kinetically controlled growth of the hyperbranched polymer chains with dynamic exchange of the end functional groups. The molecular weight distribution increasingly broadened throughout the polymerization, which was consistent with Flory's theoretical predictions for highly branched systems.[3,11]

To clarify the role and the effectiveness of the transetherification reaction during the polymerization of the above A_3 + BC system, the controlled experiment was carried out with A_2C system. As shown in Scheme 1, the hyperbranched poly(arylene ether) with the same repeating unit (CF_3-HPAE2) was synthesized through the nitro displacement of the A_2C type monomer (**1**). For comparison, the same polymerization condition was employed for both A_3 + BC and A_2C systems.

Spectroscopic analyses did not show any detectable differences between the two hyperbranched poly(arylene ether)s synthesized from the two different systems.[8] FTIR, ^{1}H NMR, and ^{13}C NMR spectra of CF_3-HPAE1 showed the same patterns as those of CF_3-HPAE2. ^{1}H NMR spectra of the both polymers

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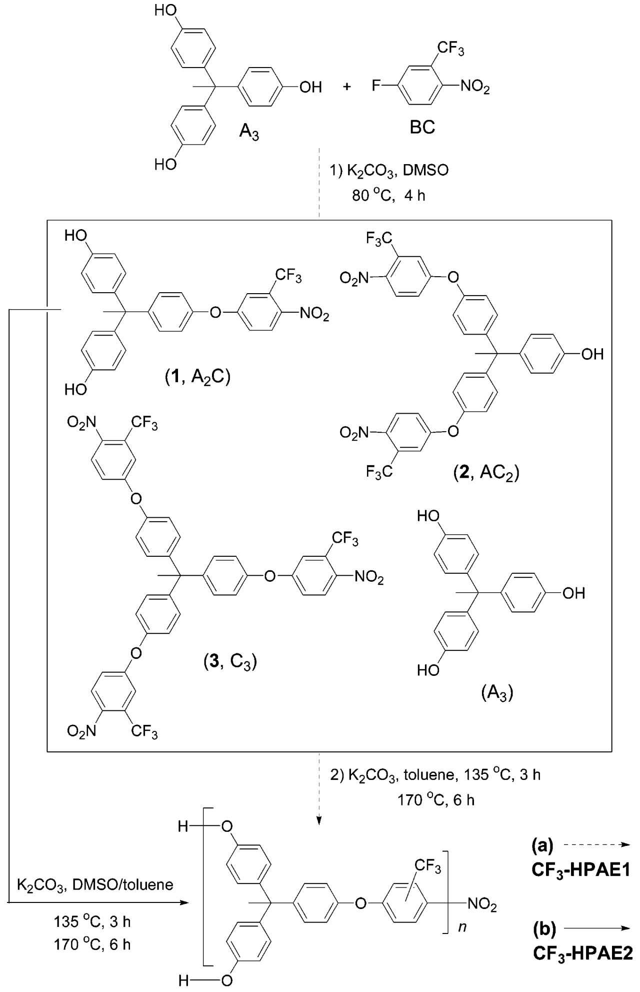
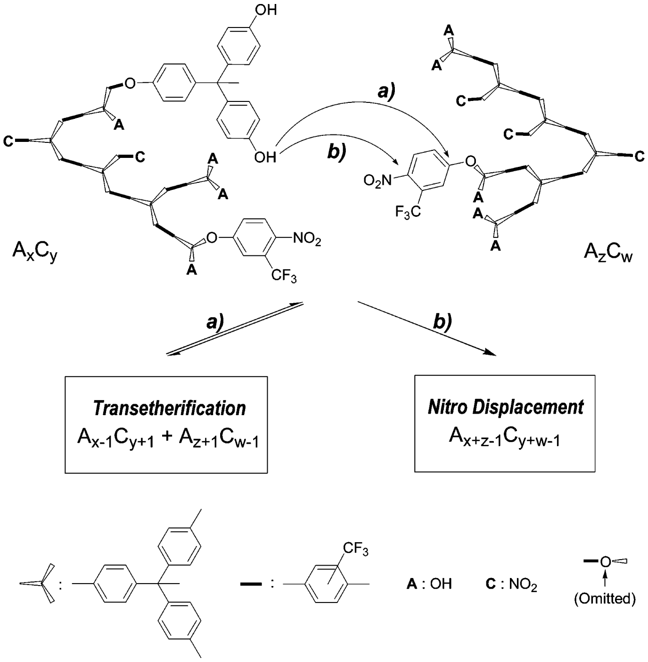
Scheme 1. Synthesis of Hyperbranched Poly(arylene ether)s from Monomers Containing Nitro Group: (a) via Selective and Sequential S_NAr (Preferential Fluorine Displacement Followed by Nitro Displacement) Reaction of A_3 and BC Type Monomers; (b) via Nitro Displacement Reaction of A_2C Type Monomer



Scheme 2. Transetherification Competing with Nitro Displacement Reaction at Ends of Growing Polymer Chains



showed the peak corresponding to the protons of hydroxy-substituted benzene rings, but the spectra did not show any peaks corresponding to the protons of nitro-substituted benzene rings. The degree of branching (DB, the number of dendritic and terminal units divided by that of total units) of the hyperbranched polymers determined from ^{13}C NMR peaks was 0.52 for CF_3-HPAE1 and 0.51 for CF_3-HPAE2.

The properties of CF_3-HPAE1 were quite similar to those of CF_3-HPAE2.[8] Both of the polymers showed good solubility in common organic solvents, such as acetone and THF as well as polar aprotic solvents (NMP, DMAc, and DMSO), and were dissolved in toluene, chlorobenzene, and chloroform on heating. The glass transition temperature (T_g) of CF_3-HPAE1 measured by DSC was 189 °C, which was slightly lower than that (194 °C) of CF_3-HPAE2. 10% weight loss temperatures (T_{d10}'s) of CF_3-HPAE1 and CF_3-HPAE2 measured by TGA were 473 and 479 °C in air, respectively. The slight difference between T_g's and T_{d10}'s of the two hyperbranched poly(arylene ether)s may be a result of the different molecular weights of the two polymers (inherent viscosity: 0.21 for CF_3-HPAE1 and 0.24 for CF_3-HPAE2). The refractive indices of each polymer film spin-coated on silicon substrate were measured with a prism coupling apparatus having two laser sources at 1310 and 632.8 nm. When measured at the wavelength of 1310 nm, the film of CF_3-HPAE1 showed the same refractive index ($n = 1.575$) as the film of CF_3-HPAE2 did ($n = 1.575$). But, the refractive indices measured at the wavelength of 632.8 nm were slightly higher than those measured at the wavelength of 1310 nm ($n = 1.599$ for CF_3-HPAE1 and $n = 1.598$ for CF_3-HPAE2). Both of the polymer films showed the low birefringences (Δn) below 0.003.

It has been reported that the hyperbranched polyimides that have the same repeating unit but are synthesized from different systems ($A_2 + B_3$ and AB_2 systems) have different microstructures and show different properties.[12] For example, T_g of the hyperbranched polyimide from $A_2 + B_3$ system was much (over 50 °C) higher than that of the hyperbranched polyimide from the AB_2 system.[12b,c] On the other hand, the hyperbranched poly(amide−imde) from the $A_2 + B^*B_2$ system, where AB_2 type intermediates had been exclusively produced, exhibited nearly identical microstructure and properties to that from the AB_2 system.[6c] The microstructures and the properties of CF_3-HPAE1 and CF_3-HPAE2 clearly indicate that the transetherification, which occurred in both $A_3 + BC$ and A_2C systems, had a great influence on the growth of the polymer chains. Regardless of the initial types, the transetherification produced various types (A_xC_y types) of growing species whose functional groups were dynamically exchanged during the polymerization, resulting in the same growing pathway of polymer chains from different systems. Thus, the "end-selective transetherification" did not significantly affect the molecular weight but had a great influence on the growing mechanism, the structure, and the property of the hyperbranched polymer.

It should be noted that both the $A_3 + BC$ and A_2C polymerization at higher monomer concentration (25 wt %) produced a gel. The same polymerization behavior from two different systems also indicated the same growing pathway of polymer chains through the transetherification. In addition, the concentration effect on the polymerization behavior implied that intramolecular cyclization (intramolecular nitro displacement) occurred in our system, as also reported in other $A_2 + B_3$ and AB_2 systems.[5d−g,13] Our deduction was further supported by the GPC result mentioned above, since the number-average molecular weight (M_n) of growing polymer chains did not significantly increase after a certain time (around 30 kDa after

4 h). Several $A_2 + B_3$[5f] and AB_2[13c] polymerization systems that underwent significant intramolecular cyclization reported the plateau in the M_n value of the growing polymer chains. The intramolecular cyclization might play a central role to produce a soluble hyperbranched polymer without gelation, while the "end-selective transetherification" kinetically hampered the consecutive intermolecular nitro displacement reaction that leads to the formation of three-dimensional cross-linked network. On the basis of the fact that the dilution of monomers favors the cyclization, we are currently investigating the variation in the microstructure of the hyperbranched polymer depending on the polymerization concentration.

In summary, hyperbranched poly(arylene ether) (CF_3-HPAE1) was synthesized from A_3 and BC type monomers through the selective and sequential S_NAr reaction, the preferential displacement of the fluorine followed by the nitro displacement. The microstructure and properties of CF_3-HPAE1 were same as those of CF_3-HPAE2 synthesized from A_2C type monomer, indicating that the transetherification, which made all the end functional groups dynamically exchangeable, had a great influence on the growth of the polymer chains. The synthetic methodology described here provides a basis for the facile preparation of 3-dimensional macromolecules with a highly branched (hydrophobic) aromatic ether backbone containing trifluoromethyl substituents in the main chain and numerous (hydrophilic) phenolic groups at the chain ends, which are expected to find numerous applications, especially as a polymeric micelle or an optical waveguide material.

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Supporting Information Available: Details of the experimental procedures, the spectral data for the synthesized compounds, FTIR and NMR spectra, TGA and DSC thermograms, refractive index data, and GPC traces of the synthesized polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The detailed experimental procedure and data are in the Supporting Information.

(9) The transetherification competing with the nitro displacement reaction at the chain ends was clearly indicated by the previous model reaction of 4-nitro-3-trifluoromethyldiphenyl ether with *m*-cresol.[7] The further analysis of the mixture after the model reaction revealed that the ratio of *m*-cresol moieties substituted at the 2-position and 5-position of benzotrifluoride ring was about 50:50.

(10) 2-Trifluoromethyldiphenyl ether, the model compound having the ether linkage activated by the trifluoromethyl group at the ortho position, did not react with *m*-cresol even at 170 °C,[8] supporting that the growing polymers did not undergo the transetherification in their main chains.

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