

"Click" Long Seesaw-Type A $\sim\sim$ B $\sim\sim$ A Chains Together into Huge Defect-Free Hyperbranched Polymer Chains with Uniform Subchains

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 Supporting Information

Hyperbranched polymers have attracted much interest because of their useful chemical and physical properties, resulting from their branching topology and a high number of end groups.^{1–4} For a given weight concentration, their smaller hydrodynamic volume and functional periphery lead to a variety of current and potential applications, including their usages as coatings and resins additives,^{5,6} viscosity modifiers,^{7,8} and novel carriers.^{4,9–11} Commonly, hyperbranched polymers are synthesized through the step-growth approach, such as polycondensation, addition step-growth reactions and cycloaddition, or the chain-growth approach, including the self-condensing vinyl copolymerization and the ring-opening multibranching polymerization. The detailed methodologies have been extensively reviewed.^{1–4,12}

Hyperbranched polymers with short subchains behave like small rigid and hard "balls" so that their properties are mainly related to their size. On the other hand, for hyperbranched polymers with longer subchains, proper microscopic conformation variation and entanglement can greatly affect their macroscopic properties. For example, the swollen and collapse of long subchains of a hyperbranched polymer additive in a solution or dispersion can alternate its macroscopic viscosity by a factor of hundreds. This is why the research and development of various hyperbranched polymers made of subchains longer than the entanglement length has attracted much attention in the past two decades. People coined different terms to describe them as Hyper-Macs,¹³ arborescent graft polymers,¹⁴ and dendrigrafts.¹⁵ Using the chain-growth approach, Gnanou et al.¹⁶ and Dworak et al.¹⁷ tried to develop different techniques for the preparation of hyperbranched chains with a desired architecture. However, their methods involved a multistage and time-consuming process, inevitably resulting in broadly distributed subchains. While in the step-growth approach, AB₂ type of macromonomers can be interconnected into hyperbranched chains with a "controllable" architecture through polyesterification^{18–20} and poly-Williamson coupling reaction¹³ between two reactive A and B functional groups. Note that for a given weight concentration a solution of long initial macromonomer chains contains a very limited number of reactive A and B groups. In order to effectively couple them together, Pan et al.²¹ utilized alkynyl–azide polycycloaddition to make hyperbranched polystyrene (PSt) chains with claimed short uniform subchains. On the other hand, Hutchings

et al.²² described an iterative convergent strategy to make dendritically branched chains using a multistaged Williamson coupling process.

In reality, there exist two types of AB₂ macromonomers—Y-type: two reactive B groups are at one end and A is at the other end; seesaw-type: each chain end is attached with one reactive B group and A is in the middle. They lead to different topologies of hyperbranched polymers. Using Y-type macromonomers, some of B groups inevitably remain unreacted during the coupling reaction. Each of them extends the subchain between two neighboring branching points by one macromonomer length because it remains as a small side substitute on the subchain, resulting in hyperbranched polymers with subchains with a broad length distribution, as shown in Scheme 1a. Note that using a reaction between a linear macromonomer A $\sim\sim$ A and a cross-linker B₃ with three functional groups is similar to using Y-type macromonomers. On the contrary, using seesaw-type macromonomers, one will be able to obtain "perfect" hyperbranched chains with uniform subchains,²³ as shown in Scheme 1b. Note that such a resultant structure is different from a dendrimer because it lacks a starting center point. Also, note that such formed hyperbranched chains are polydisperse in their overall molar mass. One has to further fractionate them into a series of hyperbranched chains with uniform subchains but different overall molar masses by using precipitation or preparative chromatography.

Further, there is a possible intrachain coupling between A and B groups, leading to a defect (self-looping). However, using the seesaw type of macromonomers could lead to no more than one defect per hyperbranched chain. Unfortunately, less attention has been paid to such a big difference in final topologies of resultant hyperbranched polymer chains using different types of macromonomers. To our knowledge, there also lacks a systematic study of effects of length and concentration of seesaw-type macromonomer chains on the polymerization (coupling) kinetics and the intrachain self-looping.

In the current study, we first prepared linear seesaw-type polystyrene macromonomers with three different lengths using

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the well-known atom transfer radical polymerization (ATRP) and end-group transformation. These seesaw-type macromonomers have one alkynyl group in the middle and one azide group at each chain end, denoted as $[N_3 \sim \text{PSt} \sim \text{alkynyl} \sim \text{PSt} \sim N_3]$.

The “click” reaction between N_3 and alkynyl groups leads to hyperbranched polystyrene chains with uniform subchains defined by the initial macromonomers preparation, as shown in Scheme 1.

The ATRP initiator of 1,3-dibromomethyl-5-propargyloxybenzene (DBMPB) was prepared with dimethyl 5-hydroxyisophthalate as a starting reagent. The ATRP polymerization of styrene was performed with CuBr/bpy as a catalyst and DBMPB as an initiator in tetrahydrofuran (THF) at different monomer/initiator ratios in order to obtain narrowly distributed macromonomer polystyrene chains with different lengths and a polydispersity index (M_w/M_n) around 1.10. Two bromide end-groups were converted into two azide groups with NaN_3 in DMF. The average azide functionality of each seesaw-type $[N_3 \sim \text{PSt} \sim \text{alkynyl} \sim \text{PSt} \sim N_3]$ chain was higher than 99%. Therefore, three seesaw-type macromonomers with number-average molar masses of 4.40×10^3 , 1.00×10^4 and 1.80×10^4 were obtained, denoted as seesaw-4.4K, seesaw-10K, and seesaw-18K, respectively. The details of synthesis and characterization are listed in the Supporting Information.

The self-polycondensation of seesaw-type polystyrene macromonomers with different chain lengths were conducted with CuBr and N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA) as catalysts under vacuum at 45°C for different durations. The CuBr and PMDETA were removed from resultant hyperbranched polystyrene chains by the repeating precipitation. The molar mass distributions of hyperbranched chains were respec-

tively determined by a gel permeation chromatograph (GPC) with a refractive index (RI) detector using a conventional linear polystyrene calibration and also with a multiangle laser light-scattering (MALLS) detector. The weight-average molar mass ($M_{w,\text{MALLS}}$) of hyperbranched polystyrene chains measured by a combination of GPC and MALLS was used to monitor the reaction kinetics.

Figure 1 shows two serial GPC-RI curves of hyperbranched polystyrene chains prepared from self-polycondensation of two seesaw-type macromonomers with different lengths. It is clear that as the self-polycondensation proceeds, the distribution of resultant hyperbranched polystyrene chains becomes broader and broader and shifts to the left, i.e., larger hydrodynamic volume and higher molar mass. In Figure 1B, a new peak with an apparent number-average molar mass of $M_n \approx 1.7 \times 10^7$ g/mol appears after 2 days. The peaks related to high molar masses increase and become more and more dominant. Similar multimodal distributions of hyperbranched polymer chains with lower molar masses were also previously reported in the literature.^{13,18,20}

In order to compare reaction kinetics of different macromonomer chains, hereafter we define a weight-averaged degree of self-polycondensation as $(DP)_w = M_{w,\text{hyperbranched}}/M_{w,\text{macromonomer}}$ based on GPC-MALLS measurements. Figure 2 shows that the self-polycondensation is fast in the first 2 days and significantly slows down after it, presumably due the decrease of macromonomer concentration in the reaction mixture. After reacted

Scheme 1. Comparison of Hyperbranched Chains Made of Two Types of Macromonomers

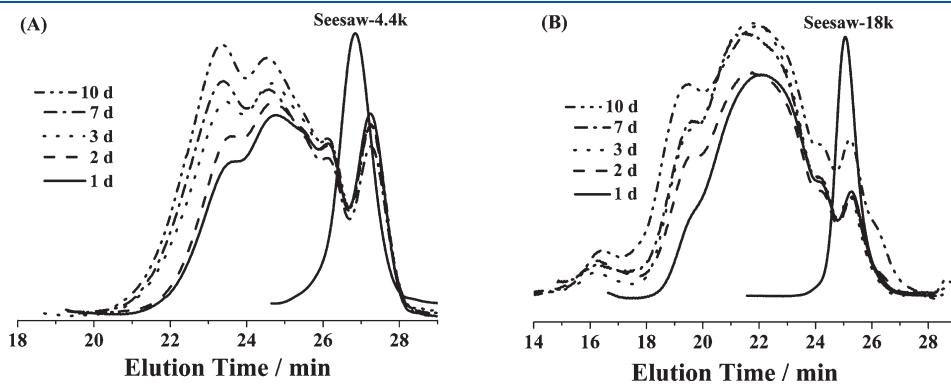
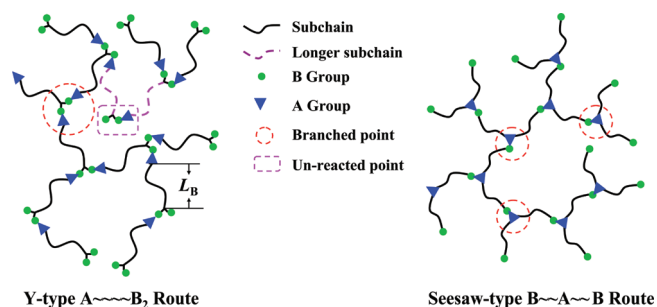


Figure 1. GPC curves of hyperbranched polystyrene chains respectively prepared from two different seesaw-type macromonomers after different reaction times, where $C_{\text{macromonomer}} = 0.5$ g/mL, $T = 45^\circ\text{C}$, and THF is solvent.

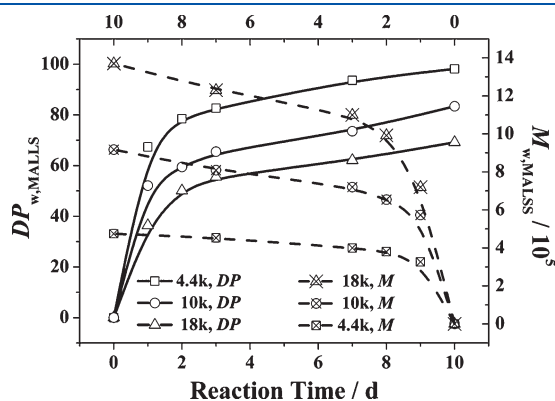


Figure 2. Self-polycondensation kinetics of three different macromonomers monitored in terms of weight-averaged degree of self-polycondensation, defined as $(DP)_w = M_{w,\text{hyperbranched}}/M_{w,\text{macromonomer}}$, where $C_{\text{seesaw}} = 0.5$ g/mL and $T = 45^\circ\text{C}$.

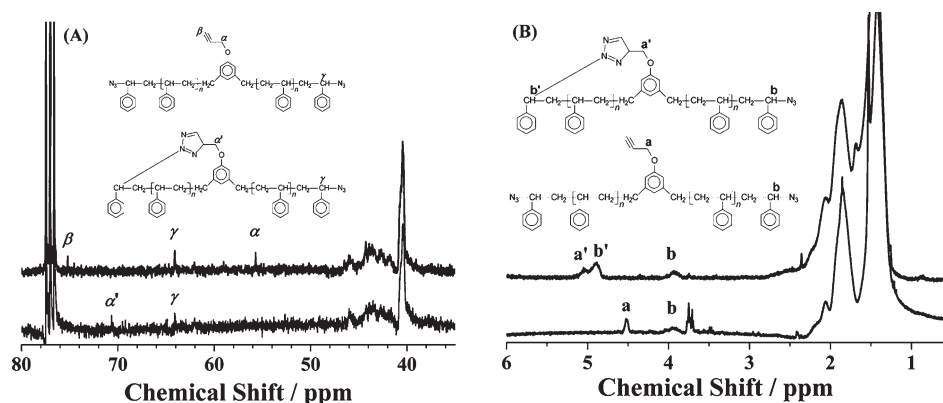


Figure 3. (A) ^{13}C NMR and (B) ^1H NMR spectra of seesaw-4.4K and its cyclic analogue.

for 10 days, the values of $(\text{DP})_{w,\text{MALLS}}$ reach 98.1, 83.4, and 69.2 for seesaw-4.4K, seesaw-10K, and seesaw-18K, respectively. As expected, the self-polycondensation of longest seesaw-18K has the lowest rate in $(\text{DP})_{w,\text{MALLS}}$ increase, which can be attributed to two reasons as follows: (1) there are a less number of reactive groups for a given weight concentration, and (2) reactive groups of longer macromonomer chains are more easily wrapped inside so that their reactivity decreases.

The increase of the weight-average molar mass ($M_{w,\text{MALLS}}$) has two stages. Initially, the increase of $M_{w,\text{MALLS}}$ is sharp but slows down after one onset time point. For a given reaction time, the degree of polycondensation increases but overall molar mass decreases as the hyperbranched chains become shorter. Previously, Hutchings et al. prepared hyperbranched chains using the Williamson coupling reaction with a long Y-type polystyrene macromonomer ($M_n = 3.73 \times 10^4$ g/mol) and obtained $(\text{DP})_w \approx 14$ after 24 h,¹³ while with a polybutadiene macromonomer ($M_n = 1.58 \times 10^4$ g/mol), $(\text{DP})_w \approx 40$ after 6 h.²⁴ Using a modified Williamson coupling reactions with cesium carbonate as the base, Hutchings et al.⁷ also obtained hyperbranched chains with $(\text{DP})_w \approx 60$, starting with a Y-type macromonomer ($M_n = 2.80 \times 10^4$ g/mol). Pan et al.²¹ used a much short Y-type macromonomer ($M_n = (1-7) \times 10^3$ g/mol) and the azide-alkyne click reaction and increased $(\text{DP})_w$ up to ~ 65 for their shortest macromonomer. Therefore, our current self-polycondensation of longer linear seesaw-type macromonomer chains via the effective alkyne-azide click reaction resulted in large hyperbranched chains with uniform subchains.

Figure 1A also shows that for shortest macromonomer chains the macromonomer peak is more clearly shifting to the right during the self-polycondensation. Hutchings et al.¹³ observed a similar phenomenon in one of their previous reports; namely, there was a shoulder appearing on the right side of their Y-type macromonomer peak, which was attributed to the self-looping of individual linear Y-type macromonomer chains because the cyclization led to a relatively smaller hydrodynamic volume. Further evidence on the intrachain cyclization of linear macromonomer chains comes from a combination of the dissolution fractionation and NMR analysis. Each resultant hyperbranched polystyrene sample was fractionated using the dissolution with ethyl ether as a solvent. The GPC analysis confirms that the first dissolution fraction (lowest molar mass, presumably the cyclized macromonomer chains) has a symmetrical peak with an apparent molar mass very similar to the corresponding macromonomer.

The chemical structure of the first dissolution fraction was further characterized by ^1H NMR and ^{13}C NMR spectra.

Figure 3 reveals that seesaw-4.4K and the first dissolution fraction (after reaction for 10 days) have some differences in their ^1H NMR and ^{13}C NMR spectra. Namely, seesaw-4.4K has signals of the methine protons next to the azide group at 3.95 ppm and the methylene protons next the alkynyl group at 4.52 ppm, while the first dissolution fraction has no signal at 4.52 ppm and a weaker signal at 3.95 ppm but two additional signals at 5.05 and 4.89 ppm appear. In the ^{13}C NMR spectra, seesaw-4.4K has signals of the alkynyl carbon at 75.3 ppm and the methylene carbon next to the alkynyl group at 55.7 ppm, while the first dissolution fraction has no signal at these two positions and the signal of the methine carbon next to the azide group becomes weaker. These results clearly indicate that some of linear macromonomer chains are cyclized via the click reaction between one azide group and the alkynyl group in the middle of the chain.

In order to find effects of the macromonomer length and concentration on the cyclization, we mathematically split and extracted the macromonomer peak from the multipeak distribution by assuming that the molar mass of macromonomers follows a Gaussian distribution and estimated the weight fraction of unreacted or cyclized macromonomer chains in the resultant product in terms of the area ratio (A_m/A_h) of the extracted macromonomer peak to the entire peak of resultant hyperbranched chains. After a long reaction time, A_m/A_h still remains a constant in each case; namely, 0.17, 0.15, and 0.10 for seesaw-4.4K, seesaw-10K, and seesaw-18K, respectively, decreasing as the macromonomer becomes longer. The results indicate that some of macromonomers are not able to further react to hyperbranched chains, presumably due to the fact that following reason.

Scheme 1B shows that each resultant hyperbranched chain could contain no more than one active alkynyl group that is most likely hidden inside. On the other hand, if a macromonomer chain undergoes an intrachain "click" reaction (cyclization) to form a loop, there is only one reactive azide group left so that those cyclized macromonomer chains will have little chance to further react with large hyperbranched chains with only one alkynyl group hidden inside. This is why the content of those cyclized macromonomer chains in the distribution remains a constant even after an extended reaction time of many days. With increasing the initial macromonomer concentration from 0.1, 0.5 to 1.0 g/mL, the value of A_m/A_h decrease from 0.22, 0.16 to 0.14. As expected, an increase of the initial macromonomer

concentration in the reaction mixture should increase the interchain clicking probability and make the intrachain self-looping of individual macromonomer chains more difficult so that its content decreases, as shown in Figure S6B.

In summary, the current study has demonstrated that ultra-large “defect-free” hyperbranched chains with long uniform subchains can be effectively prepared from narrowly distributed linear seesaw-type $[N_3 \sim \text{alkynyl} \sim N_3]$ macromonomer polymer chains via the “click” reaction. Our results have also clarified that 10–20% of linear seesaw-type macromonomer chains can undergo an intrachain clicking reaction (cyclization) to form an intrachain loop. An increase in either the macromonomer length or concentration can reduce such self-looping. Note that each resultant hyperbranched chain could have no more than one intrachain loop (defect), and such a possible defect has nearly no effect on the conformation and properties of hyperbranched chains, especially when the average degree of the self-polycondensation is high. In comparison with other types of macromonomers, seesaw-type macromonomers $[B \sim A \sim B]$ are superior in the preparation of hyperbranched polymers with long and uniform subchains because using other types of macromonomers inevitably leads to heterogeneous subchains with different lengths due to some unreacted functional groups. Armed with such “defect-free” hyperbranched polystyrene chains, we are able to further fractionate each of them into a series of hyperbranched chains with uniform subchains but different overall molar mass so that we will be able to, *for the first time*, study the structure–property relationship of large hyperbranched chains.

■ ASSOCIATED CONTENT

S Supporting Information. Details of preparing seesaw-type PSt macromonomers and hyperbranched polystyrene chains with uniform subchains. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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