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Tunable intramolecular cyclization and glass transition temperature of hyperbranched polymers by regulating monomer reactivity

Qingfu Ban, Heng Chen, Yi Yan, Nan Tian, Jie Kong*

MOE Key Laboratory of Space Applied Physics and Chemistry, Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

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ABSTRACT

In this work, the dialkynyl-functionalized A_2 monomers with different alkyls and aromatic backbones were synthesized and employed as construction units to produce multi-component $A_2 + B_3$ type hyperbranched polymers via copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC). The alkyl and aromatic backbones between two alkynyl groups were designed as hexyl (C_6), dodecyl (C_{12}), phenyl (Ar) and diphenyl (Ar_2) to regulate monomer reactivity for investigating its effect on intramolecular cyclization and glass transition temperature (T_g). It was found that both the increase of backbone rigidity and the decrease of backbone length can enhance monomer reactivity. In addition, the differences of monomer reactivity can greatly influence the backbone compositions of hyperbranched polymers. High monomer reactivity can lead to high content of corresponding backbones, which can further control the degree of intramolecular cyclization and T_g of hyperbranched polymers. Thus, regulating monomer reactivity is an effective way to tune hyperbranched topology, backbone composition and physical properties.

1. Introduction

The control of polymer backbones has always received more attentions in polymer building, since they are a matrix materials to regulate bulk or composite properties of polymers [1–5]. As a fascinating research branch, the backbone-controlled polymerization strategies, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) polymerization and etc., have been developed and widely used to produce polymers with precise structural sequence, composition, molecular weight and functional groups, and diversely linear, star, brush, cyclized/knotted, hyperbranched topology [6–20]. Further, these structural features could endow the fabricated polymers with great potentials in coating [21–25], processing aid [26], carbon or ceramic precursors [27–30], and drug or gene carriers [31–33].

Apart from these controlled polymerization methods, the monomer reactivity also plays very important role in regulating polymer architectures. For example, the monomer reactivity ratio is a very important parameter to predicate polymer compositions, determining the tendency of self-polymerization or copolymerization reactivity [34]. The monomer-activated anionic ring opening polymerization (ROP) can lead to different monomer reactivity in contrast to conventional oxyanionic ROP, producing tapered polymer structures [35]. Very recently, the latent monomer with protected monomer reactivity was ingeniously synthesized and used

* Corresponding author.
E-mail address: kongjie@nwpu.edu.cn (J. Kong).

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to generate sequence-controlled polymers by carrying out programmable temperature changes [36]. More interestingly, the difference of monomer reactivity can be used to control hyperbranched topology [37–41].

However, there is always a competition between chain growth and intramolecular cyclization in the polymerization procedure for preparing AB_n-type ($n \geq 2$) or $A_m + B_n$-type ($m \geq 2$, $n \geq 3$) hyperbranched polymers, resulting in an inevitable topological defect [42–44]. Therefore, the influence of monomer reactivity on controlling the degree of intramolecular cyclization is a very important issue for hyperbranched topology. In order to better analyzing the degree of intramolecular cyclization, some topological parameters have been developed and confirmed effective to characterize the degree of intramolecular cyclization, e.g., average number of cyclic structures (ANC) [45], terminal index (TI) [46], and macro-cyclic index (m-CI) [47]. Furthermore, numerous efforts on the polymerization routes, monomer concentration, feed ratio and feed sequences have been explored to well control the degree of intramolecular cyclization [48]. Especially, the structural difference of monomer backbones can also be used to control the degree of intramolecular cyclization, such as the increased backbone rigidity and decreased backbone length can relatively decrease the degree of intramolecular cyclization [45,47]. Also, the monomer reactivity can be greatly influenced by structural difference of monomer backbones, which provide us a facile route to control the degree of intramolecular cyclization by regulating monomer reactivity, i.e. controlling the backbone composition of hyperbranched polymers. On the other hand, the control of hyperbranched topology is able to alter their properties, such as T_g. It has been reported that the T_g of hyperbranched polymers can be influenced by many structural factors, such as polymer compositions, molecular weight, terminal groups, degree of branching (DB) and monomer sequence [49–60]. Therefore, regulating monomer reactivity should also have some undiscovered influences on T_g of the fabricated polymers because of the composition change of polymer backbones.

In the present work, the dialkynyl-functionalized A_2 monomers with different alkyl and aromatic backbones were designed and used as tunable building units to produce $A_2 + B_3$-type hyperbranched polymers via CuAAC polymerization. The influence of alkyl and aromatic backbones on monomer reactivity, and their influences on backbone composition, degree of intramolecular cyclization and T_g of these fabricated polymers were carefully investigated.

2. Experimental

2.1. Materials

1,6-Hexanediol (99.5%; Aladdin), 1,12-dodecanediol (99%, Aladdin), hydroquinone (99%, Aladdin), 4,4′-diphenol (99%, Aladdin), 1,1,1-tris(hydroxymethyl)ethane (98%, TCI), propargyl bromide (99%; Aladdin), 4-chlorobutyryl chloride (98%, Aladdin), sodium hydroxide (99.5%, J & K Chemical), sodium azide (98%; Amresco), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%; Aladdin), copper bromide (99%; Aladdin), calcium hydride (CaH_2, 99%; Aladdin) and triethylamine (TEA, 99%;Alfa) were all used as received without further treatment. Anhydrous DCM was freshly distilled under reflux using CaH_2. Anhydrous THF was freshly distilled under reflux using sodium/benzophenone.

2.2. Synthesis

2.2.1. Synthesis of A_2 and B_3 monomers

The schematic synthesis of A_2 and B_3 monomers was presented in Fig. S1. For A_2 monomers, 1,6-hexanediol, 1,12-dodecanediol, hydroquinone and 4,4′-diphenol were directly modified by propargyl bromide under the catalysis of NaOH. After refluxing for 24 h, the synthesized A_2 monomers were successfully purified via column chromatography or recrystallization. In detail, the DCM/petroleum ether (1/4, v/v), DCM/n-hexane (1/2, v/v) and DCM/petroleum ether (1/2, v/v) were used as eluent to purify A_2-C_6, A_2-C_{12} and A_2-Ar, respectively. In addition, A_2-Ar_2 was purified by recrystallization in methanol. For the B_3 monomer, a similar synthesis procedure was used according to the previous report [47].

2.2.2. Synthesis of hyperbranched polymers

CuAAC reaction was used to synthesize the hyperbranched polymers. In detail, for the hyperbranched polymers with one-part A_2 monomer backbones, the A_2 monomer (1 mmol), B_3 monomer (1 mmol), PMDETA (0.1 mmol) and 5 mL dried DMF were charged into a 25 mL flask. After evacuating with a high vacuum pump and filling with argon atmosphere three times, CuBr (0.1 mmol) was added and sealed. The mixture was stirred at room temperature for 24 h, and then evaporated to remove DMF. The residue was diluted with DCM and passed through a short neutral alumina column. Then, the filtrated organic solution was concentrated and precipitated into an excess of diethyl ether to obtain the hyperbranched polymers (yield: > 90%). For the hyperbranched polymers with bicomponent A_2 monomer backbones (yield: > 90%), two kinds of A_2 monomers were used in the $A_2 + B_3$ polymerization system (Fig. 1). The synthesis procedure was similar to the preparation of hyperbranched polymers with one-part A_2 monomer backbones.

2.3. Characterization

2.3.1. Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) measurements were recorded using a Bruker AV400 spectrometer (Bruker Bio-Spin, Switzerland) with $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard.