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Chain-Growth Click Polymerization of AB_2 Monomers for the Formation of Hyperbranched Polymers with Low Polydispersities in a One-Pot Process**

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Abstract: *Hyperbranched polymers are important soft nanomaterials but robust synthetic methods with which the polymer structures can be easily controlled have rarely been reported. For the first time, we present a one-pot one-batch synthesis of polytriazole-based hyperbranched polymers with both low polydispersity and a high degree of branching (DB) using a copper-catalyzed azide–alkyne cycloaddition (CuAAC) polymerization. The use of a trifunctional AB_2 monomer that contains one alkyne and two azide groups ensures that all Cu catalysts are bound to polytriazole polymers at low monomer conversion. Subsequent CuAAC polymerization displayed the features of a “living” chain-growth mechanism with a linear increase in molecular weight with conversion and clean chain extension for repeated monomer additions. Furthermore, the triazole group in a linear (L) monomer unit complexed Cu^I, which catalyzed a faster reaction of the second azide group to quickly convert the L unit into a dendritic unit, producing hyperbranched polymers with $DB = 0.83$.*

Nanostructured polymers with branched architectures and multiple chain-end functionalities are an important type of soft nanomaterial that can be used in a variety of applications, ranging from specialty additives and nanomedicines to catalysis.[1] Among the various nanostructured polymers that have been reported to date, hyperbranched polymers have received considerable interest owing to their attractive features, which include one-pot syntheses, arborescent structures, and a high degree of functionalization.[2] Although hyperbranched polymers are often considered as analogues of dendrimers,[3] current challenges associated with their synthesis include the lack of structural control in the polymer product, which significantly limits their potential applications as advanced soft nanomaterials.

The structural difference between hyperbranched polymers and dendrimers is rooted in their different synthetic procedures. Typical dendrimer syntheses use protected AB_2 monomers for iterative reaction and deprotection steps to achieve complete conversion of peripheral B groups with no monomer–monomer reactions in the growth of each generation.[3a] As a result, the dendrimers exhibit a spherical shape with a high degree of branching ($DB = 1$) and uniform structures ($M_w/M_n = 1$). For comparison, hyperbranched polymers are typically synthesized in homogeneous solutions by the one-pot step-growth polymerization of unprotected AB_2 monomers,[4] or by the step-growth/chain-growth polymerization of AB* inimers (containing initiator fragment B* and monomer vinyl group A in one molecule).[5] These synthetic features in hyperbranched polymers lead to bimolecular (monomer–monomer, monomer–polymer, and polymer–polymer) reactions and result in products that exhibit lower DBs and significantly broader molecular-weight distributions than dendrimers.

To produce hyperbranched polymers with controlled structures without sacrificing the advantageous features of a one-pot synthesis, several strategies have been developed to switch the polymerization to a chain-growth mechanism[6] or to carry out the polymerization in dispersed confined space.[7] In particular, methods based on the slow addition of AB_2 monomers into a dilute solution containing multifunctional cores[6d,e] and the design of special monomer/core pairs with different reactivities[6b,g–i] are often applied to achieve chain-growth polymerization with exclusive monomer–polymer reactions. However, low molar ratios of the monomers to the multifunctional cores ($<100{:}1$) were practically used in both methods to suppress undesired monomer–monomer reactions,[6d,8] preventing the synthesis of high-molecular-weight polymers. Furthermore, the delicate monomer addition techniques and the sophisticated monomer design with unequal reactivities render large-scale syntheses difficult.

Herein, we present a one-pot one-batch solution polymerization of AB_2 monomers to produce hyperbranched polymers with high molecular weights ($M_n \approx 240\,\mathrm{kg\,mol^{-1}}$), high degrees of branching ($DB = 0.83$), and a low polydispersity ($M_w/M_n < 1.3$) using copper-catalyzed azide–alkyne cycloaddition (CuAAC)[9] reactions. An AB_2 monomer that contained one alkyne group and two azide groups (Scheme 1) reacted according to a chain-growth polymerization mechanism with a linear increase in polymer molecular weight and a decrease in polydispersity with monomer conversion. Although CuAAC reactions have already been used for the synthesis of dendrimers[10] and hyperbranched polymers,[11] a one-pot one-batch CuAAC polymerization system that follows a chain-growth mechanism and produces uniform hyperbranched polymers has never been reported.

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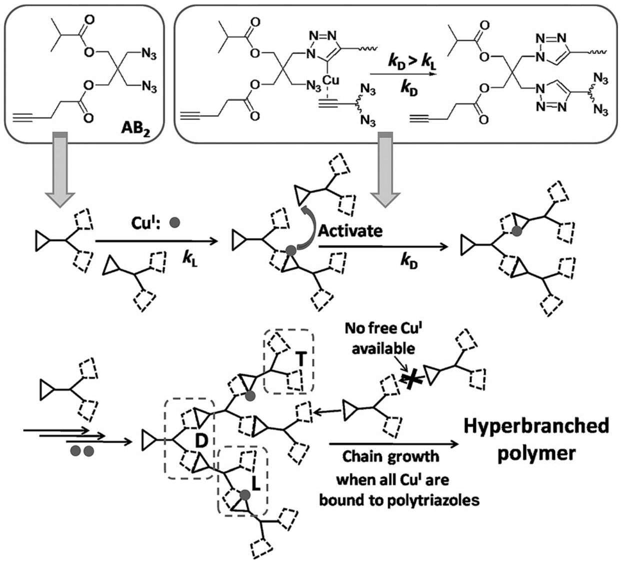

Scheme 1. Synthesis of hyperbranched polymers with low polydispersity and a high degree of branching by chain-growth CuAAC polymerization.

The CuAAC polymerization of the AB$_2$ monomer, 2,2-bis(azidomethyl)-3-(but-3-ynyloxy)propyl isobutyrate (Scheme 1; see also the Supporting Information, Figure S1), was carried out in DMF using $CuSO_4{\cdot}5\,H_2O$/ascorbic acid as the catalyst at feed ratios of $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0 = 100{:}1{:}5$. As shown in Figure 1 A, the conversion of the AB$_2$ monomer increased with reaction time and reached 96% after three hours, indicating a rapid polymerization with efficient click coupling reactions. The molecular-weight evolution of the hyperbranched polymers at different conversions was monitored using THF size exclusion chromatography (SEC). The elution chromatograms in Figure 1 B show monomodal peaks with a clean shift towards higher molecular weights with AB$_2$ conversion. The absolute number-average molecular weights ($M_{n,\text{MALLS}}$) of the hyperbranched polymers were determined by multi-angle laser light scattering (MALLS) and increased linearly with conversion (Figure 1 C). At 96% conversion, an $M_{n,\text{MALLS}}$ value of 71.1 kg mol^{-1} with a polydispersity of $M_w/M_n = 1.27$ was determined for the final product. Meanwhile, the apparent molecular weight of the polymer product based on linear poly(methyl methacrylate) standards was only $M_{n,\text{RI}} = 25.4$ kg mol^{-1}, indicating a compact molecular structure of the hyperbranched polymers.

Compared to many one-pot solution polymerizations of AB$_2$ monomers described in the literature,[12] our results in Figure 1 reveal intriguing features of a chain-growth polymerization, which was a primary target in the experimental design based on the knowledge that triazole groups formed in situ can complex with Cu^I species.[9,13] As catalytic amounts of copper, with a feed ratio of $[CuSO_4{\cdot}5\,H_2O]_0/[AB_2]_0 = 1{:}100$, were used, it was hypothesized that all Cu^I species were bound to the formed polytriazole oligomers at very low conversions, so that subsequent CuAAC reactions cannot occur between two monomers (Scheme 1). In other words, after a short period of random monomer–monomer reactions to form enough triazole groups, there were no or only very few free Cu^I species in solution. These Cu^I-containing polytriazole oligomers functioned as in situ generated multifunctional cores and reacted with the remaining AB$_2$ monomers in polymer–monomer reactions, leading to a chain-growth polymerization mechanism. Therefore, slow monomer addition is not necessary in this system, as the monomers in solution have to diffuse into the proximity of the polymer to interact with the triazole-bound copper complexes and undergo a click reaction; hyperbranched polymers are thus obtained.

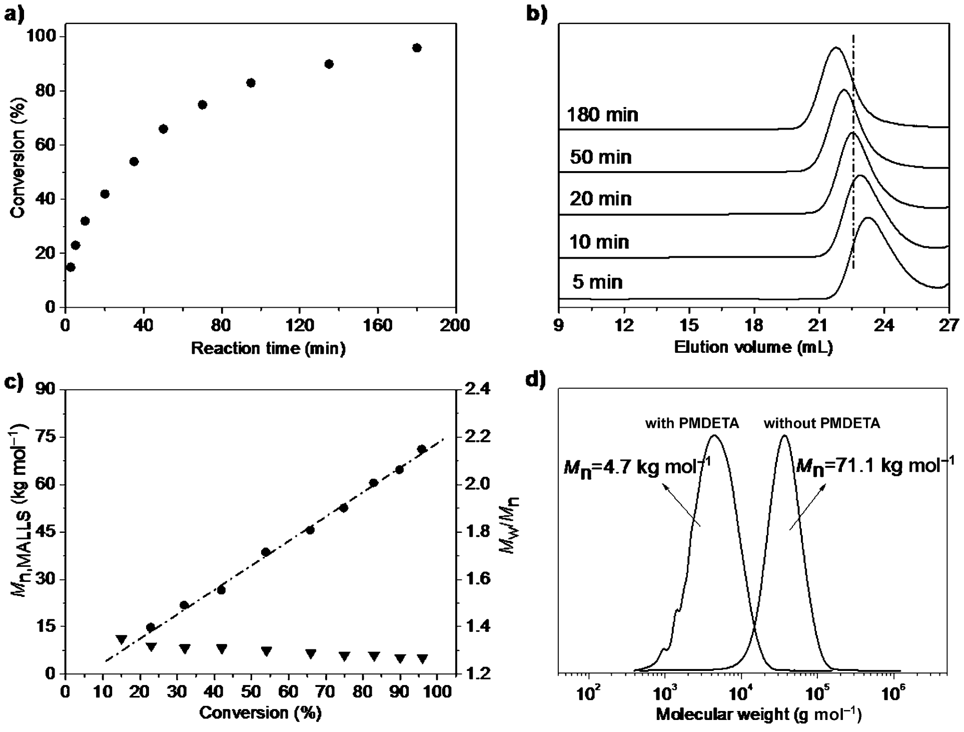

Figure 1. a) Kinetic analysis, b) SEC traces, and c) evolution of the number-average molecular weight ($M_{n,\text{MALLS}}$) and polydispersity index (M_w/M_n) of hyperbranched polymers synthesized by CuAAC polymerization of AB$_2$ monomers at feed ratios of $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0 = 100{:}1{:}5$ in DMF at 45 °C, $[AB_2]_0 = 0.5$ mol L^{-1}. d) Comparison of the SEC traces of hyperbranched polymers synthesized with and without the use of PMDETA (1 equiv) under otherwise identical conditions: $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0/[\text{PMDETA}]_0 = 100{:}1{:}5{:}y$ with $y = 1$ or 0 in DMF at 45 °C.

This hypothesis was further supported by ^{1}H NMR spectroscopy studies, which monitored the complexation of Cu^I with triazole groups in mixtures of polytriazole hyperbranched polymers and Cu^I catalysts at a molar triazole/Cu^I ratio of 3:1. Complexation of Cu^I to triazole groups was complete immediately after the addition of the Cu^I species to a solution of the polytriazole hyperbranched polymers in DMF, as confirmed by the clear change in the chemical shift of the triazole protons in the NMR spectrum (Figure S2B).[14] It is therefore reasonable to expect that the CuAAC polymerization at an initial ratio of $[AB_2]_0/[Cu]_0 = 100{:}1$ would produce enough triazole groups at low monomer conversion (< 10%) to complex all added Cu^I species and essentially switch the polymerization mechanism from step growth to chain growth. Afterwards, the CuAAC polymerization system had constant polytriazole core concentrations, and no monomer–monomer side reactions occurred, as confirmed by the linear increase in molecular weight with conversion that was observed at conversions of > 15% (Figure 1C). To corroborate our hypothesis, the CuAAC polymerization was also conducted in the presence of *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA, a strong Cu^I ligand; 1 equiv).[14] This process exhibited step-growth polymerization features and produced polymers with low molecular weights (Figure 1D), because the PMDETA ligands led to dissociation of the Cu^I/triazole complexes and freed the Cu^I catalyst into solution (Figure S2C).

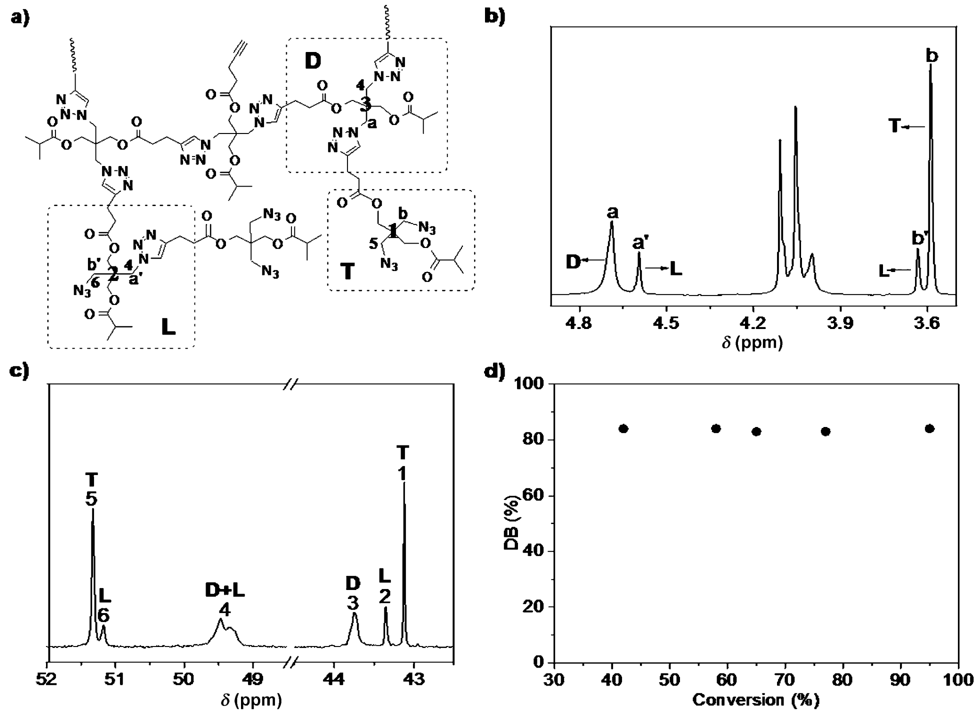

Figure 2. a) Representative structure and b) ^{1}H NMR and c) inverse-gated decoupled ^{13}C NMR spectra of a purified hyperbranched polymer sample at 96% monomer conversion. d) DB evolution as a function of monomer conversion. Polymerization conditions: $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0 = 100{:}1{:}5$ in DMF at 45 °C, $[AB_2]_0 = 0.5\ \text{mol}\,L^{-1}$.

A high degree of branching (i.e., a high fraction of dendritic (D) units in the hyperbranched polymer) was achieved because the Cu^I/triazole complex catalyzes the fast reaction of the neighboring azide group in the same monomer unit (Scheme 1), which was first reported by Rodionov and Finn in their mechanistic study of ligand-free CuAAC reactions.[15] The higher reactivity of the second azide group quickly consumed linear (L) units that were formed from terminal (T) units after reaction of one azide group (Scheme 1) and generated a high fraction of D units in the hyperbranched polymers.

The DB value of the hyperbranched polymer was determined by ^{1}H NMR spectroscopy with the assistance of ^{13}C NMR and 2D NMR spectroscopy for peak assignments (Figures S3 and S4). A typical ^{1}H NMR spectrum of the hyperbranched polymer shows well resolved peaks that represent the characteristic protons from the D, L, and T units for reliable integration (Figure 2B). Using the equation $DB = (D + T)/(D + T + L)$,[16] the DB value of the hyperbranched polymer was calculated to be 0.84, indicating that the second azide group in the L unit was ten times more reactive than the azide groups in the T unit.[17] Similar DB values were also obtained by peak integration in an inverse-gated decoupled ^{13}C NMR spectrum (Figure 2C). Analysis of all other samples withdrawn from the polymerization reaction mixture at different conversions (42–96%; Figure 2D) gave constant DB values of 0.83–0.84 independent of the conversion.

After studying the polymerization mechanism, we next explored the robustness of this novel chain-growth CuAAC polymerization method in terms of the tunability of the molecular weight and the feasibility of chain extension. In this study, four CuAAC polymerization reactions with the same monomer concentration of $[AB_2]_0 = 0.5\ \text{mol}\,L^{-1}$ but different monomer/Cu catalyst ratios ($[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0 = x{:}1{:}5$, $x = 25$, 65, 100, or 150) were carried out. Decreasing the amount of the Cu catalyst led to an increase in the molecular weight of the hyperbranched polymers at similar conversions (Figure 3). These results indicate that a smaller amount of the Cu catalyst decreases the molar concentration of polytriazole cores formed at the initial stage of the polymerization process, and results in hyperbranched polymers with higher molecular weights. Meanwhile, the DB value of the hyperbranched polymers was hardly affected by changes in the initial molar AB$_2$ monomer/Cu catalyst ratios (Table 1), further supporting the hypothesis that the

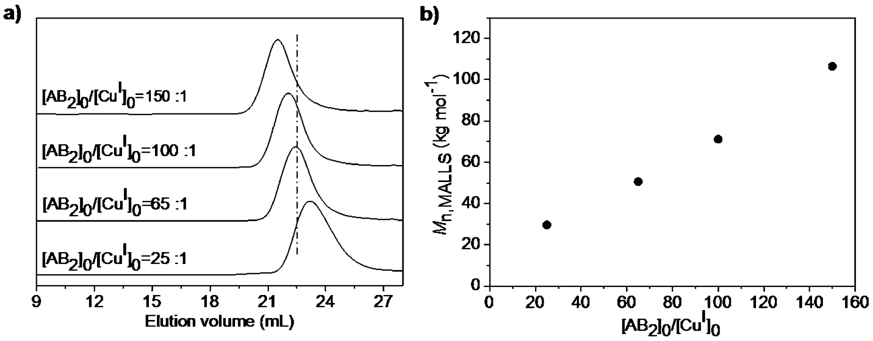

Figure 3. a) SEC traces and b) number-average molecular weights ($M_{n,MALLS}$) of hyperbranched polymers at various AB_2/Cu^I molar ratios. Polymerization conditions: $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0 = x{:}1{:}5$ in DMF at 45 °C, $[AB_2]_0 = 0.5$ mol L^{-1}.

Table 1: CuAAC polymerization of AB_2 monomers at different molar feed ratios.

Sample	$[AB_2]_0/[Cu^I]_0$	Conv.[a] [%]	$M_{n,MALLS}$[b] [kg mol^{-1}]	$M_{n,RI}$[c] [kg mol^{-1}]	M_w/M_n[c]	DB[d]
HB1	150	95	106.5	36.3	1.28	0.83
HB2	100	96	71.1	25.4	1.27	0.84
HB3	65	98	50.6	19.5	1.28	0.83
HB4	25	98	29.6	13.5	1.33	0.84

[a] Monomer conversion determined by ^{1}H NMR spectroscopy. [b] The number-average molecular weight measured by THF SEC with a MALLS detector. [c] The apparent number-average molecular weight and the molecular weight distribution measured by SEC with an RI detector, calibrated with linear poly(methyl methacrylate) standards. [d] Determined by inverse-gated decoupled ^{13}C NMR and ^{1}H NMR spectroscopy.

higher reactivity of the second azide group was due to the presence of a neighboring Cu^I/triazole complex on the same monomer unit.

We were also interested in demonstrating the possibility of sequential monomer addition in this chain-growth CuAAC polymerization for polymer chain extension. For a polymerization mixture containing $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0$ in a ratio of 25:1:5 in DMF, complete monomer conversion (>98 %) was reached after two hours and produced a hyperbranched polymer with $M_{n,MALLS} = 29.6$ kg mol^{-1} and $M_w/M_n = 1.33$. Without stopping the reaction and performing any purification, a second batch of the AB_2 monomer (25 equiv with respect to the initial amount of Cu) was added to the reaction system. The monomer conversion reached >98 % in twelve hours, producing a hyperbranched polymer with $M_{n,MALLS} = 58.1$ kg mol^{-1} and $M_w/M_n = 1.31$. The doubled molecular weight confirmed that the AB_2 monomers added in the second batch only reacted with the preformed hyperbranched polymer macroinitiators rather than with other monomers. This process could be continued by the addition of a third (50 equiv) and a fourth batch (100 equiv) of AB_2 monomers to the reaction mixture after complete conversion of the monomers in the preceding batch. For these processes, the peaks in the SEC curves shifted smoothly to lower elution volumes, and the molecular weights of the polymers doubled each time after complete monomer conversion (Figure 4). After complete reaction of the fourth monomer batch, the molecular weight of the produced hyperbranched polymer was $M_{n,MALLS} = 242.3$ kg mol^{-1} with $M_w/M_n = 1.29$. These results clearly demonstrate that this CuAAC polymerization proceeds according to a chain-growth mechanism, with the possibility of sequential one-pot monomer additions to produce hyperbranched copolymers with segmented structures.

After polymerization, the Cu catalyst in the hyperbranched polymers could be easily removed by the addition of one to two equivalents of PMDETA, which gave a colorless product (Figure S5). The purified hyperbranched polymers exhibited a glass transition temperature, T_g, of 14 °C (Figure S6), which is slightly higher than the values reported for dendrimers with similar structures.[10c] These polytriazole-based hyperbranched polymers can be easily dissolved in common organic solvents, such as DMF, acetone, THF, dichloromethane, or ethyl acetate, but are not well-soluble in methanol and hexane.

In summary, a novel chain-growth CuAAC polymerization method has been developed to produce hyperbranched polymers with high molecular weights, low polydispersities, and high degrees of branching in a one-pot solution reaction. Owing to the complexation of the Cu^I species to the in situ formed triazole groups, all Cu^I catalysts are bound to polytriazole cores at low monomer conversions, and subsequent CuAAC reactions can only occur in the proximity of the polymer between polymers and monomers. The reactions exhibited a linear increase in polymer molecular weight with conversion and clean chain extension when the monomer was added in several batches, demonstrating key features of a chain-growth polymerization mechanism. The copper(I) triazole complex enabled a fast reaction of the second azide group and quickly converted the L unit into a D unit, producing hyperbranched polymers with a high degree of branching (DB = 0.83). Considering the broad

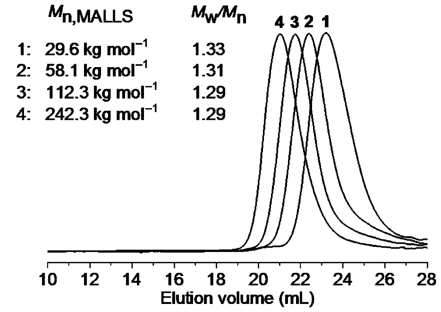

Figure 4. Evolution of the SEC traces for the sequential addition of four AB_2 monomer batches. Initial polymerization conditions: $[AB_2]_0/[CuSO_4{\cdot}5\,H_2O]_0/[\text{ascorbic acid}]_0 = 25{:}1{:}5$ with $[AB_2]_0 = 0.5$ mol L^{-1} in DMF at 45 °C; the second, third, and fourth batches contained 25, 50, and 100 equiv of the AB_2 monomers, respectively (diluted in DMF at $[AB_2] = 0.5$ mol L^{-1}), and were added at >98 % conversion of the alkyne groups without any purification.

applicability of the CuAAC reaction in polymer synthesis, the easy functionalization of AB_2 monomers, and the potential coordination of triazole moieties to metal cations, this one-pot synthetic method for chain-growth CuAAC polymerization is expected to be of broad interest in both polymer chemistry and materials science for the synthesis of polytriazole-based polymers with various architectures.

Keywords: chain growth · click chemistry · CuAAC · hyperbranched polymers · polymerization

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