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PAPER

Fast and scalable production of hyperbranched polythioether-ynes by a combination of thiol-halogen click-like coupling and thiol-yne click polymerization

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Fast and scalable production of hyperbranched polythioether-ynes was achieved by applying sequential click chemistry (SCC) *via* couple-monomer methodology (CMM). As a typical example, thiol-halogen click-like reaction employing strong base, KOH and thiol-yne click reaction *via* UV irradiation were used for precursor preparation and polymerization, respectively. Two series of hyperbranched polythioether-ynes employing two kinds of di-thiols with different reactivity have been prepared within 10 h and characterized with ^{1}H NMR spectroscopy and gel permeation chromatography. The hyperbranched polymers (HPs) derived from 1,6-hexanedithiol reached high weight-average molecular weight (M_w) of 230500, high weight-average degree of polymerization (DP_w) of 1224 and high degree of branching (DB) of 0.82–0.68. Postmodification of abundant alkyne terminal groups afford HPs with a greatly enhanced DB of 0.96. Heat-initiated polymerization was also attempted. The present study clearly demonstrates the robustness of application of SCC technique in the CMM strategy for fast, scalable preparation of multifunctional HPs.

Introduction

Hyperbranched polymers (HPs), are three-dimensional (3D) macromolecules with branch-on-branch topology and have become one of the typical subclasses of dendritic polymers since first coined in the late of 1980s.[1] By branching, HPs are endowed with a compact structure, multi end-functionalities, tridimensional scaffold, internal space and binding sites.[2] They could be used in coatings, processing additives, and nanocarriers for small functional guests.[2]

To date, three main methodologies have been developed for the preparation of HPs, including single-monomer, symmetric monomer pair (A_2 + B_3), and couple-monomer methodology (CMM).[3] Although most of the reported HPs are prepared by single-monomer methodology (SMM) or polymerization of AB_2 or AB*-type monomers, SMM still suffers from the non-commodity and tedious preparation of monomers. The A_2 + B_3 strategy holds the merit of commercial availability of monomers, but is limited by the major problem of easy to gelation, especially under conditions of relatively high monomer concentration and high conversion. CMM based on the non-equal reactivity of functional groups in asymmetric monomer pairs was coined firstly by Gao and Yan,[3] allowing *in situ* formation of AB_2-type intermediate and subsequent preparation of HPs from commercial monomers without high risk of gelation. This greatly furthers the progress of HP synthesis. However, the conventional reactions employed in CMM are relatively slow. How to fast and efficiently produce HPs *via* the protocol of CMM is to be explored so as to meet the need of fast development of HPs.

The emerging click chemistry, which relies on the most practical and nearly perfect chemical transformations, such as azide-alkyne coupling,[4–7] Diels–Alder coupling[8] and thiol-click reactions,[9] represents great technological innovation, and has revolutionized the field of polymer synthesis as a versatile tool for the production of complex polymeric architectures. However, all the preparations generally employ the AB_2 or A_2 + B_3 strategy and utilize click reaction merely in the polymerization step, while the precursor preparation still suffers from the tedious installation of clickable groups, making the whole preparation inconvenient, slow and difficult to scale-up. Therefore, how to readily and fast prepare HPs *via* click chemistry from commercial monomers is still a challenge that remains unsolved.

On the other hand, polythioether has been widely studied in recent years due to a number of merits, such as oil resistance,[10] high refractive index,[11] metal ion adsorption,[12] and so on, whereas hyperbranched polythioethers have rarely been reported.[13] Recently, an excellent and pioneering work tried thiol-yne click polymerization to prepare hyperbranched polythioether successfully.[13] However, the synthesis of AB_2 monomer employs conventional condensation reaction and requires the chromatography purification step, causing very low yield (~13%) for the monomer and thus for the final product. Therefore, the efficient

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preparation of hyperbranched polythioethers is strongly needed to be advanced so as to facilitate the following exploitation for their novel applications.

To resolve such problems mentioned above, we expanded the CMM strategy to effectively prepare hyperbranched polythioethers by applying sequential click chemistry (SCC) which means two or more click reactions are sequentially used for the preparation of monomers/precursors and HPs. SCC has been demonstrated as a versatile method in synthesis of dendrimers and networks and in modification of end groups.[14] Most recently, we first reported the SCC example for HP preparation which is the combination of thiol-Michael addition and thiol-yne click reactions, but the employed monomer of propargyl (meth)acrylate is relatively expensive.[15] Herein, to further lower the cost and enrich the SCC method, we combined thiol-halogen click-like coupling and thiol-yne click polymerization. The whole synthesis procedure can be completed within 10 h, and HP products with high yield (>80%) and high molecular weights are readily obtained. Our novel synthesis strategy possesses various advantages such as fast reaction, high efficiency, modularization for a series of monomer pairs, and generality for different click chemistry, laying the foundation for highly efficient, cost-effective and large-scale production of HPs.

Experimental section

Materials

3,6-Dioxaoctane-1,8-dithiol, **1a**, and 1,6-hexanedithiol, **1b**, were purchased from TCI. 2,2-Dimethoxy-2-phenyl-acetophenone (DMPA), 2,2′-azobisisobutyronitrile (AIBN) and toluene (HPLC grade) were purchased from Aldrich. Propargyl bromide, propargyl chloride, and n-propylthiol were purchased from Aladdin Chemical Co. China. Methanol, CH_2Cl_2 and KOH were obtained from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received.

Synthesis of model compound, 1,2-bis(2-propargylthioethoxy) ethane

3,6-Dioxaoctane-1,8-dithiol, **1a** (1.82 g, 10 mmol) was dissolved in methanol (5 mL). This solution was purged with nitrogen gas for 10 min to eliminate oxygen, and then added dropwise with a methanol (7 mL) solution of KOH (1.12 g, 20 mmol) over 10 min with vigorous stirring. The reaction system was cooled to 0 °C, and added dropwise with a methanol (3 mL) solution of propargyl bromide (2.41 g, 20.4 mmol) or propargyl chloride (1.52 g, 20.4 mmol) over 10 min. As soon as the addition started, a white precipitate of KBr or KCl appeared. After stirring for 0.5 h, methanol was removed. The residual was dissolved with CH_2Cl_2 and washed with H_2O (×2). The organic phase was collected and dried over Na_2SO_4. CH_2Cl_2 was evaporated to afford the model compound in quantitative yield. ^{1}H NMR (300MHz, $CDCl_3$): 3.715 (t, 4H, OCH_2CH_2S), 3.63 (s, 4H, OCH_2CH_2O), 3.32 (d, 4H, $CH{\equiv}CCH_2S$), 2.89 (t, 4H, OCH_2CH_2S), 2.24 (t, 2H, $CH{\equiv}CCH_2S$).

Synthesis of HPTY1 series

The whole preparation procedure for HPTY1 series can be completed within 8 h. A 10 mL methanol solution of 3,6-dioxaoctane-1,8-dithiol, **1a** (3.64 g, 20 mmol) was prepared and purged with highly pure N_2 gas for 10 min, to eliminate oxygen. To this solution, a methanol (7 mL) solution of KOH (1.12 g, 20 mmol) was added dropwise over 10 min. Then, the reaction system was cooled to 0 °C and added dropwise with a methanol (3 mL) solution of propargyl bromide (2.41 g, 20.4 mmol) in 10 min. Once the addition started, white precipitate of KBr salt was observed. After reacting for 0.5 h, methanol was removed. The residual was dissolved with CH_2Cl_2 and washed with H_2O (×2). The organic phase was collected and dried over Na_2SO_4. CH_2Cl_2 was evaporated to afford the precursor (4.39 g) in quantitative yield. The ^{1}H and ^{13}C NMR spectra are shown in Fig. 1. ^{1}H NMR (300MHz, $CDCl_3$): 3.74 (t, 2H, $OCH_2CH_2SCH_2$), 3.68–3.60 (6H, $OCH_2CH_2OCH_2CH_2SH$), 3.32 (d, 2H, $CH{\equiv}CCH_2S$), 2.89 (t, 2H, $OCH_2CH_2SCH_2$), 2.70 (dt, 2H, CH_2SH), 2.23 (t, 1H, $CH{\equiv}CCH_2S$), 1.60 (t, 1H, S*H*). ^{13}C NMR (125MHz, $CDCl_3$): 79.8 ($CH{\equiv}CCH_2S$), 72.2 (OCH_2CH_2O), 71.1 ($CH{\equiv}CCH_2S$), 70.1 ($OCH_2CH_2SCH_2$), 69.6 (OCH_2CH_2SH), 30.3 ($OCH_2CH_2SCH_2$), 23.7 (CH_2SH), 19.1 ($CH{\equiv}CCH_2S$).

In another experiment, propargyl chloride (1.52 g, 20.4 mmol) was used instead of propargyl bromide and afforded the same precursor with the same ^{1}H NMR spectrum.

The as-prepared precursor was diluted with toluene to 0.5 M and added with DMPA (96.4 mg, 0.38 mmol) to make a stock solution. The solution was divided into six 25 mL vials sealed with a rubber septum and wrapped with aluminum foil. After purged with highly pure N_2 for 10 min, the vials were unwrapped and irradiated under a UV lamp at 15 °C for given times. Then, the vials were exposed to air, and the polymer solutions were analyzed by ^{1}H NMR (Fig. 2 and Table 1). The polymers were precipitated out by pouring the polymer solutions into methanol.

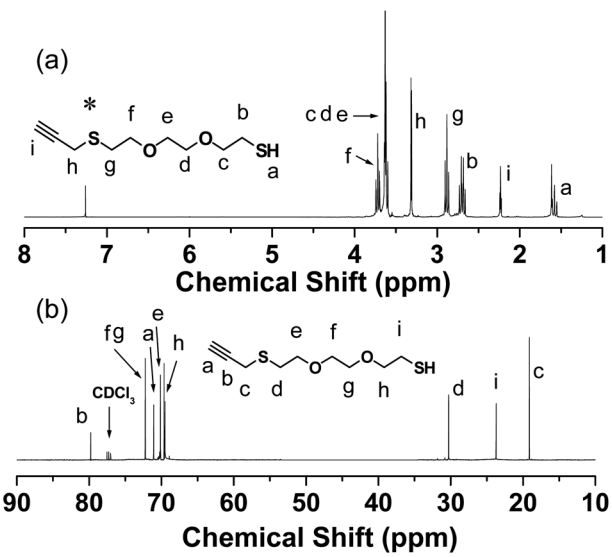


Fig. 1 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of the precursor obtained by thiol-halogen coupling of **1a** and **2a** (* because the proton signals of dithiols and di-ynes are similar to those of AB_2 monomers, we only show the signal assignment of **3a** for concision).

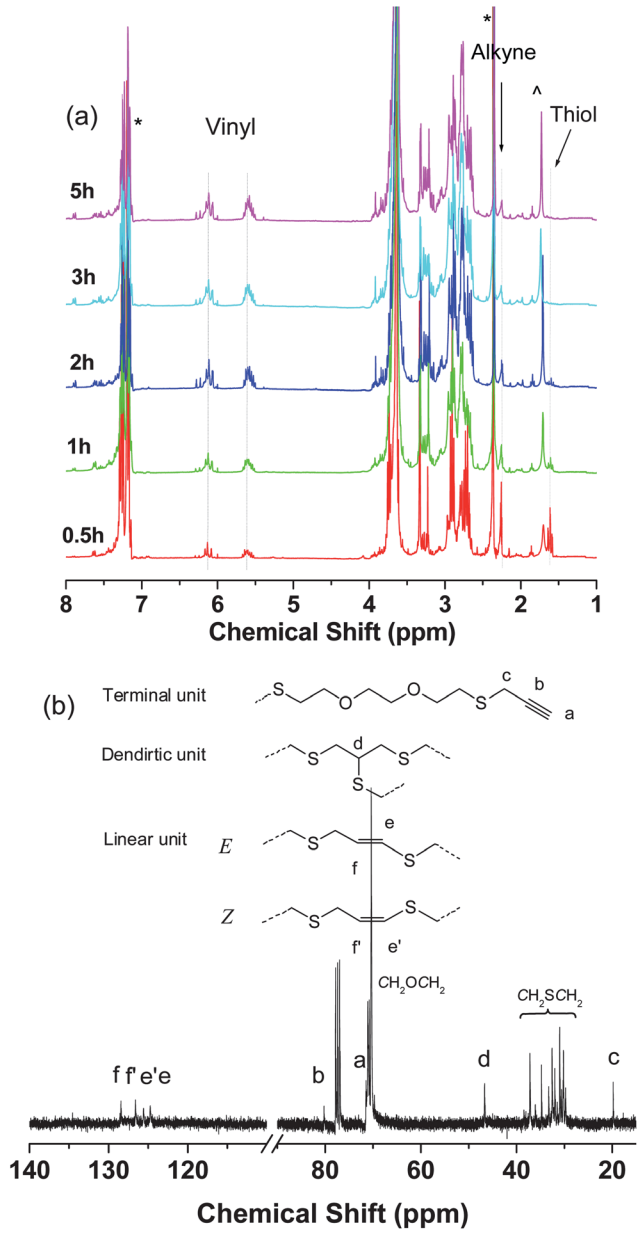


Fig. 2 (a) ^{1}H NMR spectra of precursor obtained by thiol-halogen coupling of **1a** and **2a** and corresponding HPs at different polymerization time before precipitation (* toluene, ^ H_2O); (b) ^{13}C NMR spectra of corresponding HPs irradiated for 5 h.

Both the precipitated and unprecipitated polymers irradiated for 5 h were characterized by gel permeation chromatography (GPC) (Fig. 3). Other GPC data of unprecipitated polymers are shown in Table 1.

End-capping of HPs by thiol-yne and thiol-ene click chemistry

In the interest of examining the postmodification potential of this type of HPs, the vial containing the above toluene solution of precursor was irradiated for 2 h, injected with a deoxygenated toluene (1 mL) solution of n-propylthiol (0.6 g) through an air-tight syringe, and then irradiated for another 3 h. Precipitation into methanol afforded a polymer with M_n of 6600 and M_w of 42900. The ^{1}H NMR spectrum is presented in Fig. 5, indicating that only a little amount of vinyl bonds can be found.

Table 1 Reaction conditions and results for the **HPTY1** and **HPTY2** series

Sample	Time/h	Conv[a]/%	M_n/K	M_w/K	PDI[b]	DB
HPTY1-A	0.5	47.0	1.1	1.4	1.3	0.89
HPTY1-B	1	85.8	3.5	7.7	2.2	0.61
HPTY1-C	2	94.3	6.1	33.7	5.5	0.50
HPTY1-D	3	97.7	7.5	102.2	13.6	0.49
HPTY1-E	5	98.6	7.8	150.8	19.3	0.44
HPTY2-A	1	80.1	3.1	9.5	3.1	0.82
HPTY2-B	2	90.8	4.3	27.5	6.4	0.79
HPTY2-C	3	95.6	5.7	154.3	27.1	0.76
HPTY2-D	5	98.1	6.8	211.8	31.2	0.72
HPTY2-E	8	99.2	7.9	230.5	29.2	0.68

[a] Conversion of thiol groups. [b] Polydispersity index (M_w/M_n).

Thermal-initiated thiol-yne click polymerization

Thermal-initiated polymerization was also performed. The precursor (0.46 g, 2.0 mmol) and AIBN (6.6 mg, 0.04 mmol) was dissolved in 4 mL toluene in a 25 mL Schlenk flask. After purged with highly pure N_2 for 10 min, the flask was immersed in an oil bath thermostated at 75 °C for 24 h. Then, the flask was exposed to air, and the polymer solution was analyzed by ^{1}H NMR.

Synthesis of HPTY2 series

The whole preparation procedure for the HPTY2 series can be completed within 10 h. 1,6-Hexanedithiol **1b** (3.01 g, 20 mmol) was dissolved in methanol (10 mL). The solution was purged with highly pure N_2 for 10 min to eliminate oxygen and then added with a methanol (7 mL) solution of KOH (1.12 g, 20 mmol) over 10 min with vigorous stirring. The reaction system was cooled to 0 °C, and to which, a methanol (3 mL) solution of propargyl bromide (2.41 g, 20.4 mmol) was added dropwise in 10 min. As soon as propargyl bromide was added, white KBr precipitated from the system. After reacting for 0.5 h, methanol was removed. The residual was dissolved with CH_2Cl_2 and washed with H_2O (×2). The organic phase was collected, and dried over Na_2SO_4. CH_2Cl_2 was evaporated to afford the precursor (3.75 g) in quantitative yield. The ^{1}H and ^{13}C NMR spectra are shown in Fig. 6. ^{1}H NMR (300MHz, $CDCl_3$): 3.23 (d, 2H, CH≡CCH_2S), 2.67 (t, 2H, $CH_2CH_2SCH_2$), 2.51 (dt, 2H, CH_2SH), 2.23 (t, 1H, CH≡CCH_2S), 1.60 (m, 4H,

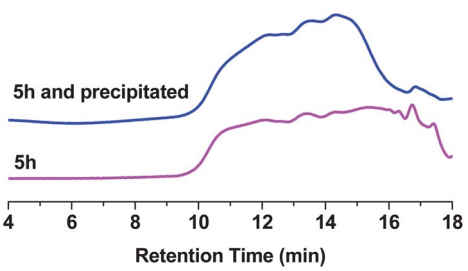


Fig. 3 GPC curves of the precipitated and unprecipitated polymers (**HPTY1** series) obtained by irradiation for 5 h.

$CH_2CH_2CH_2CH_2CH_2S$), 1.39 (m, 4H, $CH_2CH_2CH_2CH_2CH_2S$), 1.33 (t, 1H, S*H*). ^{13}C NMR (125MHz, $CDCl_3$): 80.0 ($CH{\equiv}CCH_2S$), 70.8 ($CH{\equiv}CCH_2S$), 33.7 (CH_2CH_2SH), 31.3 ($CH{\equiv}CCH_2SCH_2$), 28.6 ($CH{\equiv}CCH_2SCH_2CH_2$), 28.1–27.6 ($CH_2CH_2CH_2CH_2CH_2CH_2$), 24.4 ($HSCH_2$), 19.0 ($CH{\equiv}CCH_2S$).

The as-prepared precursor was diluted with toluene to 0.25 M and added with DMPA (96.4 mg, 0.38 mmol) to make a stock solution. The solution was divided into six 25 mL vials sealed with a rubber septum and wrapped with aluminum foil. After purged with highly pure N_2 for 10 min, the vials were unwrapped and placed under a UV lamp at 15 °C for given times. Then, the vials were exposed to air and analyzed by ^1H NMR (Fig. 7). Pouring the reaction mixtures into methanol afforded the HPs which were analyzed by GPC (see Table 1 and Fig. 8).

Measurement and techniques

Nuclear magnetic resonance spectroscopy (NMR). The ^1H NMR measurements were carried out on a Varian Mercury Plus 300 MHz NMR spectrometer at 20 °C. The ^{13}C NMR measurements were performed on a Bruker AV 500 MHz NMR spectrometer at 20 °C. The samples were dissolved with $CDCl_3$ and the solutions were measured with tetramethylsilane (TMS) as an internal reference.

Gel permeation chromatography. The molecular weights of polymers were measured on a PL PL-GPC220, using linear polystyrene as calibration, and tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL min^{-1}.

High performance liquid chromatography (HPLC). The HPLC measurement was carried out on a Shimadzu LCMS-2020 with a $\lambda = 254$ nm UV detector and CH_3OH as the eluent at a flow rate of 1 mL min^{-1}.

Results and discussion

Molecular design

The basic principle of our synthesis strategy is illustrated in Scheme 1a. Generally, click or click-like reaction between A group of A_2 monomer with C group of CB_2 monomer affords an intermediate containing AB_2 as a major component, and further click-polymerization yields HPs. This strategy represents the specific combination of CMM and sequential click chemistry (SCC), and thus can be denoted as CMM-SCC. Recently, SCC has been demonstrated as a versatile method in synthesis of dendrimers and networks and in modification of end groups.[14] However, as far as we know, SCC has never been used in HPs preparation.

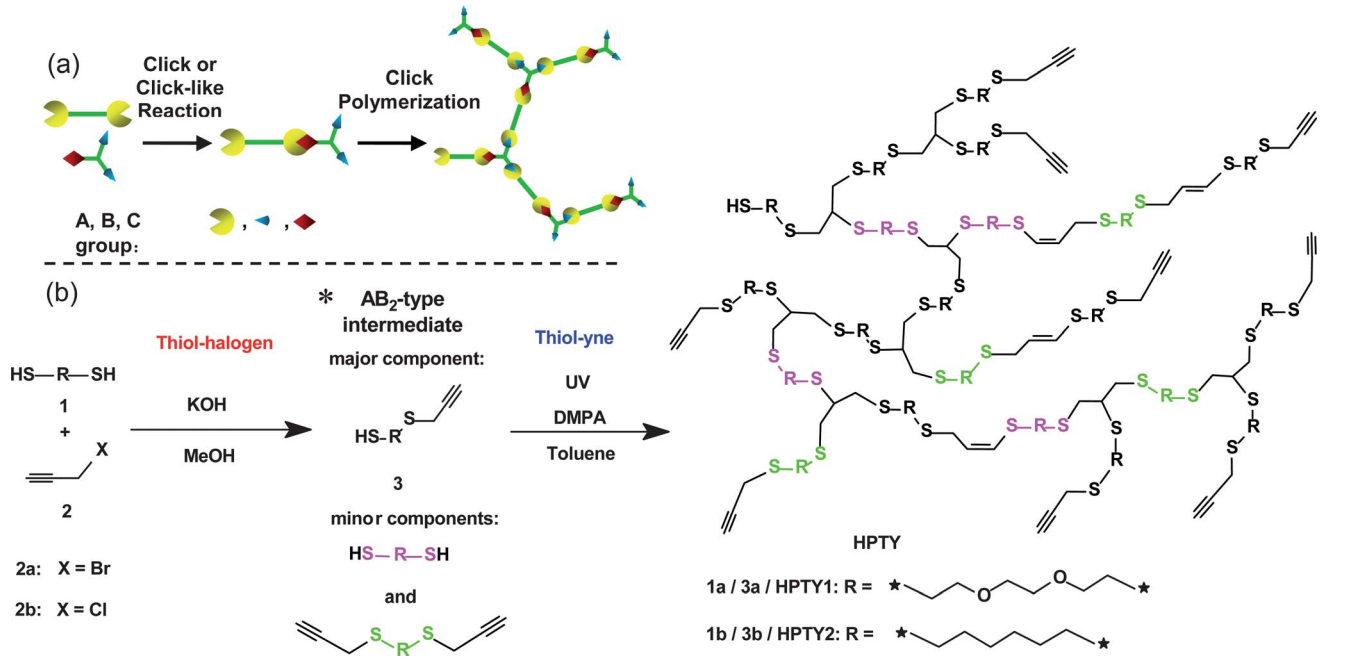
This CMM-SCC strategy holds both advantages of CMM and SCC such as, (1) commercial availability of monomers, favoring the large-scale production of precursors and HPs, (2) generality for series of monomers, allowing the tunable control of HP structure and property, and (3) fast reaction and high yield due to the merits of click chemistry.

Two reactions, thiol-yne[9,13,14,16] and thiol-halogen,[9] are chosen for the CMM-SCC strategy. Thiol-yne reaction generally proceeds *via* addition of thiol to alkyne, followed by click-addition of thiol to the resulting vinyl sulfide generating two thioether bonds in all.[17] The choice of thiol-yne as polymerization reaction seems superior, because it utilizes not only the "thiol-click" merits but also the bifunctional nature of alkyne which generates branches in polymerization. Moreover, the reaction rate of the second addition between vinyl and thiol (defined as r_2) is higher than that of the first addition between thiol and alkyne (defined as r_1),[17] which likely induces higher degree of branching (DB) than the classic equal-reactivity cases.[13,18,19] Hence, a precursor containing both thiol and alkyne groups is designed for click-polymerization. A thiol-halogen reaction, generally performed by reacting thiol with bromide employing mild organic bases such as trialkyl amines,[9] is chosen for the formation of precursor because of its high efficiency, very mild conditions and easy removal of byproduct by washing with water. Consequently, di-thiols and propargyl halides are selected as two sorts of raw materials, as shown in Scheme 1b. In the presence of a base, reaction between di-thiol and propargyl halide afforded an AB_2-type intermediate of "thiol-alkyne"; the following thiol-yne click polymerization gives HP without gelation.

It should be pointed out that controversy still exists on the viewpoint of whether the thiol-halogen reaction is a click reaction. According to the definition of click chemistry proposed by Sharpless *et al.*,[4] a click reaction can have "only inoffensive byproduct that can be removed by nonchromatographic methods", and they claimed nucleophilic substitution is click reaction. Moreover, some researchers have recently used the term of "click chemistry" for the "thiol-halogen" reaction in the effective construction of complex polymers. In contrast, others thought a click reaction should have no byproducts.[20] In this study, we slightly modified the conventional "thiol-halogen" reaction condition, and the sole byproduct is KBr salt, rather than the trialkylamine hydrohalide reported previously. Since our "thiol-halogen" reaction satisfies Sharpless's definition of click chemistry strictly, we call it "click-like" reaction to avoid the possible meaningless debating.

Synthesis and characterization

Experimentally, propargyl bromide (**2a**) was added dropwise to the methanol solution of 3,6-dioxaoctane-1,8-dithiol (**1a** or **1b**) at 0 °C in the presence of KOH. After reacting for 0.5 h, methanol was removed and the residual was dissolved in CH_2Cl_2, washed with water, dried over $MgSO_4$, followed by removal of volatiles. Then, toluene was added to perform thiol-yne click polymerization in the presence of 2 mol% photo initiator, 2,2-dimethoxy-2-phenylacetophenone, by irradiation with UV-lamp (λ = 365 nm) under N_2. The reaction time and selected results are summarized in Table 1. The hyperbranched polythioethers made from **1a** and **2a** are denoted as **HPTY1** series and those made from **1b** and **2a** are marked as **HPTY2** series. We also tried the cheaper propargyl chloride (**2b**) instead of propargyl bromide, obtaining similar results (data not shown). In addition, the thiol-halogen reaction employed cheaper and strong base, KOH, instead of commonly used organic bases.[9] It showed ultra-fast, quantitative efficiency and gave insoluble potassium halide which can be easily removed by washing with water, demonstrated by the predominant formation of AB_2 intermediate and synthesis of the model compound, 1,2-bis(2-propargylthioethoxy)-ethane.



Scheme 1 Sequential click chemistry in a couple-monomer methodology for facile synthesis of hyperbranched polymers: basic principle (a) and typical example employing thiol-halogen and thiol-yne sequential reactions (b). (* AB_2-type intermediate containing AB_2 monomer **3** as a major component, the formed di-ynes and unreacted di-thiols as minor components).

Fig. 1 shows ^{1}H NMR and ^{13}C NMR spectra of precursor resulted from the thiol-bromide reaction of **1a** and **2a**. The proton signals of thiol and alkyne groups are observed at 1.58 and 2.23 ppm, respectively, and the ratio of the integration of the proton signals of the CH_2 moiety in the propargyl group to that of the CH_2OCH_2 moiety is 1: 4. The carbon signals at 19.0, 70.8 and 80.0 ppm are assigned to the introduced propargyl group. Hence, the precursor is successfully prepared and contains equal amount of thiol and alkyne groups, indicating no side reaction occurred. HPLC results revealed that the precursor containing about 62% of AB_2 monomer (**3a**), 19% of di-thiol (**1a**) A_2 monomer and 19% of di-yne B_4 monomer (model compound, 1,2-bis(2-propargylthio ethoxy)-ethane).

In the ^{1}H NMR spectra of **HPTY1** series (Fig. 2a), the signal of thiol groups gradually weakens and the signals at 2.5–3.0 ppm which are assigned to the thioether protons gradually increase with elongation of irradiation time. This indicated that polymerization was proceeding to generate new thioether bonds. The conversion of thiol groups reached 94.3% in 2 h, indicating the polymerization undergoes very fast. The emerging signals at 6.1 and 5.6 ppm in the ^{1}H NMR spectra and 124–129 ppm in the ^{13}C NMR spectrum (Fig. 2b) imply the formation of vinyl sulfides with both *E* and *Z* structures generated by mono-addition of thiol to alkyne. By integration of the proton signals of unreacted alkynes (terminal units, abbr. *T*) and vinyl sulfides (linear units, abbr. *L*), DB can be approximately calculated according to formula: $DB = 1/(1 + (L/2T))$,[21] and is listed in Table 1. It has already been demonstrated that the second addition of thiol to vinyl sulfide (r_2) is much faster than the first addition of thiol to alkyne (r_1), and thus the reactivity ratio (γ) of r_2 to r_1 is generally larger than 1,[17] so it is rational that DB can be higher than 0.5.[13,19] In the kinetics theory with substitution effect, DB will be close to or even higher than 0.7 at conversion of 70% if $\gamma \geq 10$.[19] Interestingly, in contrast to the theoretical prediction that DB increases with conversion,[18,19] DB decreases gradually with increasing the conversion and finally approaches 0.44 at a conversion of 98.6% in our experiments (Table 1). This is probably due to three reasons: (i) thiol groups are more difficult to attack the formed vinyl bonds of macromolecules than those of oligomers because of the steric hindrance, leading to that γ becomes smaller and smaller with the reaction, (ii) intramolecular cyclization between thiol and alkyne groups, (iii) thiyl radicals have an electrophilic character and thus favor the addition to electron-rich propargyl groups.[17] In respect of reason iii, the propargyl groups are connected to electron-rich sulfur atoms that can activate alkynes more than vinyl sulfides, also resulting in smaller γ and DB.

GPC was used to determine the molecular weights and polydispersity indices (PDIs) of HPs (see Table 1). The elution curves of the precipitated and unprecipitated polymers irradiated for 5 h are shown in Fig. 3. Precipitation into methanol afforded the polymer with a yield of 81% by effectively eliminating low molecular weight oligomers that appeared at 16–18 min in the elution curve. Fig. 4 shows the evolution of M_n, M_w, theoretical PDI and experimental PDI with conversion for **HPTY1** series. It is noted that both M_n (number-average molecular weight) and M_w (weight-average molecular weight) increase rapidly with conversion, with M_w growing much faster than M_n, resulting in higher and higher PDI. The PDI grows faster at high conversion, which is in accordance with theory prediction based on the AB_2 polymerization system,[22] and could also be seen in preparations of other HPs.[2,13] Here, we highlight that the HPs prepared *via* the CMM-SCC strategy have relatively high molecular weights. For instance, two polymers presented in Table 1, **HPTY1-D** and **HPTY1-E**, exhibit high M_ws of 102,200 and 150,800, and high DP_w of 464 and 684, respectively.

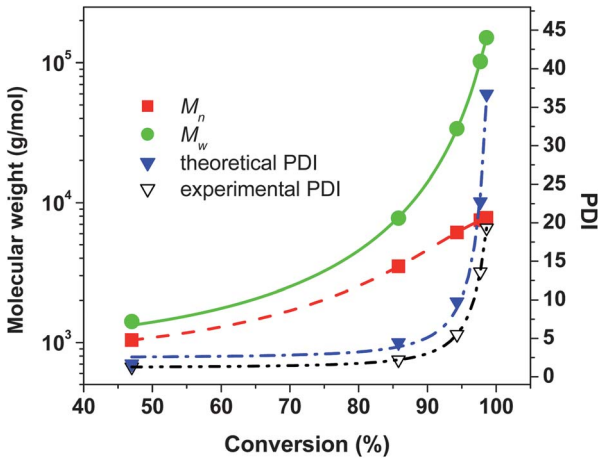


Fig. 4 Evolution of M_n, M_w, and PDI with conversion for **HPTY1** series. The theoretical PDI is obtained from ref. 22.

In addition, HPLC measurement revealed that the precursor contained about 19% di-thiol A_2 monomer and 19% di-yne B_4 monomer. No gelation was observed at a high conversion of up to 98.6%, indicating that the neat polymerization between A_2 and B_4 which has great gelation risk, has been highly compressed in the presence of predominant AB_2-type intermediate which generally does not induce gelation. This validates the advantages of CMM strategy mentioned before, and further confirms that the CMM is essentially different from the conventional AB_2 or $A_2 + B_3$ approach.

Postmodification

In the interest of examining the postmodification potential of this type of HPs, the sample **HPTY1-C** (DB = 0.5) was end-capped with n-propanethiol to transform unreacted propargyl and vinyl groups into thioethers. The ^{1}H NMR spectrum is presented in Fig. 5. The proton signal of alkyne group originally appeared at 2.23 ppm nearly vanished and residual proton signals of vinyl groups still exist. The calculated DB is 0.96. These results indicate that: (1) DB can be greatly enhanced by postmodification, demonstrating the high reactivity of vinyl and alkyne units that can be applied to create new functional materials, (2) vinyl units cannot react with small thiol molecules completely, implying the existence of steric hindrance of HPs. The second reason also implies that even small thiol molecules are not able to totally

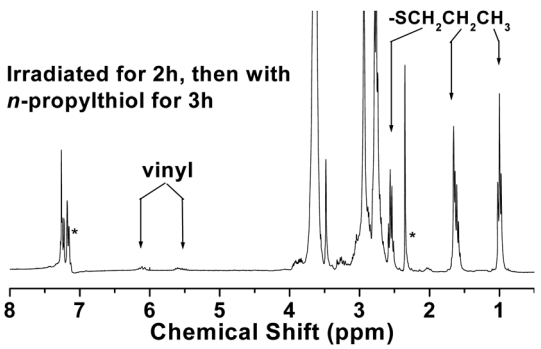


Fig. 5 ^{1}H NMR spectrum of the n-propylthiol modified HP (* toluene).

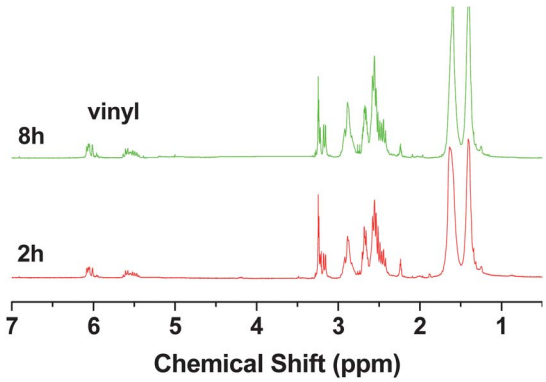


Fig. 6 ^{1}H NMR spectra of the **HPTY2** series irradiated for 2h and 8 h.

transform the vinyl groups due to the steric hindrance of HPs, we cannot expect the oligomers generated in HP polymerization to react with vinyl groups efficiently and thus, it is rational that the DB of **HPTY1** series decreases with increasing the conversion.

Thermal-initiated polymerization

Thermal-initiated thiol-yne polymerization using AIBN as a radical initiator at 75 °C for 24 h was also conducted to provide an alternative route. As a result, HP with M_n of 2200, M_w of 7100 and DB of 0.35 at the final thiol conversion of 98.2%, was acquired. We speculate that the relatively low DB is due to the smaller γ since r_1 is enhanced more greatly than r_2 at elevated temperature.

Expansion of CMM-SCC strategy: synthesis and characterization of HPTY2 series

The above example of **HPTY1** has shown the rapidness and high efficiency of CMM-SCC in the preparation of high molecular weight HPs without gelation. To testify the generality of this

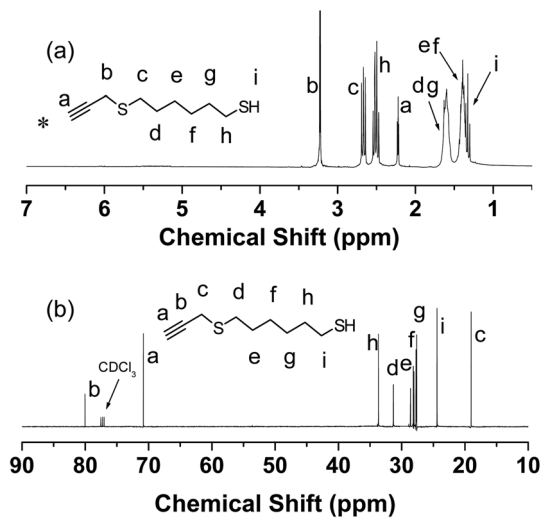


Fig. 7 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of precursor obtained by thiol-halogen coupling of **1b** and **2a** (* because the proton signals of di-thiols and di-ynes is similar to those of AB_2 monomers, we only show the signal assignment of **3b** for concision).

strategy, another di-thiol, 1,6-hexanedithiol (**1b**) is also used to prepare HPs. As compared with **1a**, **1b** has the same number of carbon atoms, but no relatively strong electronegative oxygen atom which makes the thiol group more reactive. This can be proved by the fact that the signal of thiol proton of **1a** appears at 1.34 ppm, while that of **1b** at 1.53 ppm, a relatively lower magnetic field. Fig. 7 presents the ^{1}H NMR and ^{13}C NMR spectra of the precursor. The proton signals of thiol and alkyne groups are located at 1.33 and 2.23 ppm, respectively. The new proton signal of CH_2 moiety in the propargyl group appears at 3.23 ppm and has an integration value that is half of that of the signals labelled as "d" and "g". The carbon signals appeared at 19.0, 70.8 and 80.0 ppm are ascribed to the bonded propargyl group. Thus, the precursor containing equal amount of thiol and alkyne groups is successfully prepared.

The polymers of the **HPTY2** series were also characterized with ^{1}H NMR spectroscopy (Fig. 6). Compared with the spectrum of the precursor, more and intensified signals appear at 2.4–3.0 ppm, which is indicative of the formation of thioether bonds arising from the thiol addition to alkynes. The existence of linear unit is confirmed by the appearance of proton signals at 5.5–6.1 ppm that is attributed to the monoaddition resulted vinyl sulfide. Other polymerization results are shown in Table 1. Interestingly, the DBs of the **HPTY2** series (ranging from 0.82 to 0.68) decrease only slightly with increasing the conversion, and

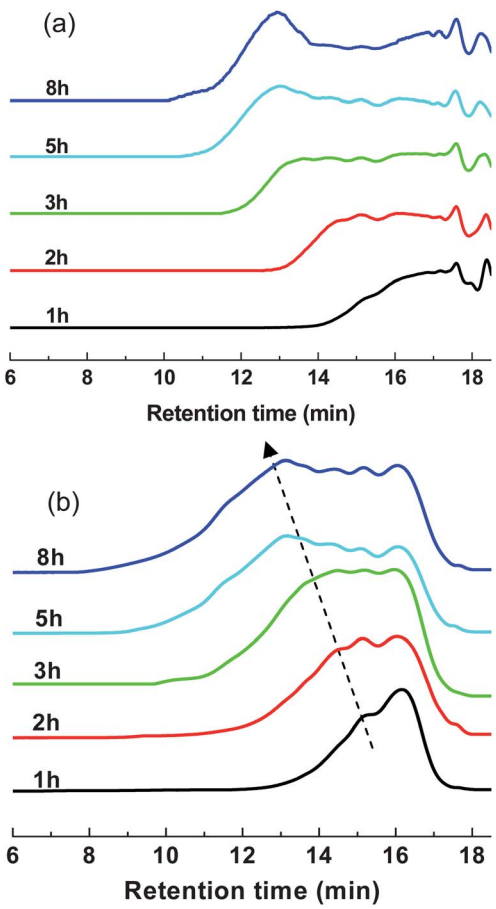


Fig. 8 GPC curves of **HPTY2** series at different polymerization time before precipitation (a) and after precipitation (b).

are higher than those of **HPTY1** series in all time scales, especially at high conversions (0.68 at conversion of 99.2%). This is likely caused by the structure difference between **1a** and **1b**. Because of the absence of electronegative oxygen atoms, the thiol group of **1b** is more reactive than that of **1a**, and enhances r_2 more greatly than r_1, inducing bigger γ than **HPTY1** cases and thus slowing down the DB's reduction. Hence, small difference of monomer structure can lead to a big difference of macromolecular topology, providing an alternative methodology to control DB of HP.[23] GPC curves of the HPs obtained before and after precipitation are shown in Fig. 8. As predicted, with increasing reaction time, the elution curves become broader and the peaks gradually appear at earlier retention times. By precipitation into methanol, the minor part of the elution volume located at 17.1–18.5 min disappeared, indicating that the oligomers can be effectively removed. Relatively high molecular weight polymers were obtained after polymerization for 5 h with a yield of 81%.

Conclusions

Sequential click chemistry strategy by combination of thiol-halogen click-like reaction and thiol-yne click reactions in a couple-monomer methodology is established successfully, and has shown its rapidness, simplicity, flexibility, generality, reproducibility, modular character, high efficiency, and cost-effectiveness for scale-up. Two series of HPs with high molecular weight and high DBs which both can be controlled through reaction time or conversion have been readily prepared from commercially available monomers within 10 h in high yield. By varying the monomer structures of dithiols and alkynes, tailor-made HPs with desired structures and properties could be created since the modular attribute of the CMM-SCC methodology with the building blocks of monomer pairs. The utilized click reactions can be extended to other thiol-click chemistry such as thiol-isocyanate, thiol-epoxy and other sorts of click reactions such as Cu(I)-catalyzed azide-alkyne, and Diels–Alder click coupling, *etc.* The breakthrough of CMM-SCC strategy will open a new avenue for facile, fast, scalable production of multifunctional dendritic materials.

The prepared hyperbranched polythioether-ynes are believed to find applications in metal ion absorption, oil resistance, anti-oxidation and so on due to their sulphur-rich feature. Such applications are currently being explored in our lab.

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