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Formation of long-subchain hyperbranched poly(methyl methacrylate) based on inhibited self-cyclization of seesaw macromonomers

Peng-Yun Li, Wei-Dong He,* Sheng-Qi Chen, Xiao-Xia Lu, Jia-Min Li, Hui-Juan Li

“Well-defined” long-subchain hyperbranched poly(methyl methacrylate) (lsc-hp PMMA) was obtained under the reaction condition in disfavor of self-cyclization of seesaw macromonomer as well as triggered by the intrinsic hindrance of 1,1-disubstituted chain ends of seesaw macromonomer. Firstly, seesaw-type alkynyl-(PMMA-Br), with one alkynyl group at the chain center and two bromine groups at each chain end was synthesized by atom transfer radical polymerization (ATRP). After the azidation of alkynyl-(PMMA-Br)₃, seesaw macromonomer of alkynyl-(PMMA-N₃)₃ underwent click reaction under high concentration in a good solvent to produce lsc-hp PMMA, almost without intrachain cyclization of macromonomer. Compared with our previous reports, steric hindrance of 1,1-disubstituted MMA units endowed almost no self-cyclization of alkynyl-(PMMA-N₃)₃ macromonomer. Therefore, lsc-hp PMMA with exact subchain length were obtained except the polydispersity of overall molecular weight. The chemical structure of lsc-hp PMMA was fully confirmed through the combination of gel permeation chromatography (GPC) with different detectors, proton nuclear magnetic resonance spectroscopy and Fourier transform infrared analyses. Furthermore, the formation kinetics for lsc-hp PMMA was monitored based on GPC with multi-angle laser light scattering detector and followed the equation: \( \ln[(DP_w + 1)/2] = \left[A_1\times10^{-16}(e^{-1}-e^{-2})/\alpha\right] \), where \( DP_w \) is absolute weight-average amount of macromonomers in hyperbranched polymers.

Introduction

Long-subchain hyperbranched polymers (LCBPs) have been of particular interest over the past years because of their unique properties such as facile synthesis, good solubility, low viscosity, globular structure, high number of terminal groups, stronger melt elasticity and storage modulus, special strain hardening in globular structure, high number of terminal groups, stronger melt properties such as facile synthesis, good solubility, low viscosity, particular interest over the past years because of their unique properties. This journal is © The Royal Society of Chemistry 20xx

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prepare hyperbranched chains, unreacted B groups inevitably lead
to the subchains with different length. However, as for seesaw
macromonomers, one unreacted B group just gives one free
subchain. Thus, our group have obtained different LCBPs with
uniform subchains by click chemistry. Moreover, unwanted
intra-subchain cyclic reaction of seesaw macromonomers
happened during the click reaction. How to effectively suppress the
cyclic side reaction?

Steric effect is a main factor that influences click chemistry. Kim
and co-workers showed that when preparing [poly(3-
dodecylthiophene)]2-P MMA miktoarm star copolymer (P3DDT-
PMA) by copper-catalyzed azide-alkyne cycloaddition (CuAAC), u-
azidopropyl-P3DDT with an alkyl spacer between azido group and
P3DDT can essentially reduce steric hindrance around the reactive
site to facilitate the click reaction. Fehér et al. prepared a series
of ferrocene-labeled steroids via CuAAC between 2β, 6β- and 16β-
azido-androstanes and alkynes with different structures, finding
considerably lower reactivity of 6β-azido-androstane towards
alkynes due to steric hindrance. It should be noted that only trace
amount of product was obtained in the CuAAC reaction of 6β-azido-
androstane and ethynylferrocene, however, when alkyne and the
bulky ferrocene moieties are separated by a spacer, product with
acceptable yield was obtained. Zhang et al. achieved high yields of
triazole-linked glycoconjugates via CuAAC by introducing a spacer
to reduce steric hindrance. Chow et al. performed systematic
analysis about the effect of dendron size on CuAAC between
dendritic diazides and dendritic diacetylenes, confirming that the
degree of polymerization decreased with increasing size of the
dendron. That is to say, steric hindrance affects the azide-alkyne
click reaction. In addition to steric hindrance, Chow and co-workers
showed that conformational freedom of the monomer has a
pronounced effect on the efficiency of click chemistry. The
intramolecular hydrogen bonds make the monomers structurally
rigid, effectively inhibiting the cyclic side reaction.

Furthermore, intra-subchain cyclic reaction of linear polymer is
usually carried out in highly dilute solution, where chains are
separated and can hardly interact with each other. Conversely,
highly concentrated solution should enable the polymer chains to
interact with each other, promoting the multi-macromolecule
chemical reaction, such as the click reaction between seesaw-type
macromolecules to form hyperbranched polymers, and suppress
the intra-macromolecule chemical reaction, for instance, the
intra-subchain cyclic reaction.

In this work, we confirm that steric hindrance of seesaw-type
macromonomer could suppress its cyclic side reaction. Methyl
methacrylate (MMA) was polymerized to prepare seesaw-type
macromonomers of alkynyl-(PMMA-N3)
2
. Compared with alkynyl-
(PST-N3)
2
with a tertiary carbon beside the azide group, moderate
steric hindrance was presence with one methyl group on the
quaternary carbon adjacent to the azide group. Moreover, we
performed the click reaction in highly concentrated solution (0.2
mL) in a good solvent to inhibit the intra-subchain cyclization of
seesaw macromonomers. Formation kinetics of this real long-
subchain hyperbranched (Isc-hp) PMMA almost without cyclic side
product was monitored.

### Experimental

**Materials**

MMA and MA (Sinopharm Chemical Reagents Co.) were dried and
distilled under vacuum over CaH2. Before use, tetrahydrofuran
(THF) was refluxed over CaH2 for 6 h, then dried and distilled over
sodium/benzophenone. N,N-dimethylformamide (DMF) was dried
and distilled under vacuum over anhydrous magnesium sulphate.
CuBr (Sinopharm Chemical Reagents Co.) was purified as followed
prior to use. After being reduced by 0.01 M Na2S2O4 aqueous
solution, filtered and washed with 1wt % HBr aqueous solution,
pure CuBr was obtained by washing with acetic acid and alcohol for
twice. AB₂-type initiator of propargyl 2,2-bis[(2'-bromo-2'-
methylpropanoyloxy)-methyl]propionate (PBMP) was prepared as
reported in the literature. 2-Bromoisobutyryl bromide (Sigma-
Aldrich), N,N,N',N",N"-pentamethylene diethylenetriamine (PMDETA,
Sigma-Aldrich) and other chemical reagents (Aladdin) were used as
received.

**Synthesis of seesaw macromonomers of alkynyl-(PMMA-N3)
2
**

A mixture of MMA (32.54 g, 325.0 mmol), PMDETA (173.3 mg, 1
mmol), PBMP (470.0 mg, 1 mmol) and THF (5 mL) were added into a
50-mL Schlenk flask equipped with a magnetic stirrer bar. The
reaction mixture was thoroughly mixed and then oxygen was
removed by subjecting the flask to three freeze-pump-thaw cycles.
Next, CuBr (143.5 mg, 1 mmol) was added to the flask under
nitrogen flow. After being sealed under vacuum, the flask
was placed in an oil bath controlled at 40 °C under stirring and
the reaction proceeded for 30 min. Then, the polymerization mixture
was cooled in an ice bath, diluted with THF, and subsequently
time passed through neutral alumina to remove the copper salt.
The mixture was concentrated under vacuum and precipitated in
methanol. Through thrice precipitation with THF/methanol and
dryness under vacuum for 24 h, PMMA with two bromine end-groups
and one central alkynyl group [alkynyl-(PMMA-Br)]
2
was
obtained. Yield: 10.4 g, M
\text{GPC}
 = 1.33 \times 10^{3} g/mol, PDI = 1.21.

Alkynyl-(PMMA-Br) (3.9 g, 0.3 mmol), NaN3 (195 mg, 3 mmol)
and DMF (25 mL) were added into a 50-mL round-bottomed flask
equipped with a magnetic stirring bar. The round-bottomed flask
was placed in an oil bath preheated at 35 °C under stirring and
reacted for 24 h. The residue was diluted with THF and
subsequently filtered through neutral alumina to remove sodium
bromide and excess NaN3. After the mixture was concentrated by
rotary evaporation, it was precipitated in methanol. White powder
(yield: 2.65 g) of PMMA with two azido end-groups and one central
alkynyl group [alkynyl-(PMMA-N3)]
2
was obtained by thrice
precipitation and dryness under vacuum for 24 h.

**Synthesis of Isc-hp PMMA via click chemistry**

Alkynyl-(PMMA-N3) (0.25 g, 0.0188 mmol), PMDETA (6.5 mg, 0.0376 mmol) and THF (1.25 mL) were added into a 5-mL Schlenk
flask equipped with a magnetic stirrer bar. After oxygen was
removed by three freeze-pump-thaw cycles, CuBr (5.4 mg, 0.0376
mmol) was added under nitrogen flow. Then, the flask
was sealed under vacuum, placed in an oil bath controlled at 70 °C
under stirring and stood for 24 h. The polymerization was stopped
by being cooled in ice bath, after which the mixture was diluted
with THF and subsequently filtered through neutral alumina to remove

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the copper salt. The mixture was concentrated under vacuum and then precipitated in methanol. The product was purified by the precipitation for three times and dried under vacuum for 24 h to obtain white powder of lsc-hp PMMA (0.14 g).

**Self-cyclization of alkynyl-(PMMA-N$_3$)$_2$ in DMF**

Alkynyl-(PMMA-N$_3$)$_2$ (0.2 g, 0.015 mmol), PMDETA (106 mg, 0.61 mmol), and DMF (350 mL) were added into a 500-mL round-bottomed flask. The reaction mixture was bubbled with N$_2$ for 12 h. Then CuBr (88 mg, 0.61 mmol) was introduced into the degassed reaction system under nitrogen flow. The click reaction was controlled at 100 °C under stirring and kept for 24 h. The reaction was stopped, cooled to room temperature and stirred for another 12 h in the air. Then the mixture was concentrated under vacuum, diluted with THF and subsequently filtered through neutral alumina to remove CuBr$_2$. After the concentration by rotary evaporation, thrice precipitation with THF/methanol and dryness under vacuum for 24 h, white powder of cyclic PMMA (0.12 g) was obtained.

**Characterization**

Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker DRX-300 NMR (300 MHz) instrument in CDCl$_3$ at room temperature with tetramethylsilane as internal standard. Fourier Transform Infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer using KBr discs. The molecular weight distribution, relative number- and weight-average molecular weights ($M_n$$_{GPC}$ and $M_w$$_{GPC}$), as well as the absolute number- and weight-average molecular weights ($M_n$$_{MALLS}$ and $M_w$$_{MALLS}$) were determined by gel permeation chromatography (GPC, Waters 1515) equipped with a refractive index (RI, Wyatt WREX-02) detector, a multiangle LLS (MALLS, Wyatt DAWN EOS) detector and three Waters Styragel columns (HR2, HR4, HR6) at ambient temperature. THF was used as the eluent at a flow rate of 1.0 mL/min and the calibration was carried out using low polydispersity linear polystyrene standards. The MALLS detector with the GaAs laser wavelength length at 685 nm are equipped with 18 diodes at a multi-angle ranging from 22.5° to 147.0°. GPC analysis was also performed on a Viscotek GPC instrument equipped with Viscotek TDA 302 detector using RI and MALLS detectors. Polypore 1 (300 x 7.8 mm), Jordi Gel DVB Mixed Bed (250 x 10 mm) and Waters Styragel HR 4(300 x 7.8 mm, 5μm) were used as the columns. HPLC grade THF from Samchun Corp. was used as the eluent. The flow rate of THF was kept as 0.7 mL/min using the BISCHOFF HPLC compact pump. The specific refractive index increment $dn/dC$ of alkynyl-(PMMA-Br)$_2$ was measured at ambient temperature in THF using a series of different concentration solutions.

**Results and discussion**

Seesaw-type macromonomer of alkynyl-(PMMA-N$_3$)$_2$ was prepared by ATRP of MMA with PBMP as initiator followed the azidation of end groups. Then lsc-hp PMMA almost without the self-cyclization of macromonomers was successfully prepared via click chemistry under high concentration of macromonomers in the good solvent of THF. Moderate steric hindrance at PMMA ends, high concentration and good solvent effectively inhibited the intrachain cyclic side reaction. The whole synthesis procedure is shown in Scheme 1.
Preparation of alkynyl-(PMMA-N$_3$)$_2$ macromonomer

Alkynyl-(PMMA-Br)$_2$ was prepared through ATRP of MMA with PBMP as the initiator in the presence of CuBr/PMDETA. To guarantee a high degree of bromines at alkynyl-(PMMA-Br)$_2$ ends, the mole ratio of monomer/initiator at the beginning of polymerization was controlled as high as 325 and the monomer conversion at the end of polymerization as low as 31.5%. To obtain alkynyl-(PMMA-N$_3$)$_2$, the azidation of alkynyl-(PMMA-Br)$_2$ was proceeded for 24 h in DMF using NaN$_3$. Fig. 1 depicts $^1$H NMR spectra of alkynyl-(PMMA-Br)$_2$ and alkynyl-(PMMA-N$_3$)$_2$.

The signals at 3.60 ppm and 0.48-1.08 ppm are assigned to –CH$_3$ and –CH$_2$ protons from MMA, respectively. In addition, the unique signal at 2.6-2.7 ppm (d’) represents methylene proton group from the end unit of alkynyl-(PMMA-Br)$_2$ chain. After the azidation, this signal disappeared, moved to a lower chemical shift and overlapped with other methylene protons from PMMA units at 1.58-2.14 ppm (d+d’), confirming the azidation. Moreover, the successful preparation of alkynyl-(PMMA-N$_3$)$_2$ is further verified by FT-IR spectra as shown in Fig. 2. The characteristic stretching peak of azido group appears at 2118 cm$^{-1}$, indicating the nucleophilic substitution of bromo group by the azido group.

Fig. 1 $^1$H NMR spectra of alkynyl-(PMMA-Br)$_2$ (A) and alkynyl-(PMMA-N$_3$)$_2$ (B) in CDCl$_3$.

Preparation of lsc-hp PMMA via click chemistry

Click chemistry was adopted to prepare lsc-hp polymers due to its high efficiency, mild reaction conditions and high yield. $^1$H NMR spectra of lsc-hp PMMA obtained from alkynyl-(PMMA-N$_3$)$_2$ at different time of click polymerization are illustrated in Fig. 3 (characteristically local scan) and Figure S2 (full scan). To identify the change of $^1$H NMR spectrum clearly, only characteristic signals are shown in Fig. 3. Comparing $^1$H NMR spectrum of lsc-hp PMMA in Fig. 3C and that of alkynyl-(PMMA-N$_3$)$_2$ in Fig. 1, it is found that the signal at 2.48 ppm attributed to the alkynyl proton sharply weakens, despite there exists one residual alkynyl group in each lsc-hp PMMA molecule. In addition, the signal of methylene protons adjacent to the alkynyl group moves from 4.70 ppm (b) to 5.19 ppm (b’) due to the formation of electron-withdraw triazole ring. Figure S2 with full scan of lsc-hp PMMA signals indicates the presence of main signals from PMMA units.

Furthermore, those characteristic signals varied with reaction time. As shown in Fig. 3A, after 1 h, the signal (b’) at 5.19 ppm is relatively weak, indicating that few branching units of lsc-hp PMMA was formed. Whereas, the signal (b) at 2.48 ppm is much strong, illustrating that most of the macromonomers still existed in the reaction mixture. At the reaction time of 2 h, the integration ratio of signal b’ to that of signal b ($A_b’/A_b$) increases to 1.01 (Fig. 3B). After 5-day click reaction, the signals at 2.48 ppm and 4.70 ppm reduce sharply and can hardly be seen in Fig. 3C. On the contrary, the signal at 5.19 ppm becomes strong obviously. Thus, it can be deduced that almost all of macromonomers have been consumed after 5 d.

Fig. 2 FTIR spectra of alkynyl-(PMMA-Br)$_2$ (A) and alkynyl-(PMMA-N$_3$)$_2$ (B).

Fig. 3 $^1$H NMR spectra of lsc-hp PMMA at different reaction time in CDCl$_3$ (A: 1 h, B: 2 h and C: 5 d).

FT-IR spectra of lsc-hp PMMA obtained at different reaction intervals are illustrated in Fig. 4. The intensity of the characteristic
stretching peak of azido group decreases with the increment of reaction time, indicating the consumption of azido-functionalized macromonomers and the formation of triazole rings of \textit{lsc-hp PMMA}.

Fig. 4 FTIR spectra of \textit{lsc-hp PMMA} at different reaction intervals (A: 1 h, B: 2 h and C: 5 d).

Fig. 5 provides Waters GPC traces of \textit{lsc-hp PMMA} obtained from alkynyl-(PMMA-N\textsubscript{3})\textsubscript{2} with $M_n$ of 13.3 k at the click concentration of 0.2 g/mL. At the reaction time of 1 h, GPC trace is almost the same as that of alkynyl-(PMMA-N\textsubscript{3})\textsubscript{2}. At the reaction time of 2 h, the signal of linear macromonomer decreases sharply. Afterwards, molecular weight distribution of the product becomes broader while the portion with higher molecular weight increases in its intensity and moves to lower elution time constantly with the extension of reaction time, suggesting that more and more \textit{lsc-hp PMMA} molecules with higher and higher overall molecular weight were produced.

Fig. 5 GPC traces of \textit{lsc-hp PMMA} obtained from alkynyl-(PMMA-N\textsubscript{3})\textsubscript{2} with $M_n$ of 13.3 k at the click concentration of 0.2 g/mL.

Waters GPC traces of \textit{lsc-hp PMMA} from alkynyl-(PMMA-N\textsubscript{3})\textsubscript{2} with $M_n$ = 8.9 k are illustrated in Fig. 6. As can be seen, GPC traces of \textit{lsc-hp PMMA} expand to lower elution time with reaction time, accompanied with the weakening of linear macromonomer signal. Moreover, it is easy to find that there is a weak shoulder in the range of long elution time for GPC traces of \textit{lsc-hp PMMA} at the concentration of 0.2 g/mL, while no shoulder was found for GPC traces of \textit{lsc-hp PMMA} at the concentration of 8.9 g/mL.

The inhibition of self-cyclization of macromonomers

Click chemistry is an excellent method to prepare \textit{lsc-hp} polymers due to its high efficiency, mild reaction conditions and high yield. However, unwanted side reaction such as intramolecular cyclization of PST seesaw-type macromonomers happened in the case of \textit{lsc-hp PST}. As for \textit{lsc-hp PMMA} in this report, high concentration of alkynyl-(PMMA-N\textsubscript{3})\textsubscript{2} was adopted. During the click polymerization of alkynyl-(PMMA-N\textsubscript{3})\textsubscript{2} macromonomers, intramolecular cyclization and hyperbranching competes with each other. However, intramolecular cyclization is a unimacromolecular reaction, the hyperbranching process, on the contrary, happens between macromonomers. Therefore, highly concentrated solution should be effective to suppress intramolecular cyclization while highly dilute solution should be necessary to obtain intramolecular cyclic structure.

The solvent is also the key issue for the growth of hyperbranched polymers through polycondensation of AB\textsubscript{2} macromonomers. Hutchings et al. found that the coupling reaction of Cl-PST-(OH)\textsubscript{2} was favoured by the solvent with high dielectric constant, resulting in
Thus, THF, a solvent better for PMMA than DMF, was used to limit the self-cyclization of alkynyl-(PMMA-N$_2$)$_2$. Moreover, di-substituted chain ends of PMMA chain would tender steric hindrance to suppress the intramolecular self-cyclization of alkynyl-(PMMA-N$_2$)$_2$ compared with mono-substituted alkynyl-(PSt-N$_2$)$_2$ and alkynyl-(PtBA-N$_2$)$_2$. The influence of steric hindrance on copper-catalyzed azide–alkyne click reaction had been reported in the preparation of ferrocene-labeled steroids with a series of azido functionalized androstanes. Considerably low reactivity of 6β-azido-androstane towards ethynylferrocene was confirmed due to the steric hindrance brought by the bulky ferrocene moiety. However, when the alkynyl group and the ferrocene moiety were separated by a spacer, acceptable yield was achieved.

ls-c-hp PMMA was prepared from alkynyl-(PMMA-N$_2$)$_2$, with different molecular weight, 8.9 k and 13.3 k, respectively. As can be seen in Fig. 6, the signal of linear alkynyl-(PMMA-N$_2$)$_2$-8.9k decreases gradually and no shoulder is found. As for the GPC traces of ls-c-hp PMMA prepared by alkynyl-(PMMA-N$_2$)$_2$-13.3k (Fig. 5), the signal of linear alkynyl-(PMMA-N$_2$)$_2$-13.3k at the elution time of 25.5 min gradually decreased, but a very weak shoulder still exists after 7-d click reaction. This observation is quite different from click polymerization of alkynyl-(PSt-N$_2$)$_2$, where alkynyl-(PSt-N$_2$)$_2$-8k has higher self-cyclization degree than alkynyl-(PSt-N$_2$)$_2$-28k.

To confirm whether the shoulder signal comes from linear or cyclic alkynyl-(PMMA-N$_2$)$_2$-13.3k, designed cyclic PMMA-13.3k was prepared from linear alkynyl-(PMMA-N$_2$)$_2$-13.3k and the dissolution fraction of ls-c-hp PMMA-13.3k was also performed with acetone/n-hexane ($V_{acetone}$ : $V_{n-hexane}$ = 50 : 37). To facilitate the self-cyclization of alkynyl-(PSt-N$_2$)$_2$-13.3k, high diluted concentration (0.25 g/350 mL), polar/poorer solvent (DMF) and higher temperature (100 ºC) were adopted. The molecular weights of designed cyclic PMMA-13.3k and its linear counterpart by Waters GPC with RI detector ($M_w$$_{GPC}$ and $M_m$$_{GPC}$) are listed in Table 1. Compared with the linear alkynyl-(PSt-N$_2$)$_2$-13.3k, designed cyclic PMMA-13.3k has a little smaller molecular weight. However, the weight-averaged molecular weight by MALSS detector ($M_w$$_{MALSS}$) for linear and cyclic PMMA is quite close with acceptable deviation.

Table 1 Comparison of cyclic and linear alkynyl-(PSt-N$_2$)$_2$-13.3k.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_w$$_{GPC}$ (g·mol$^{-1}$)</th>
<th>$M_m$$_{GPC}$ (g·mol$^{-1}$)</th>
<th>PDI</th>
<th>$M_w$$_{MALSS}$ (g·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclic PMMA-13.3k</td>
<td>12030</td>
<td>14390</td>
<td>1.19</td>
<td>17150</td>
</tr>
<tr>
<td>linear PMMA-13.3k</td>
<td>13300</td>
<td>16080</td>
<td>1.21</td>
<td>17580</td>
</tr>
</tbody>
</table>

As the cyclic polymers have smaller hydrodynamic volume than their linear analogues, the elution time of the former should be longer than the latter, making GPC a good tool to distinguish them. As shown in Fig. 5, the elution time corresponding to the designed cyclic PMMA-13.3k is 25.7 min, a little longer than linear alkynyl-(PSt-N$_2$)$_2$-13.3k, suggesting that this product should be the designed cyclic PMMA-13.3k.

The 3$^H$ NMR spectrum is used to further verify the structure of designed cyclic PMMA-13.3k. As illustrated in Fig. 7, the appearance of the signal at 5.19 ppm attributed to the methylene protons adjacent to electron-withdraw triazole ring is accompanied with the sharp decreasing of the corresponding signal at 4.70 ppm (Fig. 18, b) and the sharp decreasing of the signal of alkynyl proton at 2.48 ppm (Fig. 18, a), though very weak signal at 4.70 ppm attributed to the unreacted macromonomers still exists.

According to the fact that the proportion of cyclic macromonomer should increase with decreasing molecular weight of macromonomer, we believe that the weak shoulder in the GPC traces of ls-c-hp PMMA-13.3k should mainly attributed to the unreacted macromonomers other than cyclic macromonomers. Few bromo end-groups may be lost when preparing macromonomers by ATRP, especially for reactive a-substituted acrylates. The reservation rate of bromo end-groups of linear PMMA-13.3k is lower than PMMA-8.9K due to longer reaction time. This agrees well with the fact that a weak shoulder is found in GPC traces of ls-c-hp PMMA-13.3k and no shoulder is found in GPC traces of ls-c-hp PMMA-8.9k. Trace amount of cyclic macromonomers may also contribute to this shoulder.

![Fig. 7 3H NMR spectrum of cyclic PMMA in CDCl3.](Image)
decrease tendency. As the signal of cyclized PMMA should become stronger with the prolonged reaction time, it can be deduced that this shoulder should not be cyclized PMMA but unreacted linear macromonomers.

Moreover, click copolymerizations of alkynyl-(PMMA-N$_3$)$_2$, poly(methyl acrylate) with mono-substituted chain ends, were performed to make a comparison. As shown in Figure S9, the signal in the range of long eluent time is much obviously and can be assigned to cyclic macromonomer of alkynyl-(PMMA-N$_3$)$_2$. Being similar to lsc-hp PST, alkynyl-(PMMA-N$_3$)$_2$-17.9k has lower self-cyclization degree than alkynyl-(PMMA-N$_3$)$_2$-6.6k during click polymerization, which comes from the lower center-to-end distance of alkynyl-(PMMA-N$_3$)$_2$-6.6k.

Formation kinetics of lsc-hp PMMA based on inhibited self-cyclization of seesaw macromonomers

Since hyperbranched polymers have lower hydrodynamic radius compared with the linear similarities with the same molecular weight$^{38}$ and PST was used as the standard, GPC-RI result should deviate from the true value. Thus, GPC-MALLS was used to obtain the absolute molecular weight ($M_w$$_{MALLS}$ and $M_n$$_{MALLS}$). The specific refractive index increment (dn/dc) of alkynyl-(PMMA-Br)$_2$ was measured to be 0.097 mL/g as shown in Supporting Information. Formation kinetics of lsc-hp PMMA with the reaction time from 1 h to 7 d was monitored by Waters GPC with both RI detector and MALLS detector. The apparent number-average molecular weight ($M_n$$_{GPC}$), weight-average molecular weight ($M_w$$_{GPC}$) and $M_w$$_{MALLS}$ are summarized in Table 2. The molecular weights determined by Viscotek GPC are listed in Table 3.

![Fig. 8 GPC traces of lsc-hp and cyclic PMMA from alkynyl-(PMMA-N$_3$)$_2$ with $M_n$ of 13.3 k determined by Viscotek GPC.](image)

### Table 2 Variation of molecular weight of lsc-hp PMMA

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction time</th>
<th>$M_n$$_{GPC}$ (g∙mol$^{-1}$)</th>
<th>$M_w$$_{GPC}$ (g∙mol$^{-1}$)</th>
<th>PDI$^a$</th>
<th>$M_w$$_{MALLS}$ (g∙mol$^{-1}$)</th>
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</thead>
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<td>16.1k</td>
<td>1.21</td>
<td>17.6k</td>
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<td>1.29</td>
<td>21.0k</td>
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<td>25.7k</td>
<td>64.1k</td>
<td>2.49</td>
<td>86.3k</td>
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<td>lsc-hp PMMA$_{13.3k}$-1d</td>
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<td>38.4k</td>
<td>131.3k</td>
<td>3.42</td>
<td>267.7k</td>
</tr>
<tr>
<td>lsc-hp PMMA$_{13.3k}$-2d</td>
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<td>37.6k</td>
<td>150.2k</td>
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<td>597.0k</td>
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<tr>
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<td>162.0k</td>
<td>3.72</td>
<td>665.8k</td>
</tr>
<tr>
<td>lsc-hp PMMA$_{13.3k}$-5d</td>
<td>5d</td>
<td>42.7k</td>
<td>164.7k</td>
<td>3.86</td>
<td>716.9k</td>
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<tr>
<td>lsc-hp PMMA$_{13.3k}$-7d</td>
<td>7d</td>
<td>48.4k</td>
<td>183.2k</td>
<td>3.79</td>
<td>774.3k</td>
</tr>
<tr>
<td>linear PMMA$_{9.6k}$</td>
<td>0</td>
<td>8.9k</td>
<td>10.6k</td>
<td>1.19</td>
<td>10.6k</td>
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<tr>
<td>lsc-hp PMMA$_{9.6k}$-2h</td>
<td>2h</td>
<td>14.4k</td>
<td>36.1k</td>
<td>2.51</td>
<td>56.3k</td>
</tr>
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<td>lsc-hp PMMA$_{9.6k}$-4h</td>
<td>4h</td>
<td>14.8k</td>
<td>38.4k</td>
<td>2.59</td>
<td>57.0k</td>
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<td>lsc-hp PMMA$_{9.6k}$-8h</td>
<td>8h</td>
<td>22.9k</td>
<td>71.8k</td>
<td>3.13</td>
<td>95.2k</td>
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<tr>
<td>lsc-hp PMMA$_{9.6k}$-10h</td>
<td>10h</td>
<td>25.6k</td>
<td>127.7k</td>
<td>4.99</td>
<td>180.4k</td>
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<tr>
<td>lsc-hp PMMA$_{9.6k}$-1d</td>
<td>1d</td>
<td>34.1k</td>
<td>157.8k</td>
<td>4.77</td>
<td>460.1k</td>
</tr>
<tr>
<td>lsc-hp PMMA$_{9.6k}$-2d</td>
<td>2d</td>
<td>43.8k</td>
<td>224.6k</td>
<td>5.13</td>
<td>548.8k</td>
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<tr>
<td>lsc-hp PMMA$_{9.6k}$-3d</td>
<td>3d</td>
<td>44.8k</td>
<td>234.6k</td>
<td>5.23</td>
<td>696.2k</td>
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<tr>
<td>lsc-hp PMMA$_{9.6k}$-5d</td>
<td>5d</td>
<td>45.5k</td>
<td>240.1k</td>
<td>5.27</td>
<td>696.5k</td>
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<tr>
<td>lsc-hp PMMA$_{9.6k}$-7d</td>
<td>7d</td>
<td>45.9k</td>
<td>242.7k</td>
<td>5.29</td>
<td>700.4k</td>
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</table>

$^a$ $M_n$$_{GPC}$, $M_w$$_{GPC}$ and PDI determined by Waters GPC with refractive index detector.

$^b$ $M_w$$_{MALLS}$ determined by Waters GPC with multangle laser light scattering (MALLS) detector.

### Table 3 Molecular weights of PMMA determined by Viscotek GPC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction time</th>
<th>$M_n$$_{MALLS}$ (g∙mol$^{-1}$)</th>
<th>$M_w$$_{MALLS}$ (g∙mol$^{-1}$)</th>
<th>PDI$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear PMMA$_{13.3k}$</td>
<td>0</td>
<td>17.5k</td>
<td>20.1k</td>
<td>1.15</td>
</tr>
<tr>
<td>cyclic PMMA$_{13.3k}$</td>
<td>-</td>
<td>17.1k</td>
<td>19.6k</td>
<td>1.15</td>
</tr>
<tr>
<td>lsc-hp PMMA$_{13.3k}$-2h</td>
<td>2h</td>
<td>39.7k</td>
<td>91.8k</td>
<td>2.31</td>
</tr>
</tbody>
</table>
Plot of $M_n/M_w$ vs reaction time is shown in Fig. 9A. As can be seen, the value of $M_n/M_w$ increases fast at the beginning. This means that $M_w$ should increases much faster than $M_n$. It is a hint that there should be the linkage between hyperbranched molecules, two, three, or even more chains. At this stage, the branching degree is fairly low and the unreacted alkynyl group would not be wrapped heavily. However, as the click polymerization goes on for 1 d, the value of $M_n/M_w$ increases much slowly, namely $M_w$ increases a little faster than $M_n$. At this stage, the branching degree is high and hyperbranched molecules get larger. Consequently, the unreacted alkynyl group from one hyperbranched molecule would be wrapped tightly to hinder its linkage with azido groups from other hyperbranched molecules. Additionally, un-polymerized alkynyl-(PMMA-N$_3$)$_2$ keeps decreasing in its amount, leading to the slowdown of $M_n/M_w$. The faster increment and larger value of $M_w/M_n$ for alkynyl-(PMMA-N$_3$)$_2$-8.9k is consistent with higher reaction probability of macromonomer with lower molecular weight.

Fig. 9B depicts the variations of the overall absolute weight-average molecular weight ($M_{w \text{MALLS}}$) of lsc-hp PMMA and its absolute weight-average degree of polycondensation $DP_w$ with time, where $DP_w$ is defined as the ratio of $M_{w \text{MALLS}}$ of lsc-hp PMMA to that of alkynyl-(PMMA-N$_3$)$_2$.

The variation of $DP_w$ with time can also be divided into two stages. At the first stage, $DP_w$ increases rapidly with time, owing to the following reasons. Firstly, at the early stage of the reaction, the concentration of unreacted macromonomers is high enough to keep the reaction rate. Secondly, the wrapped alkynyl groups inside the lsc-hp PMMA molecules are few since hyperbranched polymer is not too large. When it comes to the second stage, more and more reactive groups are wrapped, resulting in the great difficulty in click polymerization. It should be emphasized that $DP_w$ of lsc-hp PMMA from alkynyl-(PMMA-N$_3$)$_2$-8.9k increases faster than that from alkynyl-(PMMA-N$_3$)$_2$-13.3 k. This can be ascribed to two reasons. Firstly, when preparing the lsc-hp PMMA at the fixed macromonomer concentration as 0.2 g/mL, the macromonomers with lower weight-average molecular weight have more reactive groups. Secondly, fewer alkynyl groups are wrapped when using macromonomer with short chain length.

The reaction time dependent $DP_w$ of lsc-hp PMMA prepared by alkynyl-(PMMA-N$_3$)$_2$ was fitted with Eq. 1.

$$\ln\left(\frac{DP_w + 1}{2}\right) = -\frac{[A]_0}{k_{AB}} \int_0^t k_{AB} dt$$

Eq. 1

where $[A]_0$ and $k_{AB}$ is the initial concentration of alkynyl groups and the reaction rate constant of alkynyl/azido groups, respectively.

With the increase of click polymerization time, lsc-hp polymer gets large and reactive groups are increasingly wrapped, making $k_{AB}$ decrease. Finally, the value of $k_{AB}$ is assumed to decrease exponentially according to Eq. 2.

$$k_{AB} = k_{AB,0} e^{-\alpha t}$$

Eq. 2

where $k_{AB,0}$ represents the initial value of $k_{AB}$ at $t = 0$ and $\alpha$ is a constant. After substitution of $k_{AB}$, Eq. 1 is rewritten as followed.

$$\ln\left(\frac{DP_w + 1}{2}\right) = -\frac{[A]_0 k_{AB,0}}{\alpha} (1 - e^{-\alpha t})$$

Eq. 3

where $[A]_0 k_{AB,0}/\alpha$ represents the maximum of theoretical $\ln((DP_w + 1)/2)$.

As can be seen from Fig. 10, the theoretical line fits well with the experiment data, indicating that time-dependent $DP_w$ of lsc-hp PMMA also obeys Eq. 1 and the assumption that $k_{AB}$ decreases exponentially is correct. The coefficients of Eq. 3 are summarized in Table 4. As can be seen, the value of $k_{AB,0}$ for 8.9 k macromonomer is higher than that for 13.3 k macromonomer. Furthermore, the value of $\alpha$ for 8.9 k macromonomer is also bigger than that for 13.3k macromonomer, indicating that the reaction rate decreases faster, probably due to the higher decrease in the reactivity of alkynyl groups being wrapped.

| lsc-hp PMMA$_{13.3k}$-3d | 3d | 218.5k | 584.5k | 2.68 |
| lsc-hp PMMA$_{13.3k}$-5d | 5d | 209.9k | 593.4k | 2.83 |

$^a$M$_{w \text{MALLS}}, M_{w \text{MALLS}}$, and PDI determined by Viscotek GPC.
Conclusions

"Well-defined" long-subchain hyperbranched poly(methyl methacrylate) with uniform long subchains and almost no self-cyclized-by-product was obtained through the combination of ATRP and azide-alkyne click reaction. To achieve this goal, seesaw type macromonomers of alkynyl-(PMMA-N$_3$)$_2$ with narrow molecular weight distribution were obtained by controlled radical polymerization, followed by their click polymerization under high concentration and moderately polar solvent of THF, which is a good solvent for PMMA. As well, di-substituted structure of PMMA chain ends endows the steric hindrance to further inhibit the self-cyclization of alkynyl-(PMMA-N$_3$)$_2$.GPC results showed that the signal attributed to alkynyl-(PMMA-N$_3$)$_2$ macromonomer diminished with the prolonged reaction time and negligible self-cyclized-by-product was found. This phenomenon is quite different from our previous report about lsc-hp PMMA, whose chain-ends are mono-substituted. During the click polymerization of alkynyl-(PMMA-N$_3$)$_2$, the formed lsc-hp PMMA gradually grew with enlarging overall molecular weight and broadening molecular weight distribution.

The growth kinetics of lsc-hp PMMA followed the equation: ln[(DP$_w$ + 1)/2] = [A]$_0$k$_{AB,0}$(1 - e$^{-\alpha t}$)/$\alpha$, where [A]$_0$ is the initial alkynyl concentration, $k_{AB,0}$ is the initial reaction rate constant between azido and alkynyl groups and $\alpha$ is a constant related to the molecular weight of macromonomers, respectively. By the comparison of GPC results and reaction parameters, alkynyl-(PMMA-N$_3$)$_2$ macromonomer with low molecular weight has higher reactivity in the click polymerization under the present conditions.

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Notes and references

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32. H. W. Ma, Q. Y. Wang, W. Sang, L. Han, P. B. Liu, H. Y. Sheng, Y. R.


Formation of long-subchain hyperbranched poly(methyl methacrylate) based on inhibited self-cyclization of seesaw macromonomers

Peng-Yun Li, Wei-Dong He,* Sheng-Qi Chen, Xiao-Xia Lu, Jia-Min Li, Hui-Juan Li

“Well-defined” hyperbranched PMMA almost without self-cyclization was obtained through click reaction, facilitated by high concentration, good solvent and di-substituted chain-ends.