Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

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

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Preparation of AB_2 ATRP initiator (PBMP)

Figure S1 shows the ^{1}H NMR spectrum of the PBMP. The typical resonance signal of $CH{\equiv}CCH_2O$- (*d*, 2 H, 4.76 ppm), -$COOCH_2$- (*m*, 4 H, 4.51~4.15 ppm) and -$CBr(CH_3)_2$ (*s*, 12 H, 1.94 ppm) suggested the successful synthesis of the initiator.

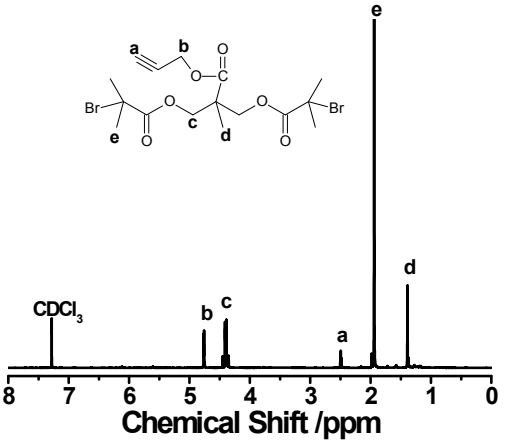

Figure S1. ^{1}H NMR spectrum of PBMP in $CDCl_3$.

^{1}H-NMR characterization of *lsc-hp* PMMA with full scan

Figure S2 reveals the full scan ^{1}H NMR spectra ($CDCl_3$) of *lsc-hp* PMMA prepared after different time. As seen, all of *lsc-hp* PMMA have the same main peaks at 0.48~1.08, 1.57~2.10 and 3.60 ppm, ascribed to $–CH_3$, CH_2 and $–OCH_3$ protons from MMA, respectively. Moreover, with the prolonged reaction time from 1 h to 5 d, the signal at 4.70 ppm (b) attributed to methylene protons adjacent to the alkynyl group weakens, while the corresponding signal at 5.19 ppm (b′) gradually gets sharp due to the formation of electron-withdraw triazole ring.

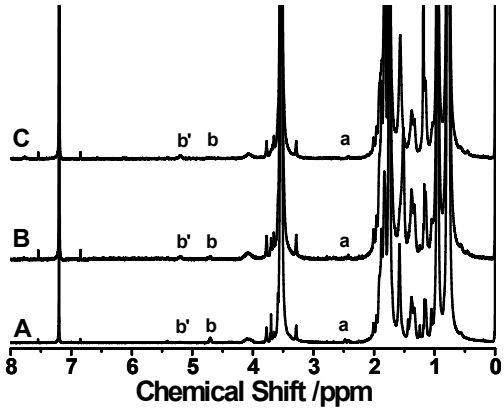

Figure S2. Full scan ^{1}H NMR spectra of *lsc-hp* PMMA at different time (A: 1 h, B: 2 h and C: 5 d).

Determining d*n*/d*C* of PMMA

The refractive index increment (d*n*/d*C*) of PMMA in THF was determined with a precise differential refractometer equipped with a position-sensitive detector (Hamamatsu S 3932), a temperature-controlled refractometer cuvette (Hellma 590.049-QS) and a laser light source. Concentration dependence of voltage (*V*/*C*) of alkynyl-$(PMMA\text{-}Br)_2$ and NaCl were measured at room temperature. The measured data points and the fitting curves are shown in Figure S3. The d*n*/d*C* of alkynyl-$(PMMA\text{-}Br)_2$ is

calculated by the following equations:

$$\frac{dn_{NaCl}}{dC_{NaCl}} = \frac{dn_{NaCl}}{dV_{NaCl}} \times \frac{dV_{NaCl}}{dC_{NaCl}} \qquad \text{Eq.1}$$

$$\frac{dn_{PMMA}}{dC_{PMMA}} = \frac{dn_{PMMA}}{dV_{PMMA}} \times \frac{dV_{PMMA}}{dC_{PMMA}} \qquad \text{Eq.2}$$

dn_{NaCl}/dV_{NaCl} and dn_{PMMA}/dV_{PMMA} is the same for the same detector. Moreover, dn_{NaCl}/dC_{NaCl} is 0.176 mL/g according to the literature.[1] The value of dV_{NaCl}/dC_{NaCl} and dV_{PMMA}/dC_{PMMA} calculated from the slope of fitting curves are -0.191 and -0.105 v·L·g^{-1}, respectively. Finally, dn_{PMMA}/dC_{PMMA} is calculated as 0.097 mL/g.

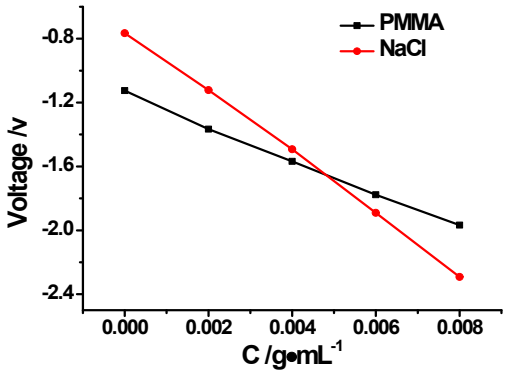

Figure S3. Concentration dependences of voltage obtained for aqueous solutions of NaCl (solid dots) and THF solutions of seesaw-type PMMA macromonomers (solid squares) at room temperature.

The solvent to dissolve alkynyl-(PMMA-N_3)$_2$-13.3k from *lsc-hp* PMMA

As can be seen from Figure 5B, a weak shoulder signal appears at the right region of GPC traces of *lsc-hp* PMMA obtained from alkynyl-(PMMA-N_3)$_2$-13.3k. To confirm whether this weak shoulder comes from the unreacted linear PMMA or the cyclic PMMA, the solvent that can selectively dissolve the fraction with molecular weight the same as/below the linear macromonomers was determined. Firstly, 30 mg of alkynyl-(PMMA-N_3)$_2$-13.3k was dissolved in 10 mL acetone in a round-bottom flask with a

magnetic stirring bar at 15 °C. Then *n*-hexane was slowly injected into the round-bottom flask through micro-injector at the rate of 30 mL/h, until the solution turns a little cloudy. The total amount of *n*-hexane added was 7.4 mL. That is to say, the solvent consists of acetone/*n*-hexane at the volume ratio of 50:37.

Fractional dissolution of the first fraction of *lsc-hp* PMMA by selective solvent

At 15 °C, 55 mg *lsc-hp* PMMA prepared by click reaction for 7 d was added to a 50-mL round-bottom flask equipped with a magnetic stirring bar, then 26.1 mL selective solvent (V_{acetone}:$V_{n\text{-hexane}}$=50:37) was added and the reaction was stirred for 12 h. Then the dissolved product was filtered and further purified by passing through a 0.22-μm nylon membrane filter. After the concentration under reduced pressure and 24-h dryness under vacuum, trace amount of product adhered to the round-bottom flask was obtained.

Supplementary GPC results for the first fraction of *lsc-hp* PMMA

Figure S4 depicts the GPC traces of the first fraction of *lsc-hp* PMMA, linear alkynyl-(PMMA-N_3)$_2$-13.3k as well as the cyclic PMMA-13.3k. As can be seen, the first fraction of *lsc-hp* PMMA has a broad distribution ranges from 23.5 min to 28.0 min, indicating dissolution of partial higher molecular weight fraction, possibly due to the slightly temperature change during the fractional dissolution. As the elution time of the linear and the cyclic alkynyl-(PMMA-N_3)$_2$-13.3k are 25.490 min and 25.718 min, respectively. Consequently, GPC trace of the first fraction was processed by multiple peak fitting, with two selected peaks at 25.490 min, 25.718 min and another peak around 24.4 min corresponding to the higher molecular weight fraction. As shown in

Figure S4B, the fitted sum curve (curve C) fits well with GPC trace of the first fraction, made up of three main curves with the peak position at 25.902 min (curve D), 25.122 min (curve E) and 24.377 min (curve F). Curve D can be ascribed to the formation of cyclic PMMA, while curve E and curve F can be assigned to the unreacted alkynyl-(PMMA-N_3)$_2$-13.3 k and the higher molecular weight fraction, respectively. Though the portion of cyclic PMMA in GPC traces was found not to be zero, the amount of cyclic PMMA produced is still negligible because the first fraction of *lsc-hp* PMMA obtained by dissolution fractional is in trace amount over the whole product. That is to say, the suggestion about the formation of long-subchain hyperbranched PMMA based on inhibited self-cyclization of seesaw macromonomers is reliable.

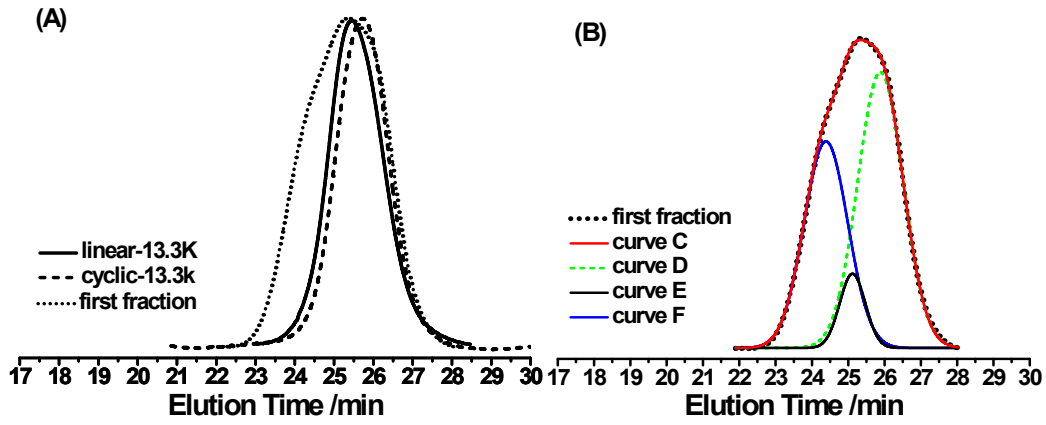

Figure S4. Waters GPC traces of linear, cyclic alkynyl-(PMMA-N_3)$_2$-13.3k and the first fraction of *lsc-hp* PMMA-13.3k (A) and multiple peak fitting of the first fraction of *lsc-hp* PMMA-13.3k (B).

Preparation of *lsc-hp* poly(methyl acrylate) (PMA)

To better confirm the steric hindrance of 1,1-disubstituted chain ends of seesaw macromonomer to inhibit the self-cyclization of seesaw macromonomers for *lsc-hp* PMMA, the analogue seesaw macromonomer with monosubstituted chain ends,

alkynyl-(PMA-Br)$_2$, was synthesized and click reacted.

Synthesis of monosubstituted seesaw-type alkynyl-(PMA-N_3)$_2$

MA (34.436g, 400 mmol), PMDETA (173.3 mg, 1 mmol), PBMP (470.0 mg, 1 mmol) and THF (2 mL) were added into a 50-mL Schlenk flask equipped with a magnetic stirrer bar. After being degassed by three freeze-pump-thaw cycles, CuBr (143.5 mg, 1mmol) was added under nitrogen flow. Then the flask was sealed under vacuum and immersed in an oil bath at 70 °C. After 4 h, the reaction was stopped by being cooled in ice bath and exposure to air. Then the reaction mixture were diluted with THF and passed through neutral alumina to remove the copper salt. After concentrated by rotary evaporation, the polymer was precipitated in methanol/water (1/1; v/v) and dried under vacuum until constant weight. Then alkynyl-(PMA-Br)$_2$ was obtained as a colorless glass. Yield: 10.2 g, $M_{n,NMR}$=11540 g/mol, $M_{n,GPC}$ = 1.788 × 10^4 g/mol, PDI = 1.20.

Alkynyl-(PMA-Br)$_2$ (5.54 g, 0.48 mmol), NaN_3 (0.312 g, 4.8 mmol) and DMF (25 mL) were added into a 50-mL round-bottomed flask which was preheated at 35 °C under stirring. After 24 h, the residue was diluted with THF and passed through neutral alumina to remove sodium bromide and excess NaN_3. Then the mixture was concentrated, precipitated in methanol/water (1/1; v/v) and dried under vacuum to gain a colorless product.

Figure S5 presents the ^{1}H NMR spectra of alkynyl-(PMA-Br)$_2$ and alkynyl-(PMA-N_3)$_2$ of different chain length. The signal at 3.6 ppm, 2.24 ppm and 1.3~2.1 ppm can be attributed to the protons of the methyl group, methylidyne group and methylene group, respectively. As can be seen, the signal at 4.18 ppm ascribed to the methylidyne group

beside the bromine group disappeared after azidation. This evidence in combination with the appearance of the characteristic peaks of azide group at 2110 cm^{-1} in Figure S6B clearly illustrates the successful preparation of alkynyl-(PMA-N_3)$_2$. The detail data of molecular weights of linear PMA are summarized in Table S1.

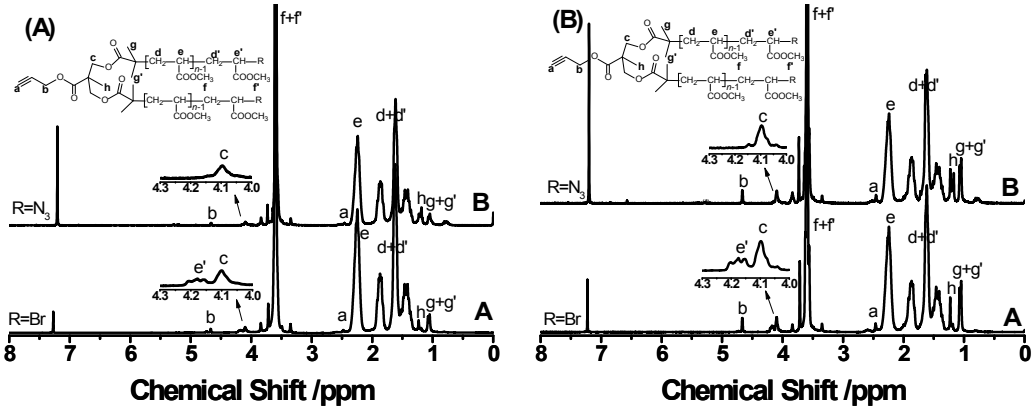

Figure S5. ^{1}H NMR spectra of alkynyl-(PMA-Br)$_2$-17.9k, alkynyl-(PMA-N_3)$_2$-17.9k (A) and alkynyl-(PMA-Br)$_2$-6.6k, alkynyl-(PMA-N_3)$_2$-6.6k (B) in $CDCl_3$.

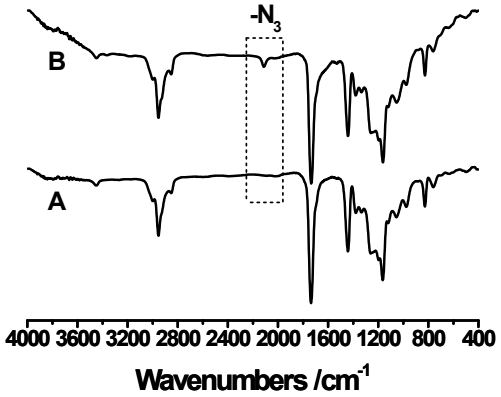

Figure S6. FTIR spectra of alkynyl-(PMA-Br)$_2$-17.9k (A) and alkynyl-(PMA-N_3)$_2$-17.9k (B).

Synthesis of lsc-hp PMA via click chemistry by seesaw-type alkynyl-(PMA-N_3)$_2$

The typical procedure employed was as follows. A mixture of alkynyl-(PMA-N_3)$_2$ (0.8 g, 0.07 mmol), PMDETA (24.3 mg, 0.14 mmol) and THF (4 mL) were added to a 5-

mL Schlenk flask. Then CuBr (20.1 mg, 0.14 mmol) was added under nitrogen flow after three freeze-pump-thaw cycles were performed. After sealed under vacuum, the flask was immersed in an oil bath at 70 °C. The reaction was proceeded for 7 d and then stopped by cooling in ice and exposed to air. Then the reaction mixture was diluted with about 50 mL of THF, filtered through alumina to remove the copper salt. After concentration by rotary evaporation, precipitation in methanol/water (1/1; v/v) and dryness under vacuum, *lsc-hp* PMA as a glass was obtained.

Self-cyclization of alkynyl-(PMA-N_3)$_2$ with different chain length in DMF

The typical procedure was as follows. Alkynyl-(PMA-N_3)$_2$-17.9k (0.2627 g, 0.0228 mmol), PMDETA (178.5 mg, 1.03 mmol), and DMF (450 mL) were added into a 500-mL round-bottomed flask under stirring at ambient temperature. After degassed by bubbling with N_2 for 12 h, the reaction mixture was heated to 100 °C under stirring. Then CuBr (147.8 mg, 1.03 mmol) was introduced into the reaction system under nitrogen flow. The reaction was proceeded for 24 h, then stopped, cooled to room temperature and stirred for another 12 h in the air. After concentrated under vacuum, the mixture was diluted with THF and subsequently filtered through neutral alumina to remove copper salt. After precipitation with methanol/water (1/1; v/v) and dryness under vacuum, cyclic PMA as a glass was obtained.

^{1}H NMR spectra of *lsc-hp* PMA prepared by macromonomers with different chain lengthd are shown in Figure S7**.** Compared with Figure S5, the signal at 4.67 ppm attributed to the methylene protons adjacent to the alkynyl group disappeared, while the corresponding signal at 5.28 ppm appeared, confirming the successful preparation

of *lsc-hp* PMA. The reaction conditions and detailed data of molecular weights of *lsc-hp* PMA are summarized in Table S2.

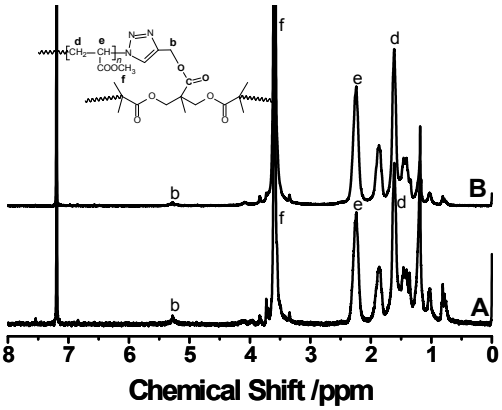

Figure S7. ^{1}H NMR spectra of *lsc-hp* PMA prepared from macromonomers of different molecular weight (A: 6.6k, B: 17.9k).

Figure S8 depicts the ^{1}H NMR spectra of cyclic PMA. The disappearance of signal at 4.67 ppm and the appearance of the signal at 5.28 ppm demonstrate the formation of cyclic PMA. GPC-MALLS is used to further characterize the cyclic as well as the *lsc-hp* PMA.

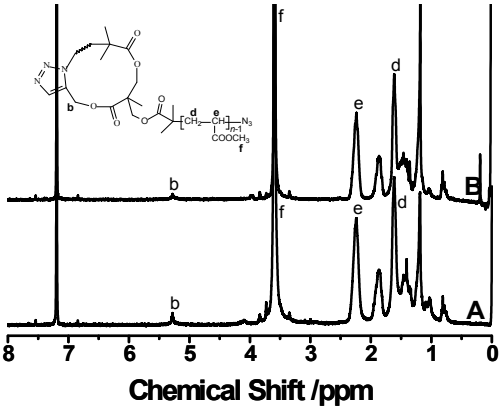

Figure S8. ^{1}H NMR spectra of cyclic PMA prepared from macromonomers of different molecular weight (A: 6.6k, B: 17.9k).

As can be seen in both Figure S9A and Figure S9B, the elution time of the designed cyclic PMA is slightly longer than the linear analogues. When it comes to the *lsc-hp*

PMA, a shoulder separated from the main peak appeared, especially in Figure S9B. The stronger shoulder of *lsc-hp* PMA-6.6k than *lsc-hp* PMA-17.9k agrees with the fact that the proportion of cyclic macromonomer should increase with decreasing molecular weight of macromonomer, as mentioned in the reference,[2] indicating the shoulder should be cyclic PMA. So there is self-cyclization of the monosubstituted seesaw-type alkynyl-(PMA-N_3)$_2$ when preparing *lsc-hp* PMA. Opposite to the phenomenon of *lsc-hp* PMA, GPC traces of *lsc-hp* PMMA prepared by high molecular weight has weak shoulder, while GPC traces of *lsc-hp* PMMA prepared by low molecular weight has no shoulder, indicating that the shoulder of GPC traces of *lsc-hp* PMMA should come from unreacted macomonomer other than cyclic PMMA. From the analysis above, we can conclude that almost no cyclic by-product was formed when using disubstituted macromonomer, while self-cyclization happened when using monosubstituted macromonomer, confirming that steric hindrance plays an important role in inhibiting the self-cyclization of macromonomers.

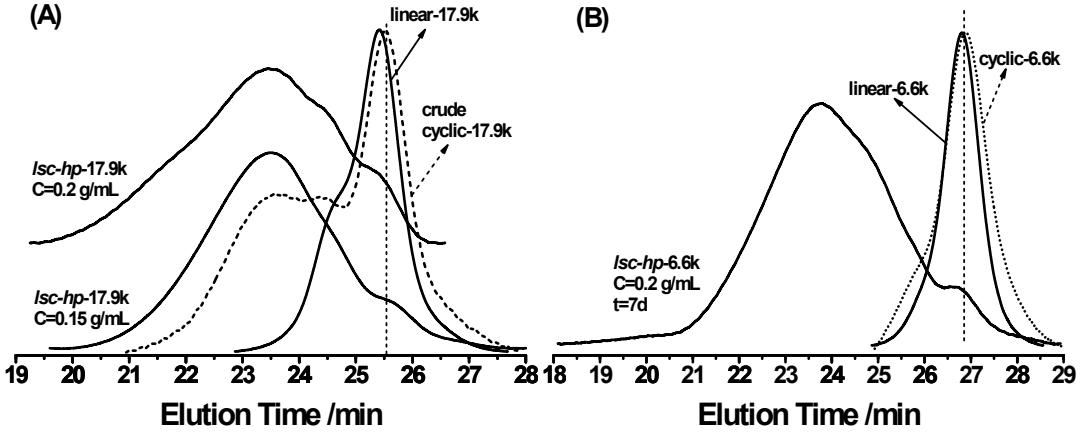

Figure S9. GPC traces of *lsc-hp* PMA obtained from alkynyl-(PMA-N_3)$_2$ with M_n of 17.9 k and 6.6 k at the concentration of 0.2 g/mL (THF as the eluent).

Table S1. Molecular weight data of linear PMA

Samples	$M_{n,\,NMR}$[a] (g·mol^{-1})	$M_{n,\,GPC}$[b] (g·mol^{-1})	$M_{w,\,GPC}$[b] (g·mol^{-1})	PDI[b]	$M_{w,\,MALLS}$[c] (g·mol^{-1})
Linear $PMA_{17.9K}$	11540	17880	21500	1.20	12410
Linear $PMA_{6.6K}$	5250	6580	7280	1.12	6860

a: Determined by ^{1}H NMR analysis.

b: Determined by GPC with refractive index detector.

c: Determined by GPC with multiangle laser light scattering (MALLS) detector using the value of dn/dC = 0.097 mL/g.

Table S2. Reaction conditions and molecular weight data of *lsc-hp* PMA

Samples	C_0 (g·mL^{-1})	$M_{n,GPC}$[a] (g·mol^{-1})	$M_{w,GPC}$[a] (g·mol^{-1})	PDI[a]	$M_{w,MALLS}$[b] (g·mol^{-1})
lsc-hp $PMA_{17.9k}$-7d	0.20	50810	115390	2.27	154900
lsc-hp $PMA_{17.9k}$-7d-2	0.15	43560	86180	1.98	74850
lsc-hp $PMA_{6.6k}$-7d	0.20	26690	78420	2.94	118700

a: Determined by GPC with refractive index detector.

b: Determined by GPC with multiangle laser light scattering (MALLS) detector using the value of dn/dC = 0.097 mL/g.

References

1. B. E. Knuckles, W. H. Yokoyama and M. M. Chiu, *Cereal Chem*, 1997, **74**, 599-604.
2. L. R. Hutchings, J. M. Dodds and S. J. Roberts-Bleming, *Macromolecules*, 2005, **38**, 5970-5980.