

Supplementary Information

The synthesis and oligomerization of a monofunctional bottlebrush-shaped polymer terminated with an azide group

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EXPERIMENT SECTION

Materials and Characterization Styrene (St, Adamas, 99%) was washed with 5 % NaOH aqueous solution and water successively, then dried over anhydrous MgSO₄ and CaH₂ sequentially, and finally distilled under reduced pressure. *tert*-Butyl acrylate (*t*BA, 99%) and 2-butanone was dried by CaH₂ and distilled under reduced pressure prior to use. CuBr (98%, Sigma-Aldrich) was stirred in acetic acid overnight, filtered, then washed with ethanol and diethyl ether successively, and finally dried under vacuum. N,N'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. 2-Hydroxyethyl acrylate (HEA, Aladdin, 97%), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 99%), 2-bromoisobutryl bromide (98%), DBCO-NHS ester, PEG_{20K} with linear and three-arm structures terminated with amino groups (95%, 9i Technology Co., Ltd, China) were commercial available and used as received. All other reagents were of analytical grade and used as received.

¹H NMR and ¹³C NMR spectra were recorded on a Varian MERCURY plus-400 spectrometer with deuterated chloroform (CDCl₃) as the solvents at 298 K. The chemical shifts were referenced to residual peaks of TMS. Fourier transform infrared (FT-IR) spectra were measured as KBr pellets on a Perkin Elmer Spectrum 100 FTIR spectrometer (U.K.) in the range of 4000-450 cm⁻¹. The molecular weight and polydispersity index (PDI) of the polymers were determined by size exclusion chromatography on a Malvern GPC with polystyrene as standard. Tetrahydrofuran (THF) was used as the eluent at a flow

rate of 1.0 mL/min at 35 °C. Atomic force microscopy (AFM) measurements were performed on a Burkert Multimode Nanoscope III atomic force microscope.

Synthetic Details

CTA-N3 was synthesized by esterification between 2-(propylthiocarbonothioylthio)-2-methylpropionic acid¹⁻² and 2-[2-(2-azidoethoxy)ethoxy]ethanol³. The ¹H- and ¹³C-NMR spectra of CTA-N3 in CDCl₃ were shown in **Fig. S1**. ¹H-NMR (400 MHz, CDCl₃, ppm) δ 4.28–4.23 (m, 2H), 3.72–3.61 (m, 8H), 3.39 (t, $J = 5.1$ Hz, 2H), 3.26 (dd, $J = 7.6, 6.9$ Hz, 2H), 1.70 (s, 8H), 1.00 (t, $J = 7.4$ Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 172.97, 70.75, 70.14, 68.96, 65.17, 55.98, 50.76, 38.75, 25.37, 21.51, 13.54.

BIEA was synthesized according to previous reports⁴⁻⁵ and further purified by distilling under reduced pressure. The ¹H- and ¹³C-NMR spectra of BIEA in CDCl₃ were shown in **Fig. S2**. ¹H-NMR (400 MHz, CDCl₃, ppm) δ 6.43 (dd, $J = 17.3, 1.4$ Hz, 1H), 6.13 (dd, $J = 17.3, 10.5$ Hz, 1H), 5.86 (dd, $J = 10.4, 1.4$ Hz, 1H), 4.42 (s, 4H), 1.92 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃, ppm) δ 171.34, 165.67, 131.41, 127.85, 63.42, 61.67, 55.31, 30.58.

Monofunctional Polymer Brushes were synthesized by sequential reversible addition fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP).

PS-N3 (P1-N3) was synthesized by RAFT polymerization at 60 °C for 16 hours with styrene (10.4 g, 100 mmol), CTA-N3 (56 mg, 0.10 mmol) and AIBN (4.9 mg, 0.03 mmol) after freeze-pump-thaw three times. The polymerization was

quenched by liquid nitrogen, precipitated in methanol three times and dried under vacuum at 50 °C overnight.

PBIEA-*b*-PS-N3 (P2-N3) was prepared by RAFT polymerization at 60 °C for 22 hours with P1-N3 (400 mg, 0.02 mmol) as macromolecular CTA, AIBN (0.5 mg, 0.003 mmol) and BIEA (1.06 g, 4 mmol) in 2-butanone (0.8 mL) after freeze-pump-thaw three times. The polymerization was quenched by liquid nitrogen, precipitated in methanol three times and dried under vacuum at 50 °C overnight.

(PBIEA-*g*-P*t*BA)-*b*-PS-N3 (P3-N3) was obtained by ATRP at 60 °C for 4 hours with P2-N3 (145 mg, 0.004 mmol, 0.24 mmol Br), CuBr (69 mg, 0.48 mmol), PMDETA (100 μL, 0.48 mmol) and *t*BA (7.0 mL, 48 mmol) in 2-butanone (7 mL). P3-N3 was obtained after quenching with liquid nitrogen, passing through neutral aluminum oxide column, precipitating in cold methanol/water (v:v = 4:1) and drying under vacuum at 50 °C overnight.

PEG_{20K}-(DBCO)₂ was synthesized according to previous reports⁶⁻⁷. NH₂-PEG_{20K}-(NH₂)₂ (200 mg, 0.01 mmol), DBCO-NHS ester (64 mg, 0.16 mmol) and trimethylamine (5 μL) were dissolved in CH₂Cl₂ (3 mL) and stirred at room temperature for 72 hours. Then the solution was precipitated in cold diethyl ether and centrifuged to remove the excess DBCO-NHS. PEG_{20K}-(DBCO)₂ was obtained after drying under vacuum at 50 °C overnight. The ¹H-NMR spectrum of PEG_{20K}-(DBCO)₂ in CDCl₃ were shown in **Fig. S7**.

PEG_{20K}-(DBCO)₃ was synthesized similar with PEG-(DBCO)₂ with three-arm PEG_{20K} terminated with amino groups. Generally, PEG_{20K}-(NH₂)₃ (120 mg,

0.006 mmol), DBCO-NHS ester (64 mg, 0.16 mmol) and trimethylamine (5 μ L) were dissolved in CH_2Cl_2 (3 mL) and stirred at room temperature for 72 hours. Then the solution was precipitated in cold diethyl ether and centrifuged to remove the excess DBCO-NHS. $\text{PEG}_{20\text{K}}\text{-(DBCO)}_3$ was obtained after drying under vacuum at 50 $^\circ\text{C}$ overnight. The $^1\text{H-NMR}$ spectrum of $\text{PEG}_{20\text{K}}\text{-(DBCO)}_3$ in CDCl_3 were shown in **Fig. S8**.

Polymer brush dimer (P3-P3) was synthesized by click reaction between P3-N3 (140 mg, 1 μ mol calculated from NMR) and $\text{PEG}_{20\text{K}}\text{-(DBCO)}_2$ (10 mg, 0.5 μ mol) with molar ration 2:1 in CH_2Cl_2 (20 mL) and stirred at 50 $^\circ\text{C}$ for 72 hours. Then the solution was cold to room temperature and dry under vacuum for characterizations.

Polymer brush trimer was synthesized by click reaction between P3-N3 (140 mg, 1 μ mol calculated from NMR) and $\text{PEG}_{20\text{K}}\text{-(DBCO)}_3$ (6.6 mg, 0.33 μ mol) with molar ration 3:1 in CH_2Cl_2 (20 mL) and stirred at 50 $^\circ\text{C}$ for 72 hours. Then the solution was cold to room temperature and dry under vacuum for characterizations.

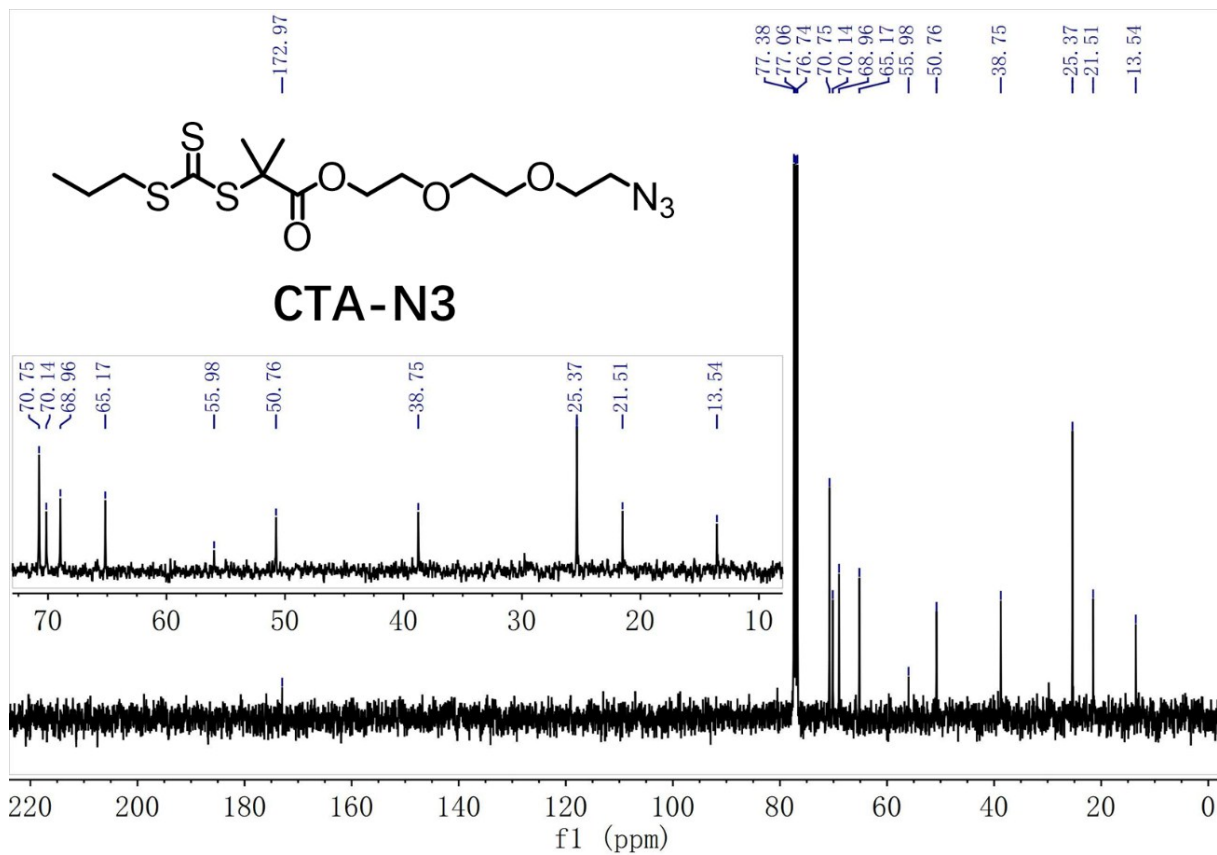
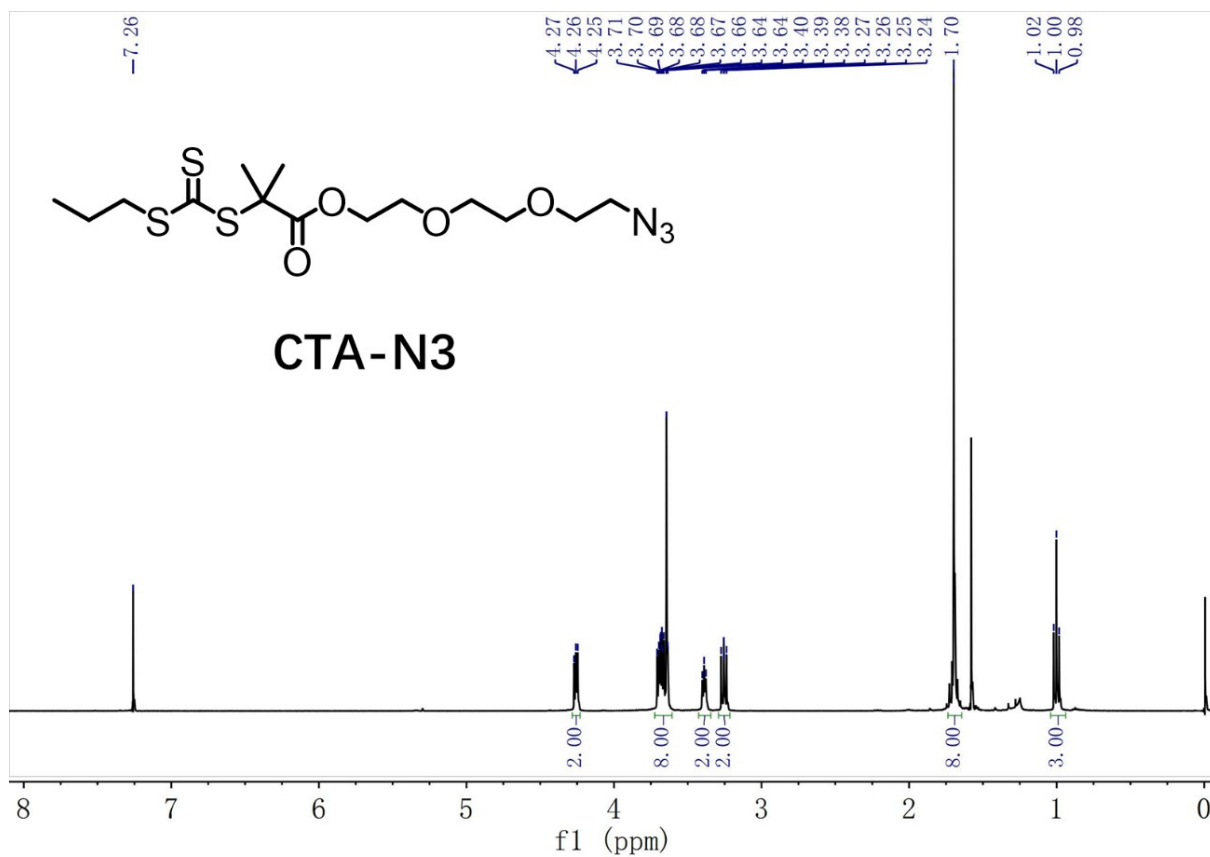


Fig. S1 ^1H - and ^{13}C -NMR spectra of **CTA-N3** in CDCl_3 .

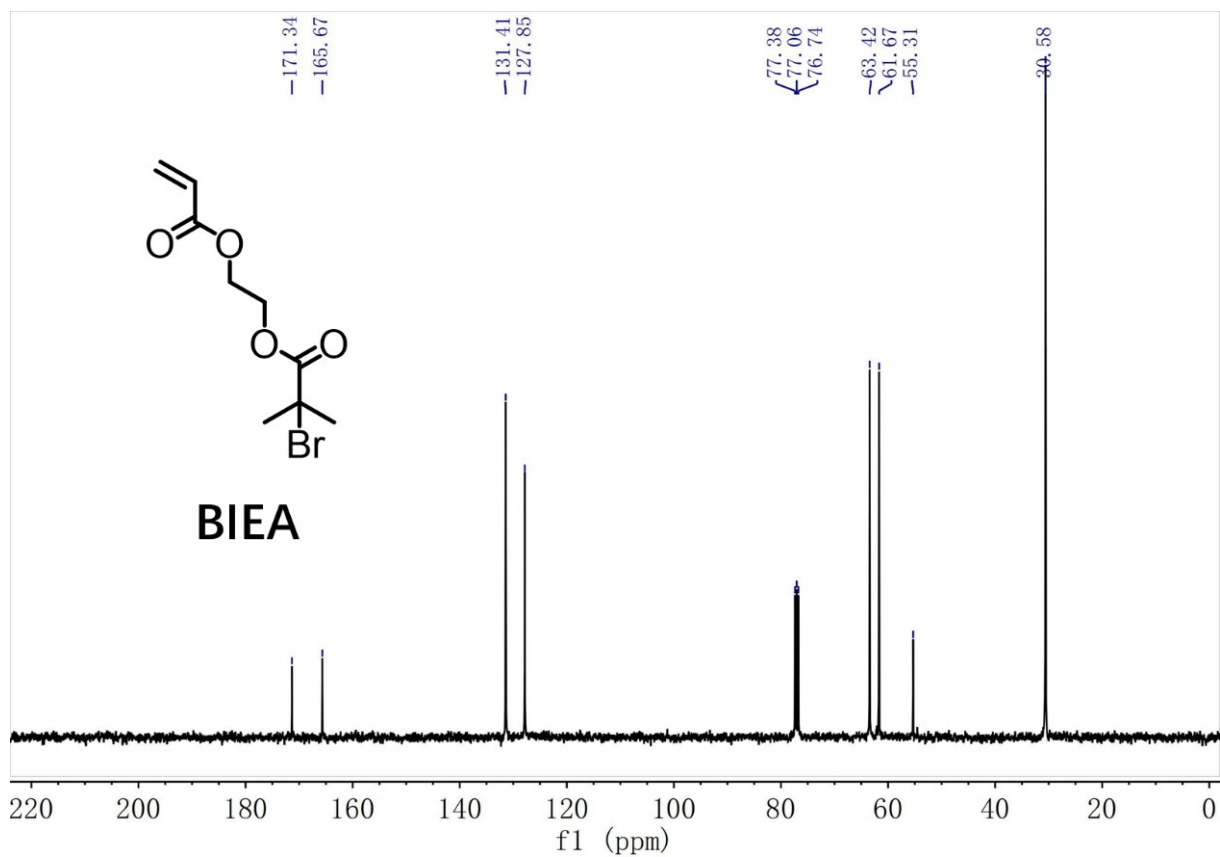
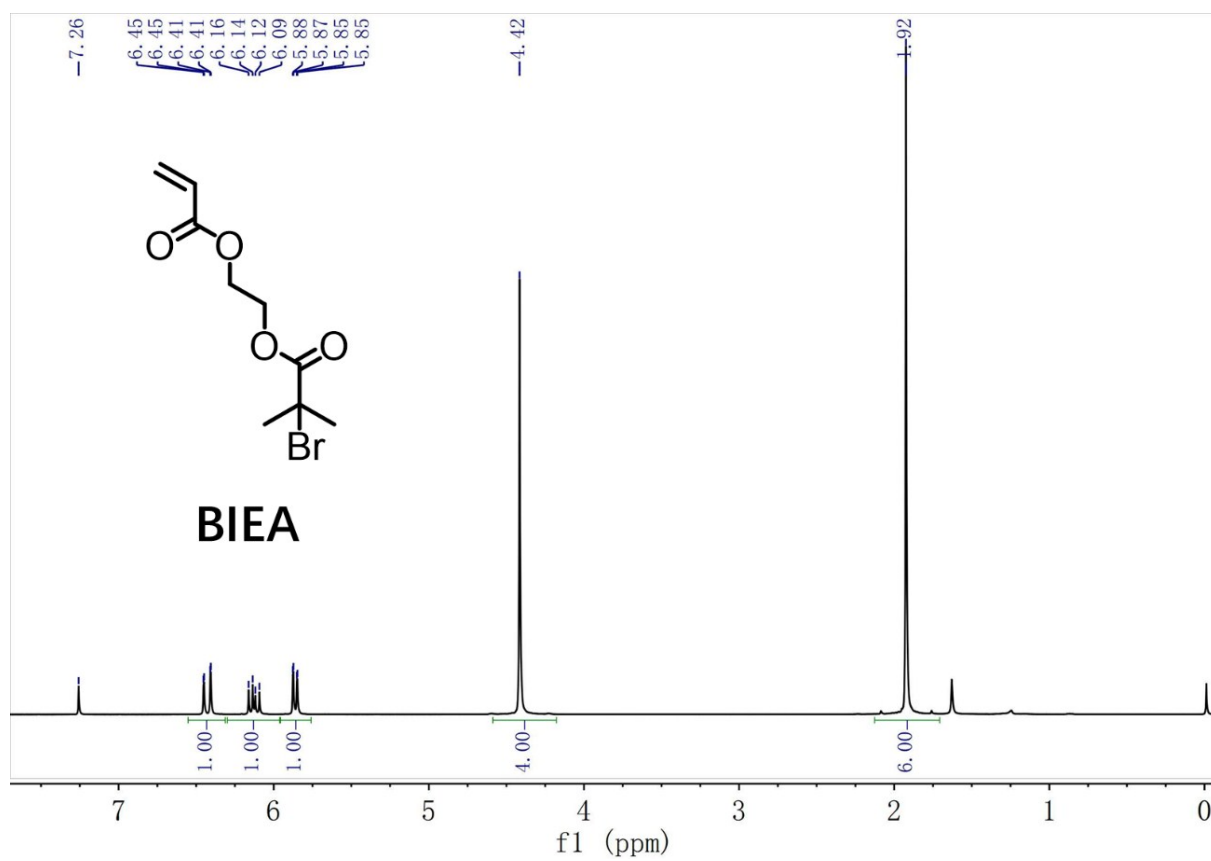


Fig. S2 ¹H- and ¹³C-NMR spectra of monomer, **BIEA**, in CDCl₃.

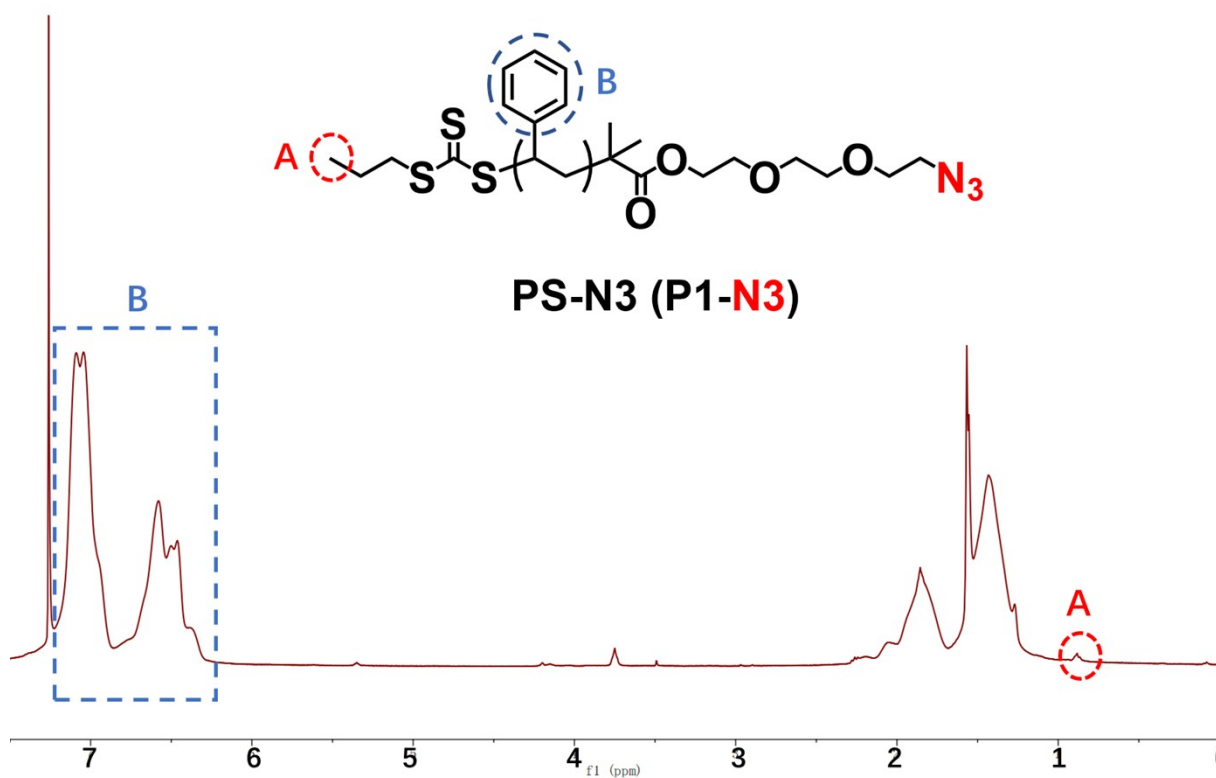


Fig. S3 $^1\text{H-NMR}$ spectrum of PS-N3 (**P1-N3**) in CDCl_3 .

$M_{n,P1-N3}$ of **PS-N3 (P1-N3)** was calculated from $^1\text{H-NMR}$ data (**Fig. S3**) based on the following equation:

$$M_{n,P1-N3} = \frac{I_B/5}{I_A/3} \times 104.15 + M_{n,CTA-N3}$$

I_B and I_A are the integral area of the protons in phenyl group within PS chains and the integral area of the terminal methyl protons at the P1-N3, respectively. 104.15 is the molecular weight of unit styrene.

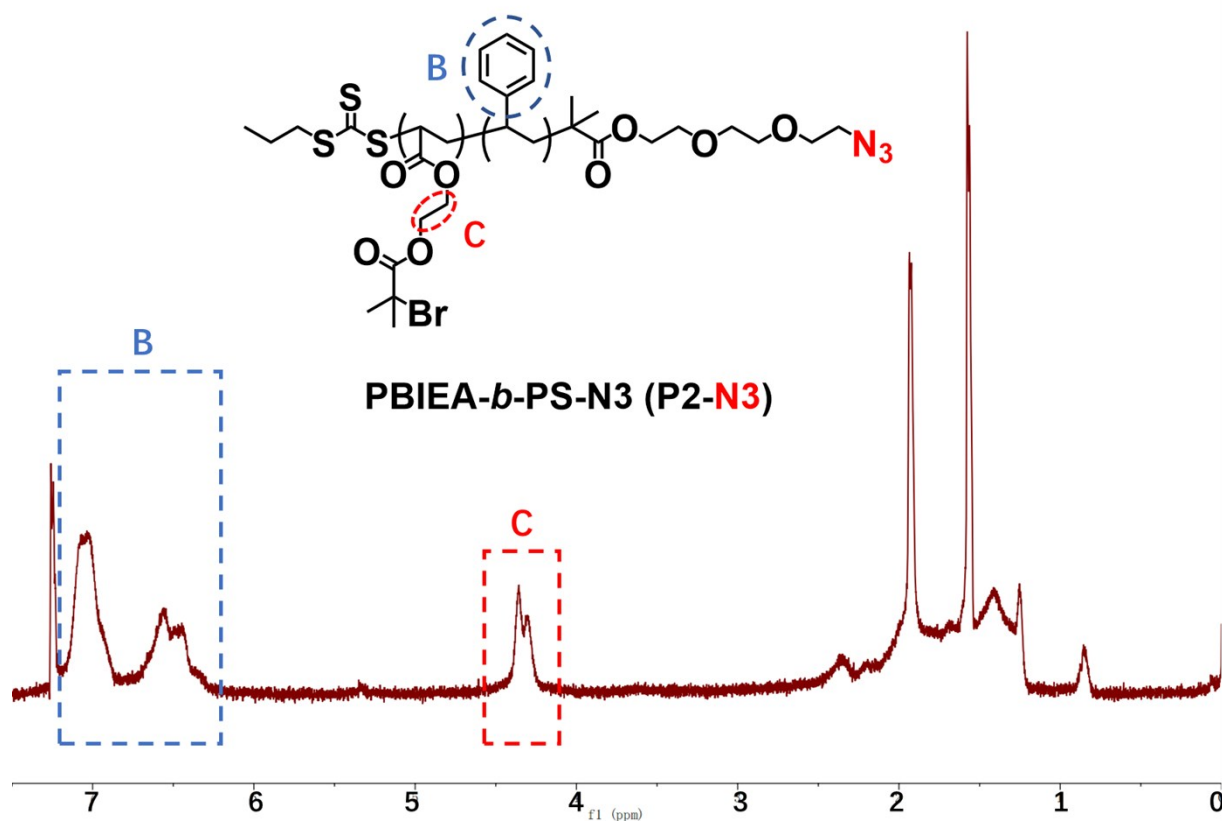


Fig. S4 $^1\text{H-NMR}$ spectrum of PBIEA-*b*-PS-N3 (**P2-N3**) in CDCl_3 .

$M_{n,P2-N3}$ of PBIEA-*b*-PS-N3 (**P2-N3**) was calculated from $^1\text{H-NMR}$ data (**Fig. S4**)

based on the following equation:

$$M_{n,P2-N3} = \frac{I_C/4}{I_B/5} \times \frac{M_{n,P1-N3} - M_{n,CTA-N3}}{104.15} \times 265.10 + M_{n,P1-N3}$$

I_C and I_B are the integral area of the protons in methylene groups within the PBIEA block and the integral area of the protons in phenyl group within PS block, respectively. 104.15 and 265.10 are the molecular weights of unit styrene and BIEA, respectively.

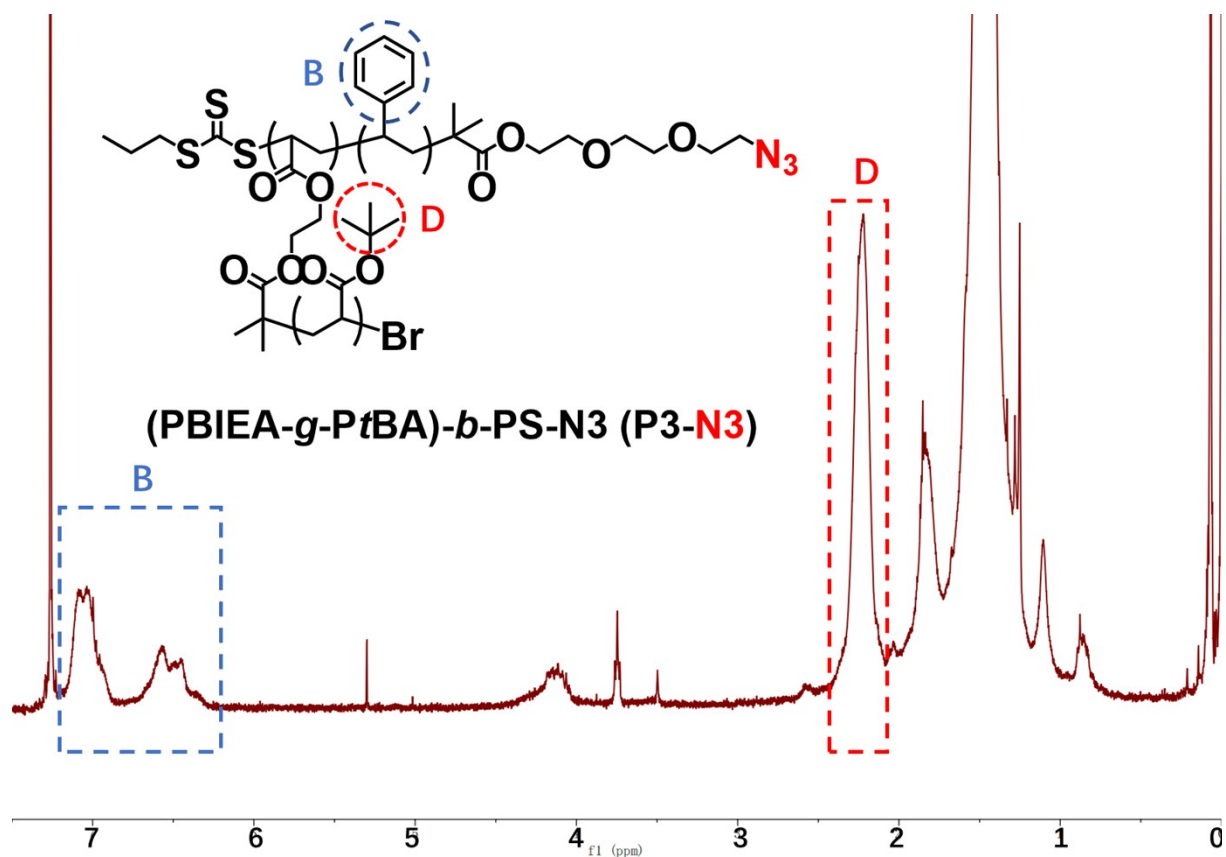


Fig. S5 $^1\text{H-NMR}$ spectrum of (PBIEA-*g*-PtBA)-*b*-PS-N3 (**P1-N3**) in CDCl_3 .

$M_{n,P3-N3}$ of (PBIEA-*g*-PtBA)-*b*-PS-N3 (**P3-N3**) was calculated from $^1\text{H-NMR}$ data (**Fig. S5**) based on the following equation:

$$M_{n,P3-N3} = \frac{I_D/9}{I_B/5} \times \frac{M_{n, P1-N3} - M_{n, CTA-N3}}{104.15} \times 128.17 + M_{n, P2-N3}$$

I_D and I_B are the integral area of the protons in tertiary butyl groups within the PtBA brush and the integral area of the protons in phenyl group within PS block, respectively. 104.15 and 128.17 are the molecular weights of unit styrene and *t*BA, respectively.

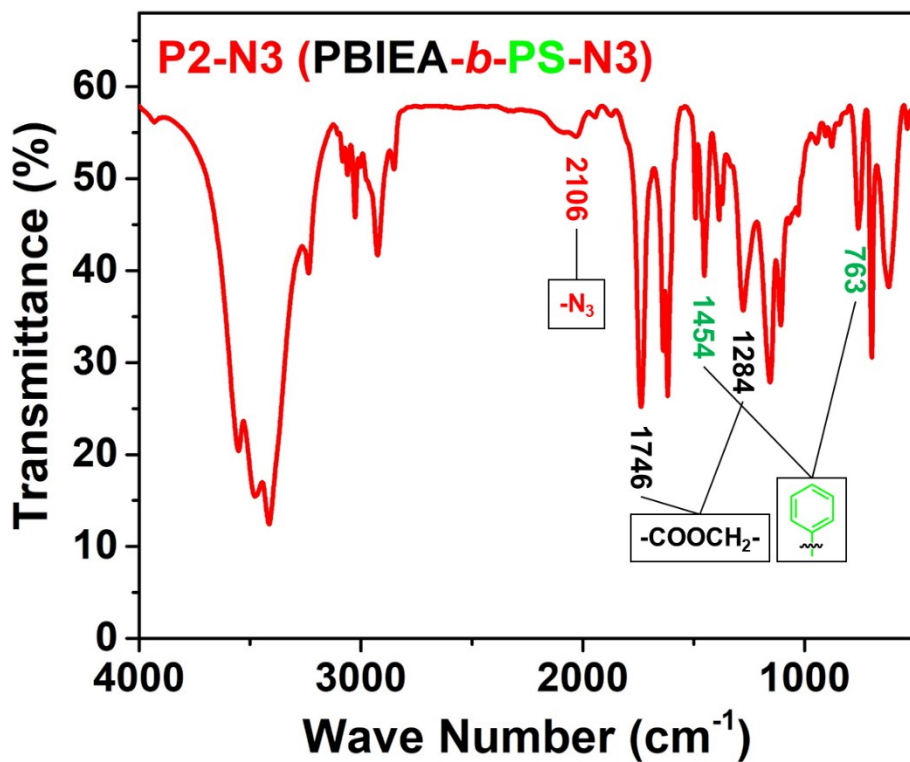


Fig. S6 FT-IR spectrum of P2-N3.

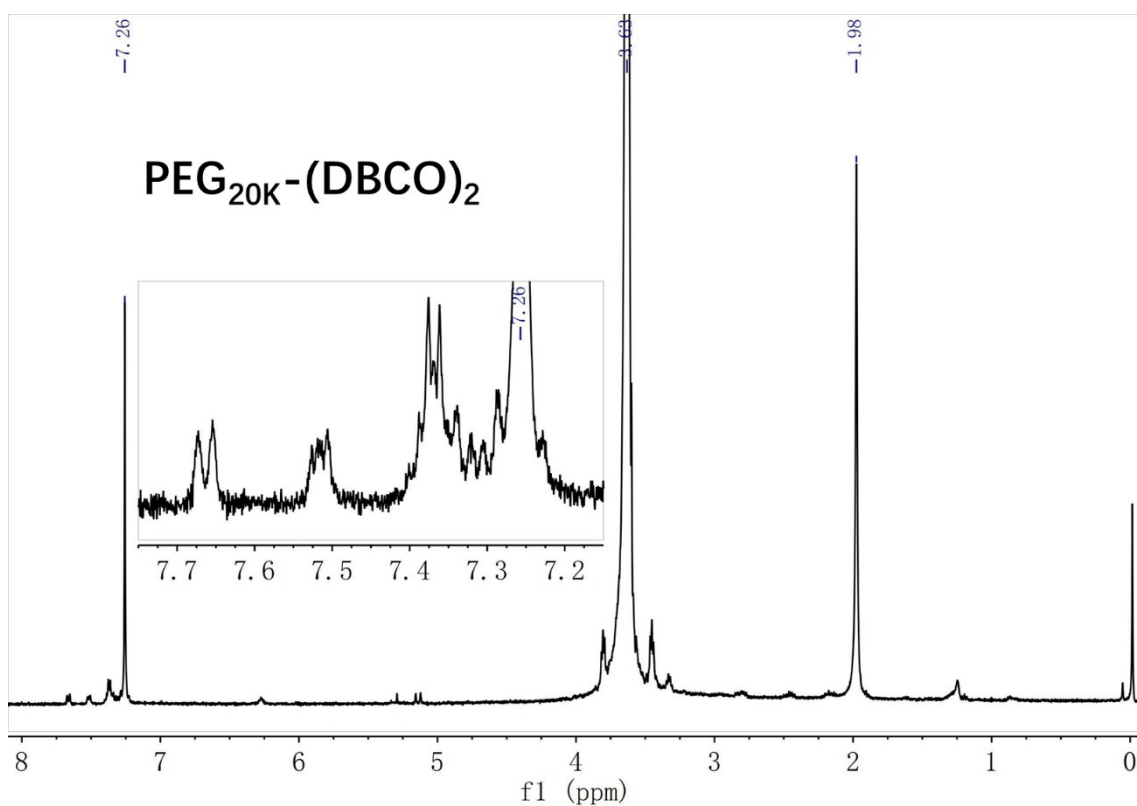


Fig. S7 $^1\text{H-NMR}$ spectrum of PEG_{20K}-(DBCO)₂ in CDCl_3 .

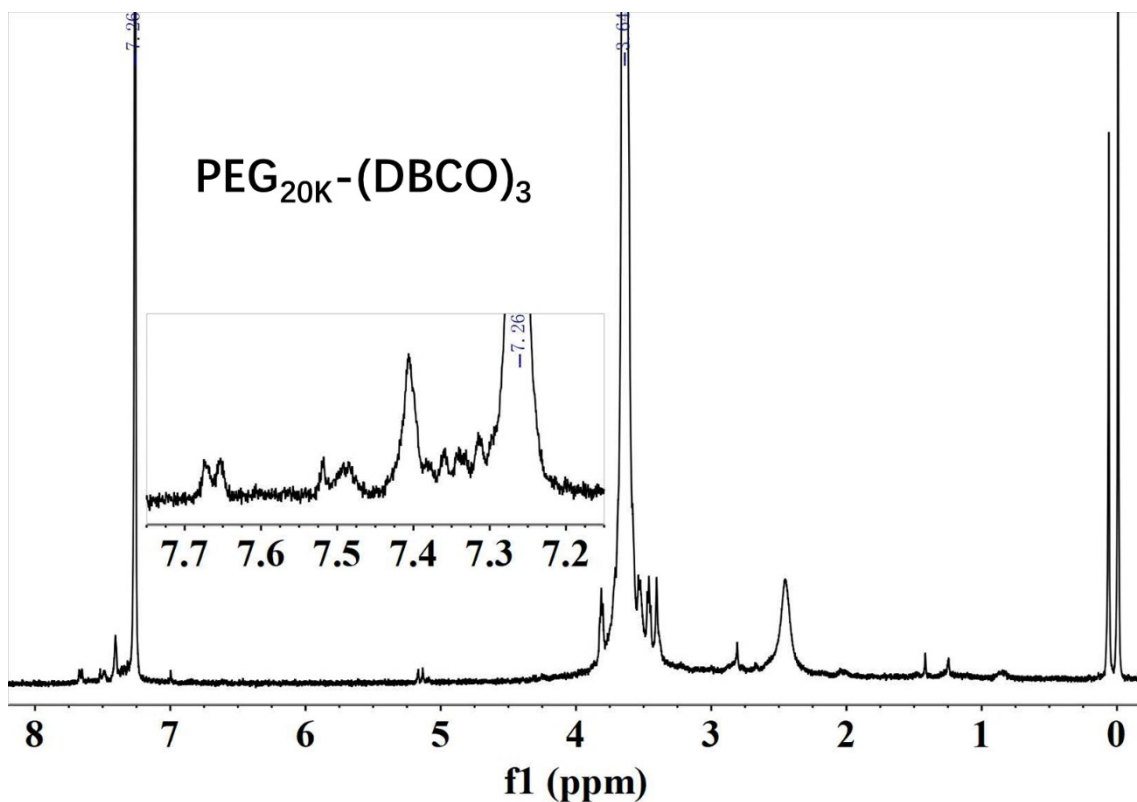


Fig. S8 ¹H-NMR spectrum of PEG_{20K}-(DBCO)₃ in CDCl₃.

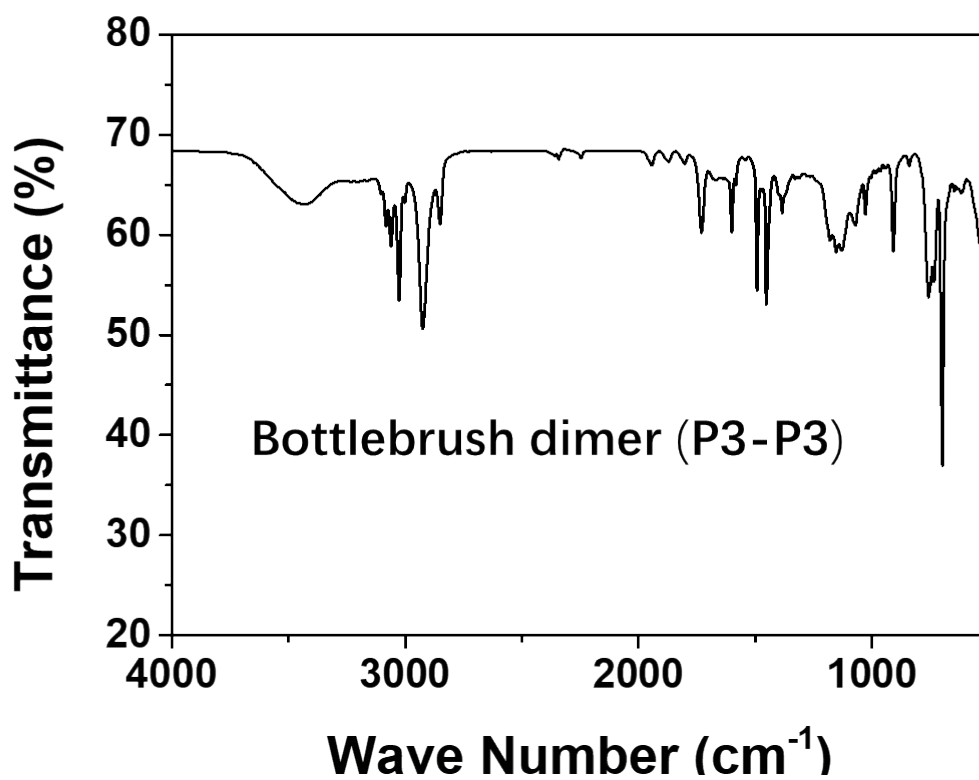


Fig. S9 FT-IR spectrum of bottlebrush dimer (P3-P3).

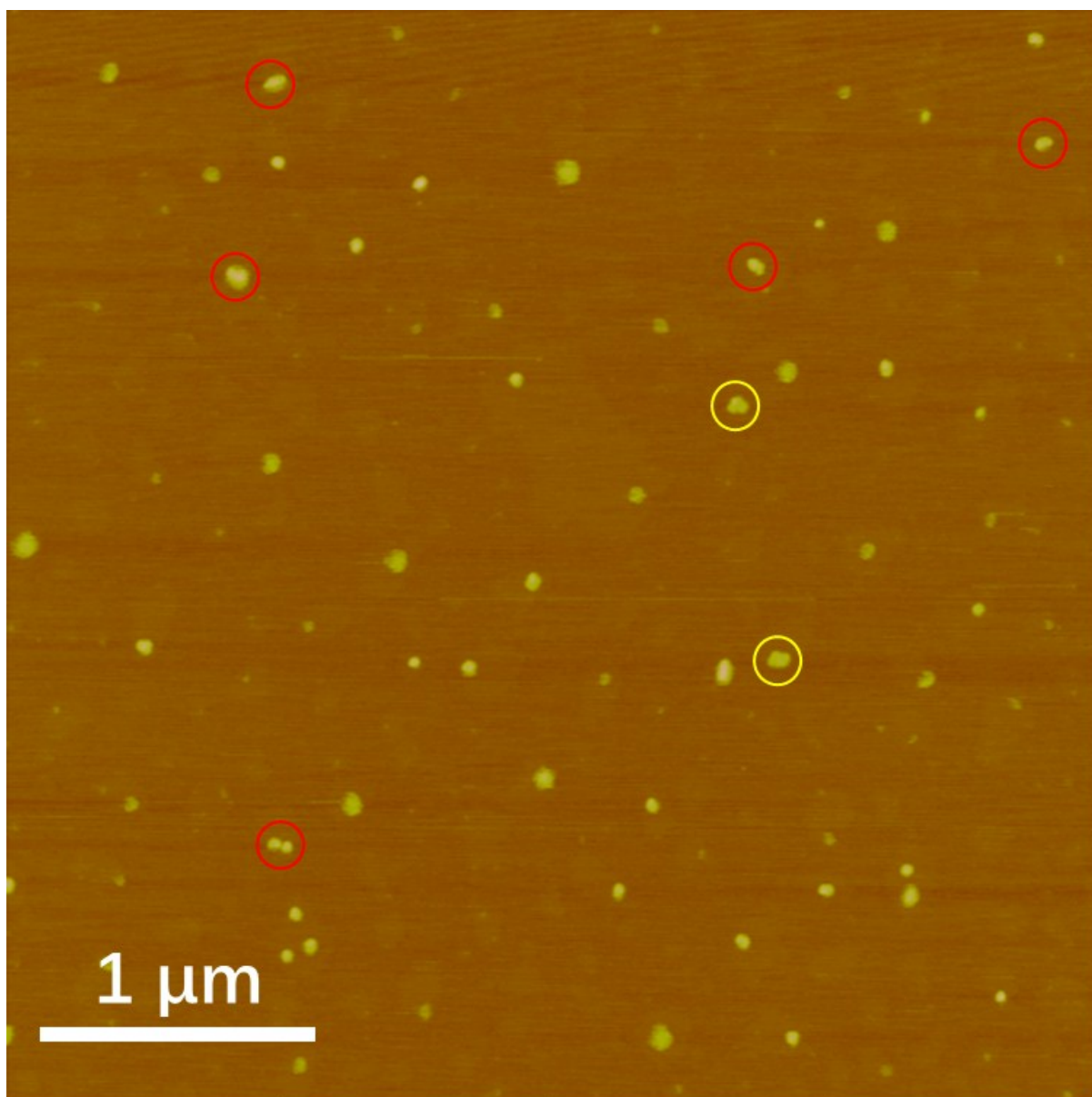


Fig. S10 AFM image of **bottlebrush trimer** associated with dimer and unimer.

Supplementary References

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