

SUPPORTING INFORMATION

Cyclic Polymers Based on UV-Induced Strain Promoted Azide-Alkyne Cycloaddition

Reaction

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Experimental

Materials

Sodium azide (NaN_3), 3-bromopropionic acid, 4-(dimethylamino)pyridine (DMAP), N,N'-dicyclohexylcarbodiimide(DCC), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy (HTEMPO), styrene (St), copper(I) bromide (CuBr), sodium chloride, hydrochloric acid (HCl), alkaline alumina, magnesium sulphate (MgSO_4), acetonitrile, anisole, methanol, toluene, petroleum ether, ethyl acetate, dichloromethane (DCM), tetrahydrofuran (THF) and dimethylsuloxide (DMSO) were purchased as reagent grade from Alfa Aesar, Aldrich, Acros, J&K Chemical, or Beijing Chemical Reagent Co. and used as received unless otherwise noted. St was dried over calcium hydride overnight and distilled under the reduced pressure. CuBr was washed by acetic acid and ethanol three times respectively, and then dried under vacuum. For making dry solvents: DCM was refluxed over calcium hydride; THF was distilled from sodium/benzophenone. Me_6TREN ^[1], **I-1** ^[2] were synthesized according to the previous literature. A low pressure mercury lamp (120 W) (CEL-LPH120-254, Beijing China Education Au-light co. Ltd) was used as the UV light source.

Characterization

$^1\text{H-NMR}$ spectra were recorded on a Bruker Avance 400 spectrometer at room temperature.

FT-IR spectra were recorded on a Thermo Nicolet Avatar-330 Spectrometer at room temperature.

UV/Vis adsorption spectra were recorded using a TU-1901 Ultraviolet Spectrophotometer. The samples were dissolved in THF with a concentration of 5×10^{-5} mol/L. The spectra were

measured from 200 to 600 nm with a resolution of 1 nm and slit width of 2 nm in a 1 cm UV cuvette.

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) mass spectra were recorded on a Autoflex III MALDI-TOF mass spectrometer equipped with a 355 nm YAG laser. It was operated at an accelerating potential of 20 kV in linear modes. The MALDI mass spectra represent averages over 256 consecutive laser shots (3 Hz repetition rate). The polystyrene were dissolved in THF with a concentration of 5 g/L. 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix and dissolved in THF with a concentration of 15 g/L. The sample was prepared by mixing 10 μ L of the polystyrene solution with 50 μ L of the matrix solution. A 1 μ L portion of the final solution was deposited onto the sample target and allowed to dry in air at 25°C. Internal standards (peptides or porphyrine derivatives) were used to calibrate the mass scale using the two-point calibration software 3.07.1 from Autoflex III systems.

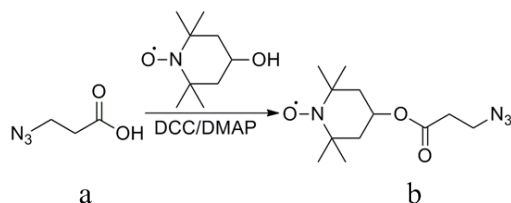
Matrix-Assisted Laser Desorption/Ionization Fourier Transform Ion Cyclotron Resonance (MALDI-FT-ICR) mass spectra were recorded on a Solarix FT-ICR (Bruker Daltonics) mass spectrometer equipped with MALDI sources set to operate over m/z 202.1-5000.0. Positive ionization mode was used when analyzing the sample. The plate offset was -100 V. The deflector plate was -180 V. A YAG laser operating at 355 nm was used for desorption/ionization. The medium focal length was chosen. The maximum energy was 100 μ J. The polystyrene were dissolved in THF with a concentration of 5 g/L. 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix and dissolved in THF with a concentration of 15 g/L. The sample was prepared by mixing 10 μ L of the polystyrene solution with 50 μ L of the matrix solution. A 1 μ L portion of the final solution was deposited onto the sample target and allowed to dry in air at 25°C. Internal

standards (peptides or porphyrine derivatives) were used to calibrate the mass scale using the cal3 Solarix control. Data Analysis 4.1 software was chosen.

Gel permeation chromatography (GPC) in THF was performed using four Waters Styragel columns (HT 2, HT 3, HT 4, and HT 5), a Waters 1515 isocratic HPLC pump, and a Waters 2414 RI detector. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration.

Preparation of 4-(3-azidopropionyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO-N₃)

(b)



Compound a: 3-bromopropionic acid (3.83 g, 25 mmol) and sodium azide (3.2 g, 50 mmol) were dissolved in acetonitrile (40 mL). After refluxing the mixture for 4h, the reaction mixture was concentrated on a rotary evaporator. The resulting residue was suspended in ethyl acetate (50 ml) and extracted with 0.1 M HCl (3 x 50 ml), water (3 x 50 ml) and brine (1 x 50 ml). The organic phases were dried by MgSO₄ and concentrated on a rotary evaporator to afford the compound **a** (0.87g, 30%). ¹H -NMR (CDCl₃), δ (ppm): 3.59 (t, 2H), 2.64 (t, 3H).

Compound b: 3-azidopropionic acid (0.87 g, 7.6 mmol) and HTEMPO (1.56 g, 9.1 mmol) were dissolved in dry DCM (15 ml), to which DCC (3.10 g, 15.13 mmol) in dry DCM (5 ml) and DMAP (0.18 g, 1.5 mmol) in dry DCM (2 ml) were separately added at 0 °C. After stirring overnight at room temperature, the reaction mixture was filtered and the filtrate was concentrated on a rotary evaporator. The crude product was purified by a silica column with petroleum ether

/ethyl acetate (v/v = 20/3) as the eluent to afford the compound **b** (0.4 g, 20%). ¹H-NMR (CDCl₃ with 2 drops of TFA-d), δ (ppm): 5.23 (m, 1H), 3.60 (t, 2H), 2.62 (t, 2H), 2.30 (m, 2H), 2.07 (t, 2H), 1.54 (s, 6H), 1.46 (s, 6H).

Preparation of Linear PS-Br

Initiator **I-1** (69.7 mg, 0.144 mmol), PMDETA (25.0 mg, 0.144 mmol) and St (1.5 g, 14.4 mmol) were mixed into a 25 mL Schlenk tube. After degassing through four freeze-evacuate-thaw cycles, the CuBr (20.7 mg, 0.144 mmol) was added to the mixture in frozen state under N₂. After another three evacuate cycles, the reaction was stirred at 90 °C for 25 min and then quenched by exposing to air. The reaction mixture was diluted with approximately 100 mL THF and passed through a short basic alumina column to remove the catalyst. The THF solution was concentrated and then precipitated into methanol. The same precipitation process was repeated three times to obtain the pure PS.

Preparation of Linear PS-N₃

Linear PS-Br (0.1 g, 0.042 mmol), Me₆TREN (12.4 mg, 0.054 mmol), and TEMPO-N₃ (18.1 mg, 0.067 mmol) were dissolved in the mixture of toluene (0.4 ml) and DMSO (0.4 ml) in a 25 mL Schlenk tube. After degassing through four freeze-evacuate-thaw cycles, CuBr (7.8 mg, 0.054 mmol) was added to the mixture in frozen state under N₂. After another three evacuate cycles, the reaction was stirred at room temperature for 20 min and then quenched by exposing to air. The reaction mixture was diluted with approximately 50 mL THF and passed through a short basic alumina column to remove the catalyst. The THF solution was concentrated and then precipitated into methanol. The same precipitation process was repeated three times to obtain the pure linear PS-N₃.

Preparation of Cyclic PS

Linear PS-N₃ (7.0 mg) was dissolved in mixed solvents of THF/MeOH (30 ml, v/v = 1/2). After stirring the solution under UV irradiation for 5 h at room temperature, the reaction mixture was kept stirring for another 36 h without UV irradiation. The pure cyclic PS was conveniently collected by evaporation of the solvents.

Cyclic PS Cleavage

The cyclic PS (7.0 mg) was dissolved in xylene (21 ml) in a 50 mL Schlenk tube. After degassing through three freeze-evacuate-thaw cycles, the tube was heated at 150 °C for 48 h under N₂ to cleave the cyclic PS.

Batchwise Operation for Cyclic PS

A batchwise operation for the formation of cyclic PS was illustrated with a yield increase of 3 times more. 21 mg linear PS-N₃ was evenly batchwised in 30 mL mixed solvents of THF/MeOH (v/v = 1/1) in 3 times alternating every 5 h UV irradiation, by which the starting polymer concentration was 7 mg/30 mL. After the addition, the cyclization reaction was allowed to perform for 24 more hours. The pure cyclic PS (19 mg) was collected by precipitating in methanol three times with a yield of 90.5%.

References

- (1) M. Ciampoli, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41.
- (2) P. Sun, G. W. Yan, Q. Q. Tang,; Y. M. Chen, K. Zhang, *Polymer* **2014**, <http://dx.doi.org/10.1016/j.polymer.2014.10.041>.

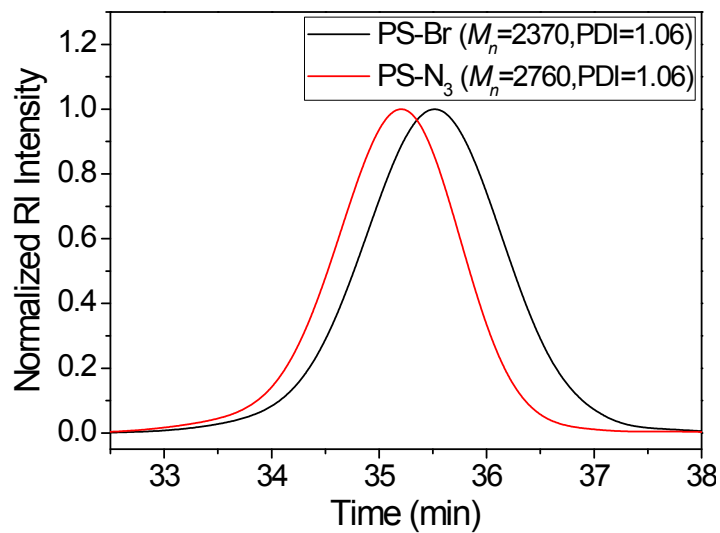


Figure S1. The GPC data of PS-Br (black) and the resultant PS- N_3 (red). THF was used as the eluent and PS standards were used for the calibration.

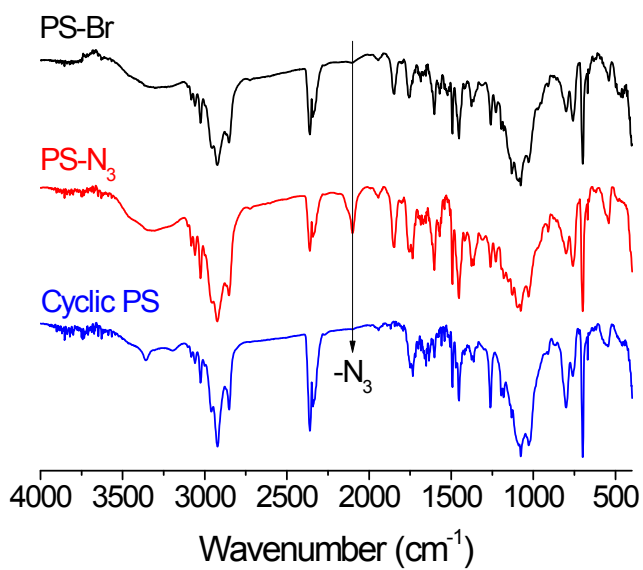


Figure S2. FT-IR spectra of PS-Br (black) and the resultant PS- N_3 (red) and cyclic PS (blue).

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	20	Calibration Date	Tue Apr 14 02:57:24
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	18	Data Processing Size	2097152
Broadband High Mass	5000.0 m/z	Laser Power	32.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

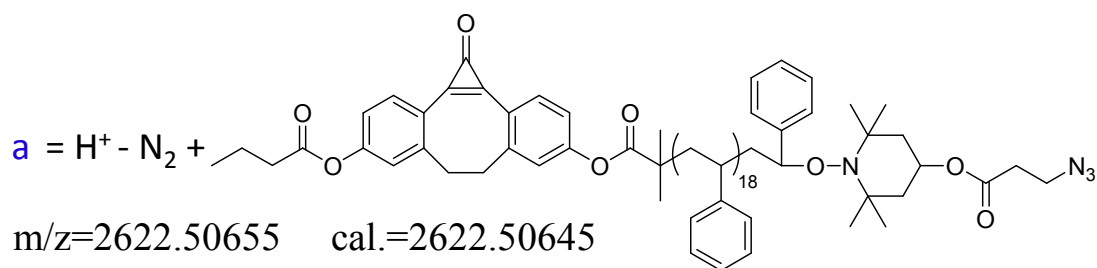
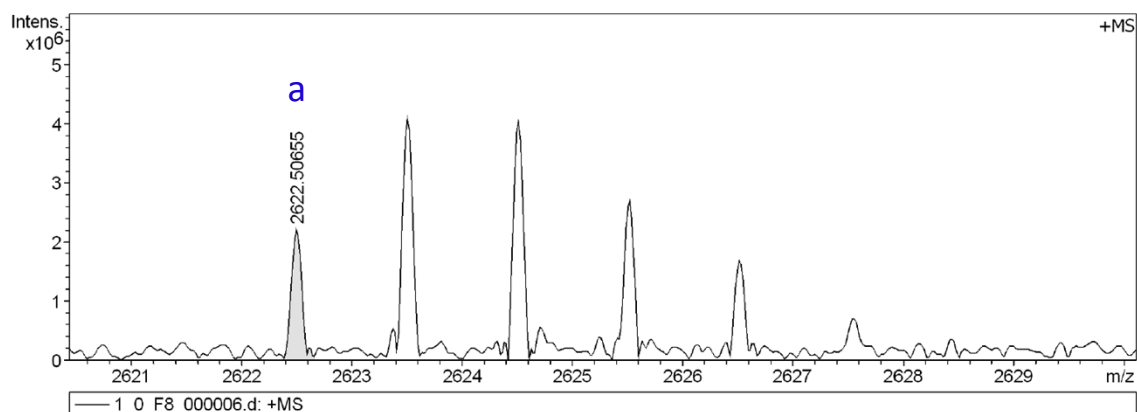
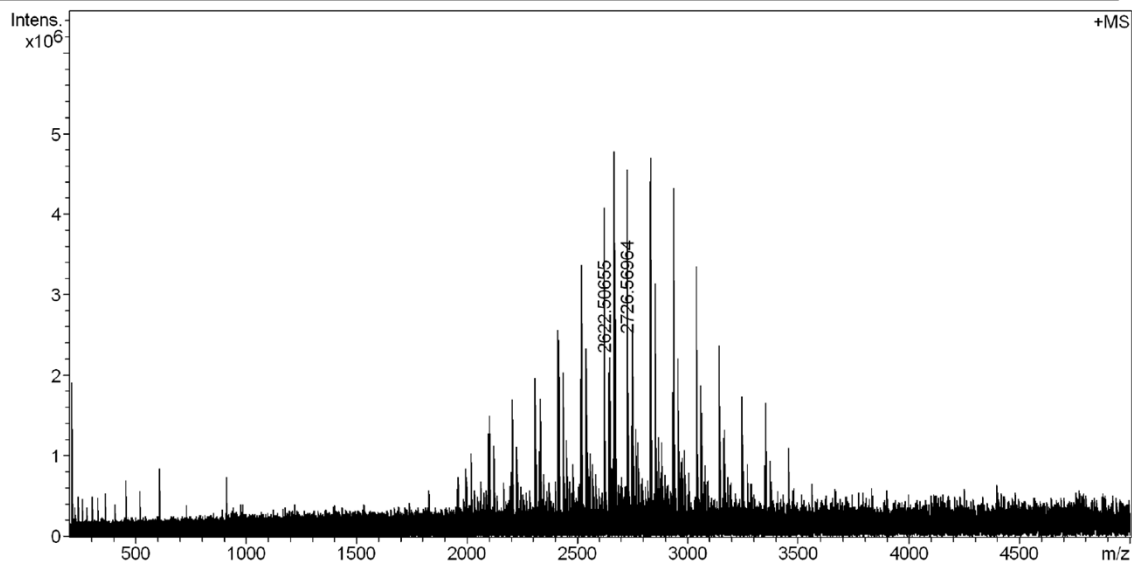


Figure S3. Matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry characterization of linear PS-N₃ precursor.

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	20	Calibration Date	Tue Apr 14 02:57:24
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	20	Data Processing Size	2097152
Broadband High Mass	5000.0 m/z	Laser Power	40.2 Ip	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

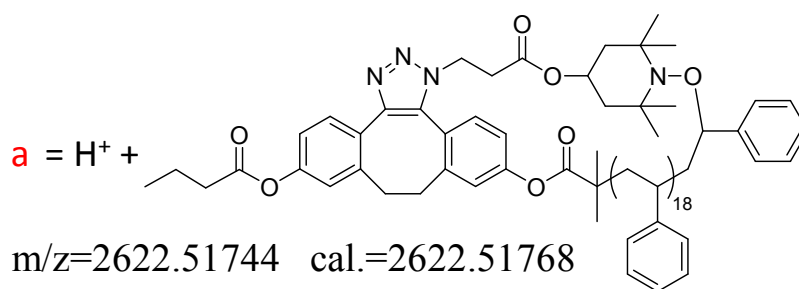
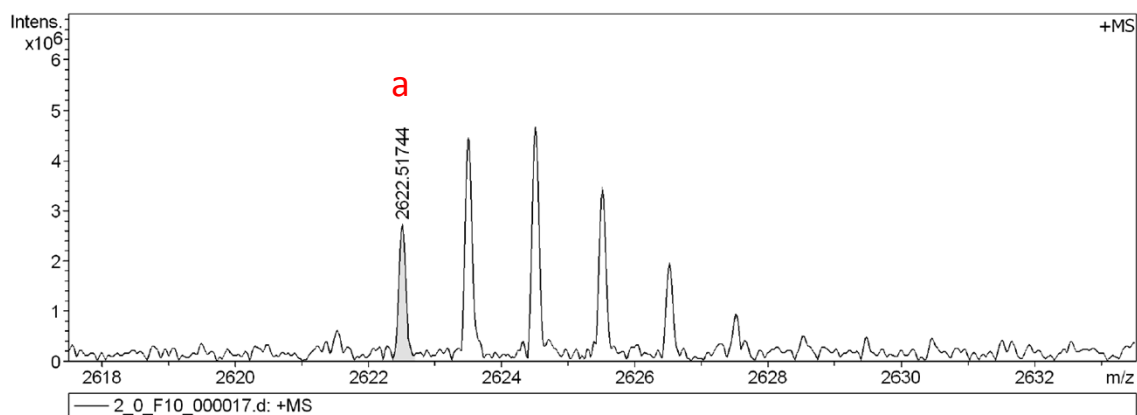
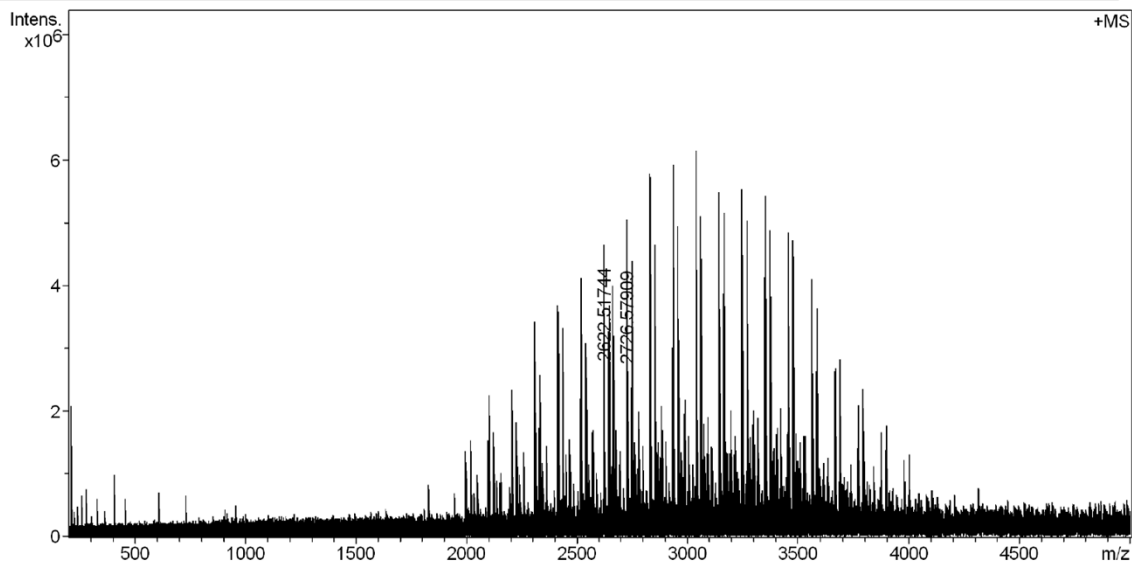


Figure S4. Matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance mass spectrometry characterization of the resultant cyclic PS.

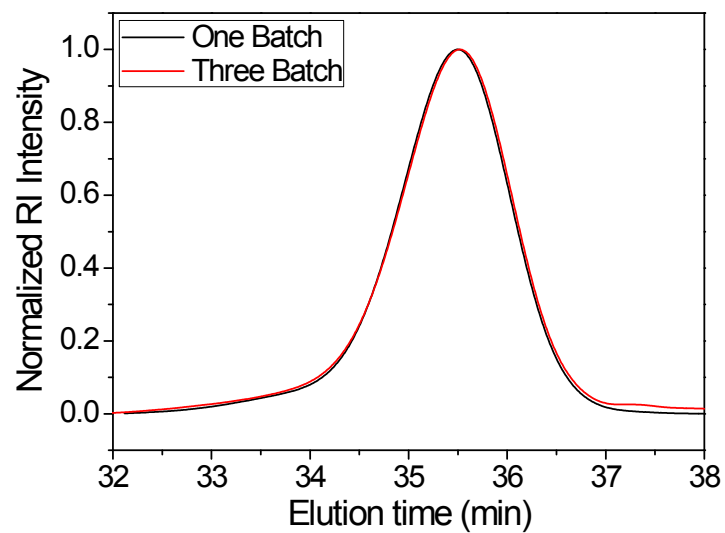


Figure S5. GPC curves of cyclic PS prepared in one batch (black) and three batch (red) methods.

THF was used as the eluent, and polystyrene standards were used for the calibration.