

SUPPORTING INFORMATION

Ring-Closure Method for Preparing Cyclic Polymers from Unconjugated Vinyl Monomers

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Experimental

Materials

Dicyclohexylcarbodiimide (DCC), n-BuLi (2.5 M), 2-aminoethanol, 2-hydroxybenzaldehyde, potassium carbonate (K_2CO_3), 4-dimethylaminopyridine (DMAP), triphenylphosphine, Pd on charcoal (10%), aluminum chloride ($AlCl_3$), sodium bicarbonate ($NaHCO_3$), sodium azide (NaN_3), 3-methoxybenzyl chloride, 3-methoxybenzaldehyde, 3-bromopropanol, 2-bromopropanoic acid, tetrachlorocyclopropenone, sodium hydroxide, and carbon disulfide were purchased as reagent grade from Aldrich, Acros, Alfa Aesar, J&K and used as received. Ethyl acetate, petroleum ether, diethyl ether, methanol, dichloromethane (DCM), acetone, tetrahydrofuran (THF), and hexane were purchased as reagent grade from Beijing Chemical Reagent Co. and used as received unless otherwise noted. Vinyl acetate (VAc) and N-vinylpyrrolidone (NVP) were distilled before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and stored at 4°C. 3-azidopropanol ^[1] and 3-methoxybenzyl(chloro)triphenylphosphorane ^[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

¹H-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.

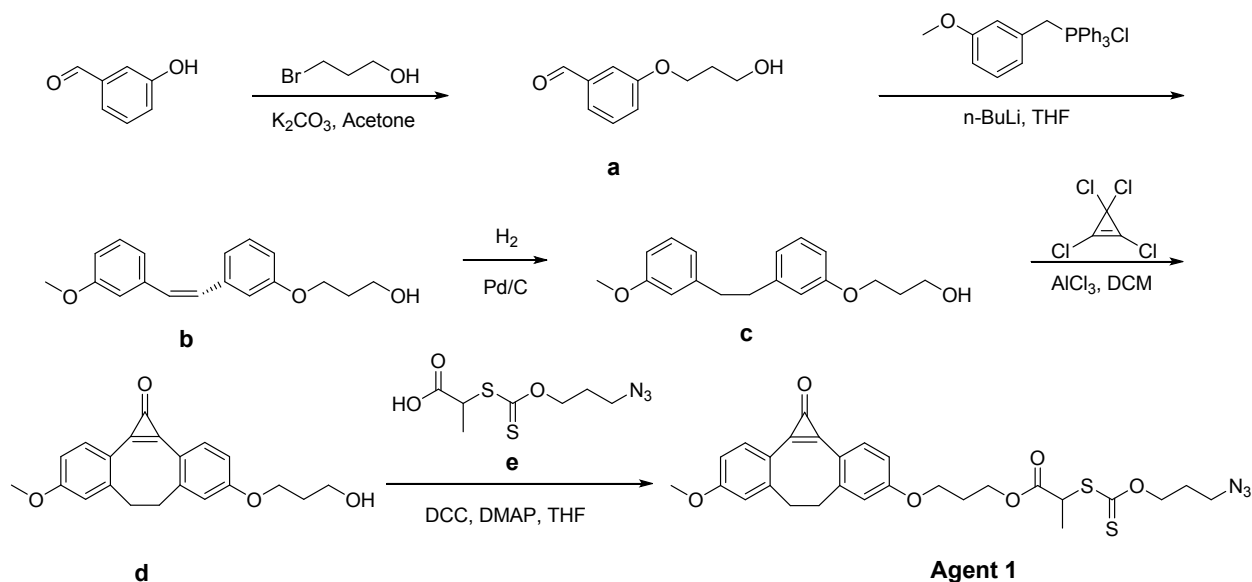
UV/Vis adsorption Spectra were recorded using a TU-1901 Ultraviolet Spectrophotometer.

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 PVAc 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 L of the PVAc solution with 50 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.

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.

Gel permeation chromatography (GPC) in DMF was conducted on a system comprised of a Waters 515 HPLC pump, and a Waters 2414 RI detector equipped with four Waters Styragel columns (HT 2, HT 3, HT 4, and HT 5). DMF with 0.01 M LiBr was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration.

Preparation of RAFT Agent 1



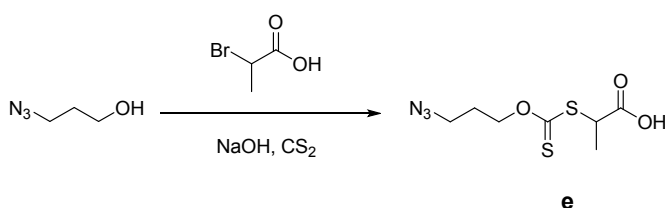
Compound a: 2-hydroxybenzaldehyde (8 g, 65.6 mmol) and bromopropanol (10 g, 71.9 mmol) were added into a suspension of K_2CO_3 (10 g, 72.5 mmol) in acetone (160 mL). The mixture was then refluxed overnight. After cooling to room temperature, the mixture was filtered and the filtrate was concentrated. The crude product was purified by column chromatography (SiO_2 , petroleum ether/ethyl acetate = 5/1) to afford the product as an oil (9.44 g) with a yield of 80.3%. $^1\text{H NMR}$ (CDCl_3), δ (ppm): 9.96 (s, 1H), 7.40-7.45 (m, 3H), 7.17 (m, 1H), 4.18 (t, 2H), 3.87 (t, 2H), 2.07 (m, 2H), 1.76 (s, 1H).

Compound b: 3-methoxybenzyl(chloro)triphenylphosphorane (27.9 g, 66.6 mmol) was dissolved in dry THF (120 mL) under N_2 and cooled to $0\text{ }^\circ\text{C}$. $n\text{-BuLi}$ (29 mL, 72.5 mmol) was added and the mixture was stirred for 90 min at $0\text{ }^\circ\text{C}$. Compound **a** (5 g, 27.8 mmol) in dry THF (30 mL) was dropwise added at $0\text{ }^\circ\text{C}$. After stirring for 7 h at $0\text{ }^\circ\text{C}$, the reaction mixture was quenched with 1 N HCl (50 mL). After 15 min, the organic phase was collected and the water phase was extracted with diethyl ether (3 x 70 mL). The combined organic phases were dried by anhydrous MgSO_4 and concentrated on a rotary evaporator. The crude product was purified by column chromatography (SiO_2 , petroleum ether/DCM = 2/1) to afford the oil products (7.9 g, 93%).

Compound c: compound b (4.5 g, 15.8 mmol) was dissolved in ethyl acetate/methanol (180 mL, 5:1). Pd on charcoal (10%) (0.3 g) was then added and the mixture was hydrogenated for 4 h. The mixture was filtered over Celite and concentrated on a rotary evaporator to produce oil product c (4.3 g, 95.9%). ¹H NMR (CDCl₃), δ(ppm): 7.20 (m, 2H), 6.74-6.81 (m, 6H), 4.11 (t, 2H), 3.87 (t, 2H), 3.79 (s, 3H), 2.89 (s, 4H), 2.04 (m, 2H), 1.90 (s, 1H).

Compound d: tetrachlorocyclopropenone (0.76 g, 4.3 mmol) and AlCl₃ (0.76 g, 5.7 mmol) were dissolved in dry CH₂Cl₂ (130 mL) under N₂ and cooled to -20 °C ~ -40 °C, in which a solution of c (1 g, 3.5 mmol) in dry CH₂Cl₂ (30 mL) was dropwised. After stirring for 3 h at -20 °C ~ -40 °C, the reaction was quenched with water (60 mL) and washed sequentially by saturated aqueous NaHCO₃ solution and then extracted with DCM (3 x 70 mL). The combined organic phases were dried by anhydrous MgSO₄ and concentrated on a rotary evaporator. The crude product was purified by crystallization in DCM to afford pale yellow solid product d (0.53 g, 45.2%). ¹H NMR (CHCl₃), δ(ppm): 7.93 (t, 2H), 6.89 (m, 4H), 4.21 (t, 2H), 3.88 (m, 5H), 3.33 (d, 2H), 2.61 (d, 2H), 2.10 (m, 2H), 2.06 (s, 1H).

Compound e:



3-Azidopropanol (1 g, 10 mmol) was treated with freshly crushed sodium hydroxide (0.4 g, 10 mmol) and carbon disulfide (7.6 g, 0.1 mol) in THF (10 mL). After stirring 6 h at room temperature, 2-bromopropanoic acid (0.79 g, 5.2 mmol) was added, and then the reaction mixture was kept stirring for another 12 h. The resultant was suspended in water (pH=3) (50 ml) and

extracted with DCM (3 x 50 ml). The organic phases were dried by MgSO₄ and concentrated on a rotary evaporator. The crude product was purified by column chromatography (SiO₂, DCM/MeOH = 50/1) to afford the product as a yellow oil (0.62 g) with a yield of 51.7 %. ¹H NMR (CDCl₃), δ(ppm): 11.58 (s, 1H), 4.65 (m, 2H), 4.39 (m, 1H), 3.44 (t, 2H), 2.06 (m, 2H), 1.59 (t, 3H).

RAFT Agent 1: compound a (500 mg, 1.5 mmol) and compound e (740 mg, 3.1 mmol) were dissolved in THF (150 mL), to which DCC (800 mg, 3.9 mmol) in THF (5 mL) and DMAP (42 mg, 0.34 mmol) in THF (2 mL) were added in sequence at 0 °C. After stirring overnight at room temperature, the reaction mixture was filtered and the filtrate was concentrated. The crude product was purified by column chromatography (SiO₂, DCM/MeOH = 100/1) to afford the product as a yellow oil (0.38 g) with a yield of 45.8 %. ¹³C NMR (CDCl₃), δ(ppm): 212.15, 171.36, 162.59, 161.63, 153.83, 147.96, 147.90, 142.62, 142.38, 135.94, 135.90, 116.81, 116.61, 116.41, 115.92, 112.39, 111.99, 70.92, 64.53, 62.43, 55.65, 48.07, 47.55, 37.29, 28.55, 27.88, 16.89. HRMS (MALDI) m/z calculated for C₂₈H₂₉N₃O₆S₂Na [M + Na⁺] 590.1395, found 590.1394.

Preparation of Linear Poly(vinyl acetate) (PVAc)

A mixed solution of VAc (0.86 g, 10 mmol), RAFT agent **1** (55.7 mg, 0.1 mmol) and AIBN (3.4 mg, 0.02 mmol) was degassed via three freeze-thaw-pump cycles. After stirring for 6 h at 60 °C, the reaction was terminated by exposure to air. Polymer was precipitated from an excess of hexane three times. The white product was obtained after drying overnight in a vacuum oven at room temperature.

Preparation of Linear Poly(N-vinylpyrrolidone) (PNVP)

A mixed solution of NVP (1.8 g, 16 mmol), RAFT agent (15 mg, 0.027 mmol), and AIBN (0.8 mg, 0.005 mmol) was degassed via three freeze-thaw-pump cycles. After stirring for 2 h at 60 °C,

the reaction was terminated by exposing system to air. The polymer was precipitated from an excess of diethyl ether three times. The white product was obtained after drying overnight in a vacuum oven at room temperature.

Preparation of Cyclic Polymers

All of the cyclic polymers were prepared with the same procedure by ring-closing the corresponding linear precursors. After dissolving linear precursors (5 mg) in MeOH (100 mL), the solution was stirred under UV light irradiation for 5h at room temperature. The UV light irradiation was then removed and the reaction solution was kept stirring for another 24 h. The pure cyclic polymers were conveniently collected by evaporation of the solvent.

Cyclic Polymer Cleavage

All of the cyclic polymers were cleaved by the same procedure. After the cyclic polymers (5.0 mg) were dissolved in THF (2 ml), 2-aminoethanol (5 mg) was added in the solution. The reaction solution was stirred for 1 h and then concentrated. The resultant polymers were directly characterized by GPC.

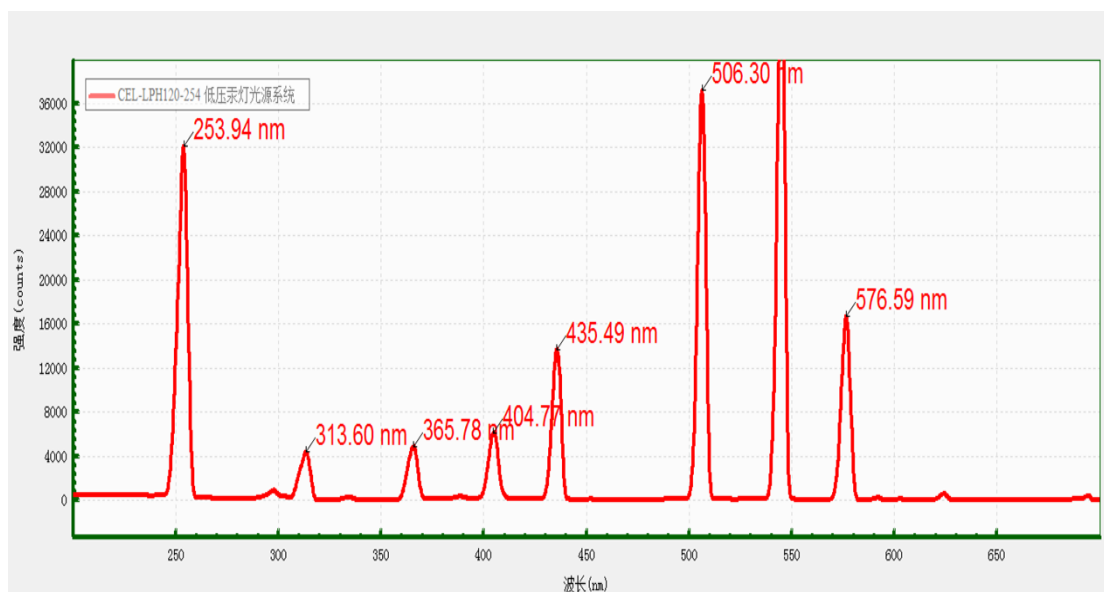


Figure S1. The full emission spectrum of the used low pressure mercury lamp (120 W) (CEL-LPH120-254, Beijing China Education Au-light co. Ltd).

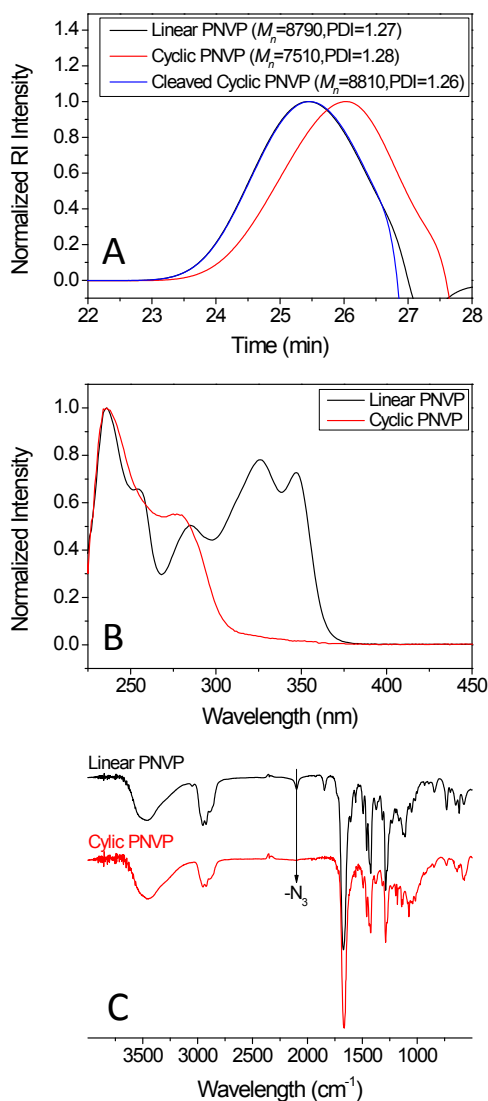


Figure S2. (A) GPC curves of linear PNVP (black), cyclic PNVP (red), and cleaved cyclic PNVP (blue), in which DMF with 0.01 M LiBr was used as the eluent and PS standards were used for the calibration. (B) UV-Vis adsorption spectra of linear PNVP (black) and cyclic PNVP (red), in which THF was used as solvent for measurements. (C) FT-IR spectra of linear PNVP (black) and cyclic PNVP (red).

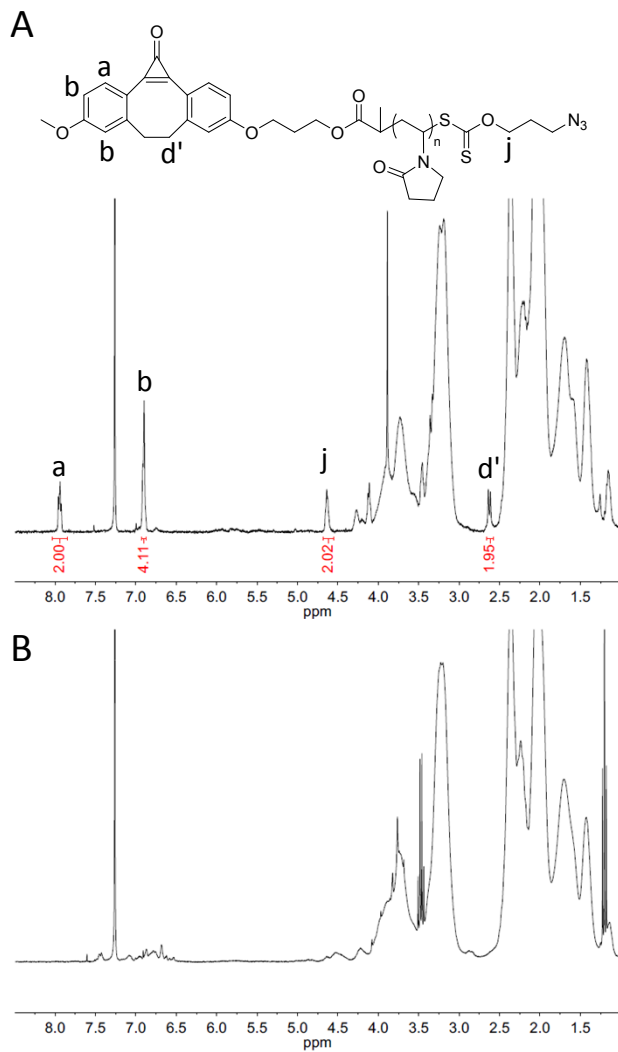


Figure S3. $^1\text{H-NMR}$ spectra of linear PNVP (A) and the corresponding cyclic PNVP (B). CDCl_3 was used as deuterated solvent.

References

- (1). Pak, J. K.; Hesse, M. *J. Org. Chem.* **1998**, *63*, 8200.
- (2) Sun, P.; Yan, G. W.; Tang, Q. Q.; Chen, Y. M.; Zhang, K. *Polymer* **2015**, *64*, 202.