

## Supporting Information for

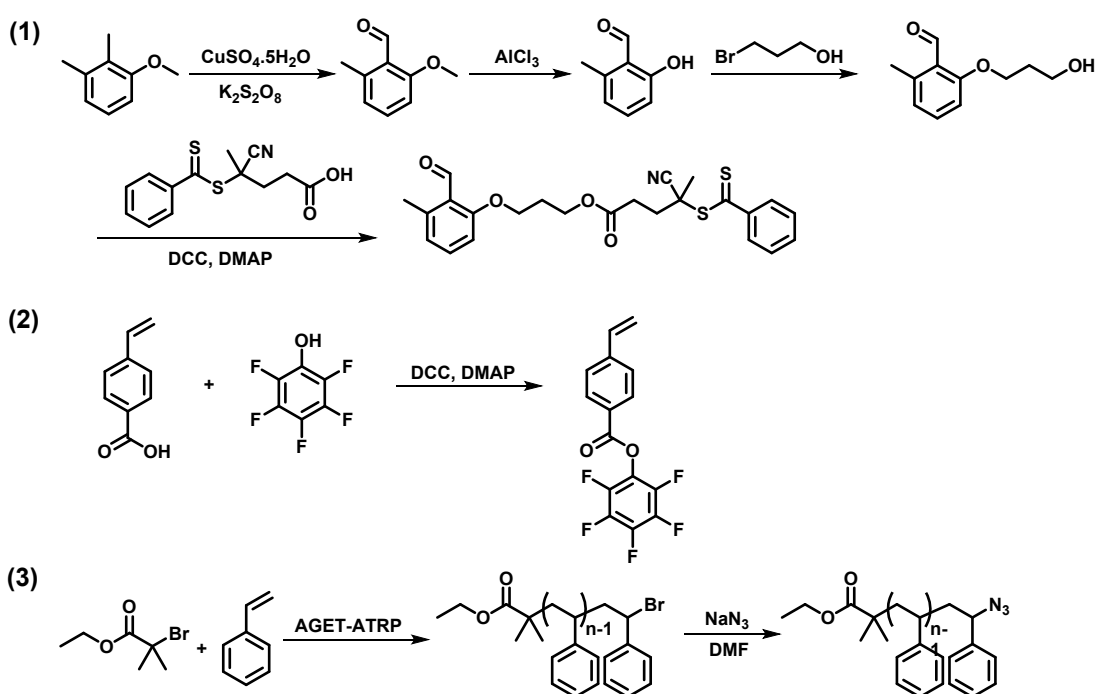
### Synthesis of cyclic-brush polymer with high grafting density using activated ester chemistry as “grafting onto” approach

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#### Experimental part

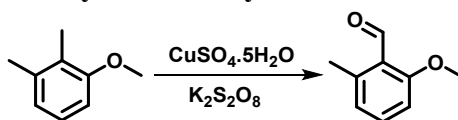
#### Synthesis.

#### Synthetic routes



**Scheme S1** Illustration of synthetic routes of RAFT agent, monomer (PF4VB) and linear polystyrene (*l*-PS- $\text{N}_3$ ).

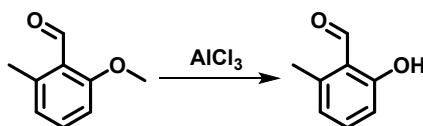
#### 1. Synthesis of 2-methoxy-6-methylbenzaldehyde<sup>1</sup>



2,3-Dimethyl anisole (4.08 g, 30 mmol), copper sulfate pentahydrate (7.86g, 31.5 mmol), potassium peroxodisulfate (24.33 g, 90 mmol) and a mixture of acetonitrile /water (1/1, 360 mL) were added into a round bottom flask. The suspension was vigorously stirred at 90 °C until thin layer chromatography (TLC) displayed that all the material (2,3-dimethyl anisole) had been consumed. The aqueous phase was extracted with DCM three times and the organic phase was

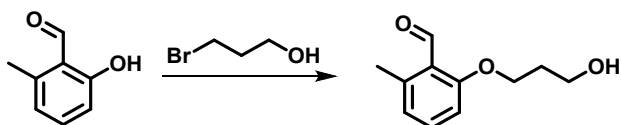
dried using  $\text{MgSO}_4$ . After evaporation under reduced pressure, the crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to get a yellow solid (2.46 g, yield: 54.6%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm): 10.67 (s, 1H, *CHO*), 7.37 (t, 1H, *ArH*), 6.81 (t, 2H, *ArH*), 3.87 (s, 3H, *OCH}\_3*), 2.56 (s, 3H, *CH}\_3*).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 Hz, ppm): 192.94, 163.29, 142.16, 134.57, 124.22, 123.46, 109.16, 55.89, 21.99.

## 2. Synthesis of 2-hydroxy-6-methylbenzaldehyde<sup>1</sup>



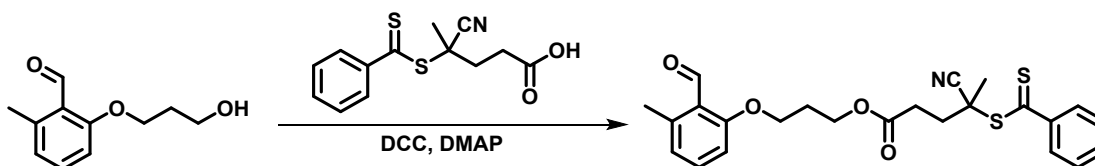
2-Methoxy-6-methylbenzaldehyde (1.5 g, 10 mmol) was dissolved in anhydrous DCM (20 mL) with 0 °C ice-bath.  $\text{AlCl}_3$  (4.0 g, 30 mmol) was added into the solution and stirred at room temperature overnight. The mixture solution was quenched with water. The aqueous phase was extracted three times with DCM (40 mL $\times$ 3). The organic phase was dried by  $\text{MgSO}_4$ . After evaporating, the final purification was gained by flash silica gel chromatography (petroleum ether/ethyl acetate = 16/1). (1.22 g, yield: 89.6%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm): 11.90 (s, 1H, *OH*), 10.32 (s, 1H, *CHO*), 7.35 (t, 1H, *ArH*), 6.80 (t, 1H, *ArH*), 6.70 (t, 1H, *ArH*), 2.60 (s, 3H, *CH}\_3*).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 Hz, ppm): 195.36, 163.16, 142.17, 137.40, 121.82, 118.53, 116.05, 18.04.

## 3. Synthesis of 2-(3-hydroxypropoxy)-6-methylbenzaldehyde<sup>2</sup>



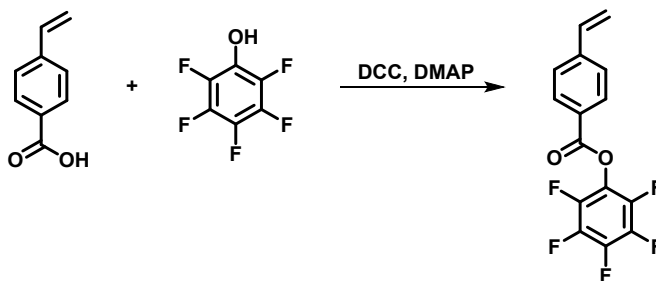
2-Hydroxy-6-methylbenzaldehyde (1 g, 7.34 mmol) and bromopropanol (1.02 g, 7.34 mmol) were added into a suspension of  $\text{K}_2\text{CO}_3$  (3.03 g, 22.02 mmol) in DMF (50 mL). The mixture was reacted at 80 °C overnight. After cooling to room temperature, the mixture was filtered and washed by 1 M HCl solution. The organic phase was extracted three times with EA and washed by water. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 2/1). (0.72 g, yield: 50.5%)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm): 10.61 (s, 1H, *CHO*), 7.36 (t, 1H, *ArH*), 6.86 (t, 2H, *ArH*), 4.21 (t, 2H, *CH}\_2*), 3.85 (t, 2H, *CH}\_2*), 2.72 (s, 1H, *OH*), 2.56 (s, 3H, *CH}\_3*), 2.09 (t, 2H, *CH}\_2*).  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ , 75 MHz, ppm): 192.21, 162.18, 142.40, 134.78, 124.14, 123.24, 110.09, 66.14, 59.84, 32.04, 21.23.

## 4. Synthesis of RAFT agent<sup>2</sup>



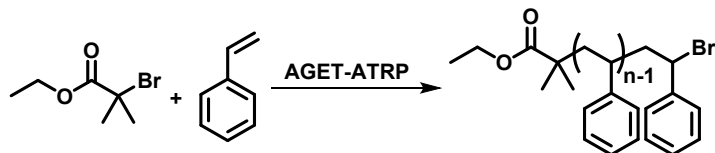
2-(3-Hydroxypropoxy)-6-methylbenzaldehyde (358.1 mg, 1.84 mmol) and 4-cyano-4-(thiobenzoylthio)pentanoic acid (429.2 mg, 1.54 mmol) were dissolved in DCM (5 mL) at 0 °C. DCC (633.6 mg, 3.07 mmol) and DMAP (37.54 mg, 0.31 mmol) dissolved in DCM (4 mL) were added into above solution. After stirring at room temperature for 24 h, the reaction mixture was filtered and the filtrate was evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to get a red oil. (497.8 mg, yield: 71.0%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 10.62 (s, 1H, CHO), 7.85 (d, 2H, ArH), 7.53 (t, 1H, ArH), 7.36 (q, 3H, ArH), 6.79 (m, 2H, ArH), 4.29 (t, 2H, CH<sub>2</sub>), 4.10 (t, 2H, CH<sub>2</sub>), 2.35-2.75 (m, 7H, CH<sub>2</sub>, CH<sub>3</sub>), 2.16 (m, 2H, CH<sub>2</sub>), 1.89 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): 222.28, 192.00, 171.39, 162.22, 144.48, 142.06, 134.48, 133.05, 128.57, 126.66, 124.32, 123.36, 118.46, 109.81, 64.96, 61.74, 45.70, 33.35, 29.71, 28.47, 24.14, 21.45.

### 5. Synthesis of pentafluorophenyl 4-vinylbenzoate (PF4VB)



4-vinylbenzoic acid (13.3 g, 90 mmol), 2,3,4,5,6-pentafluorophenol (14.7 g, 80 mmol) and DMAP (1.95 g, 16 mmol) were dissolved in THF (150 mL). DCC was dissolved in THF and then dropwise added into the mixture solution. The solution was stirred for 24 h. The mixture was filtered and purified by fast silica gel-column chromatography using hexane as eluent. The gained crude product was recrystallized using hexane under -20 °C. (13.24 g, yield: 52.7%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 8.14 (d, 2H, ArH), 7.57 (d, 2H, ArH), 6.79 (dd, 1H, CH=CH<sub>2</sub>), 5.97 (d, 1H, CH<sub>2</sub>=CH-), 5.49 (d, 1H, CH<sub>2</sub>=CH-). <sup>13</sup>C NMR: (CDCl<sub>3</sub>, 75 MHz, ppm): 162.35, 143.78, 143.08, 141.21, 139.69, 137.85, 136.27, 135.66, 131.06, 126.53, 125.87, 117.75. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 564 MHz, ppm): -152.59 (2F, pentafluorophenyl, *ortho*), -158.17 (1F, pentafluorophenyl, *para*), -162.50 (2F, pentafluorophenyl, *meta*).

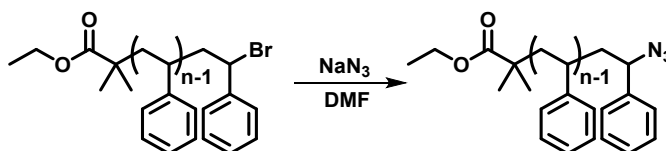
### 6. Synthesis of linear polystyrene (*l*-PS-Br) by ATRP



Styrene (9.06 g, 87.00 mmol), EBiB (339.4 mg, 1.74 mmol), CuBr<sub>2</sub> (111.7 mg, 0.05 mmol), PMDETA (173.30 mg, 1.5 mmol), AA (176.13 mg, 1.0 mmol) and 10 mL anisole were added into a 25 mL Schlenk flask. The flask was placed in an oil bath at 90 °C and stirred for 2.5 h. The mixture solution was cooled to room temperature. the mixture was purified by filtration through a short Al<sub>2</sub>O<sub>3</sub> column to remove the catalyst and concentrated to precipitate into methanol. The white polymers were gained by filtration and dried under vacuum. (3.23 g, conv. %: 34.4%) ( $M_{n,th} = 2000$ )

g/mol,  $M_{n,NMR} = 2500$  g/mol,  $M_{n,GPC} = 2400$  g/mol,  $M_w/M_n = 1.06$ ).

## 7. Synthesis of linear polystyrene (*l*-PS- $N_3$ ) by azidation with $NaN_3$



Polymer (1.2 g, 0.5 mmol),  $NaN_3$  (488.0 mg, 7.5 mmol) and DMF (8 mL) were added into a 25 mL round bottom flask and stirred at room temperature for 24 h. The reaction mixture was diluted and purified by filtration through a short  $Al_2O_3$  column to remove excess sodium azide, followed by precipitation in methanol. The white polymer was gained by filtration and dried under vacuum. (974.8 mg, yield: 81.2%) ( $M_{n,GPC} = 2500$  g/mol,  $M_w/M_n = 1.05$ ).

Linear polystyrene (*l*-PS- $N_3$ ) was prepared by atom transfer radical polymerization (ATRP) and the azidation of end group from polymer chain. The main methods for verifying the successful preparation of azide-containing polystyrene (*l*-PS- $N_3$ ) were NMR, GPC, MALDI-TOF mass spectroscopy and FT-IR.  $^1H$  NMR spectroscopy (Fig. S5) was used to measure the molecular weight ( $M_{n,NMR}$ ) of the polymers and to prove the chemical transformations caused by the changing of the end groups. The calculated number average molecular weight ( $M_{n,NMR}$ ) of the linear polystyrene (*l*-PS-Br) precursor was 2400 g/mol, corresponding to the  $M_{n,NMR}$  of 2400 g/mol (Fig. S6). After azidation,  $^1H$  NMR spectroscopy showed the transition process from bromine end-groups (4.3-4.6 ppm) to azides (3.8-4.1 ppm) completely, which provide convincing evidence for the formation of azide-containing polymer (*l*-PS). After azidation, the SEC curves (Fig. S6) don't have obvious changes. From Fig. S7, appearance of azide ( $2094\text{ cm}^{-1}$ ) also proved the formation of azide. As shown in Fig. S8, the representative experimental peak  $m/z$  value (2109.15 Da), was consistent with the theoretically calculated value ( $[18\text{mer-}N_2 + Ag]^+$ , Calcd 2109.11 Da). The difference between two adjacent peaks (104.06 Da) is equal to the mass of one styrene repeat unit. Therefore, the above data confirmed the successful preparation of *l*-PS- $N_3$ .

## Reference

1. K. K. Oehlenschlaeger, J. O. Mueller, N. B. Heine, M. Glassner, N. K. Guimard, G. Delaittre, F. G. Schmidt, and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2013, **52**, 762-766;
2. Q. Tang, Y. Wu, P. Sun, Y. Chen and K. Zhang, *Macromolecules* 2014, **47**, 3775-3781.

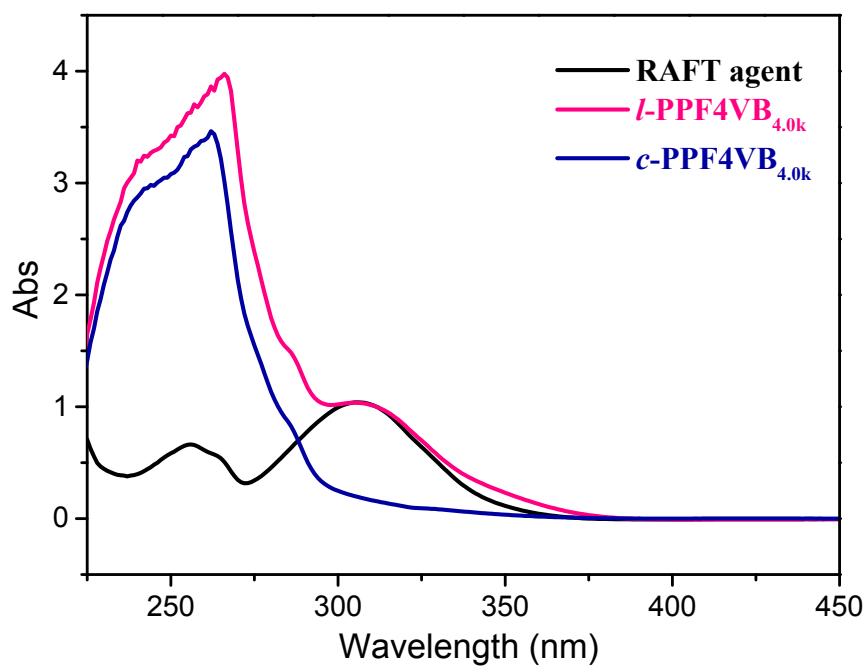


Fig. S1 UV-vis spectrum of RAFT agent, *l*-PPF4VB<sub>4.0k</sub> and *c*-PPF4VB<sub>4.0k</sub>.

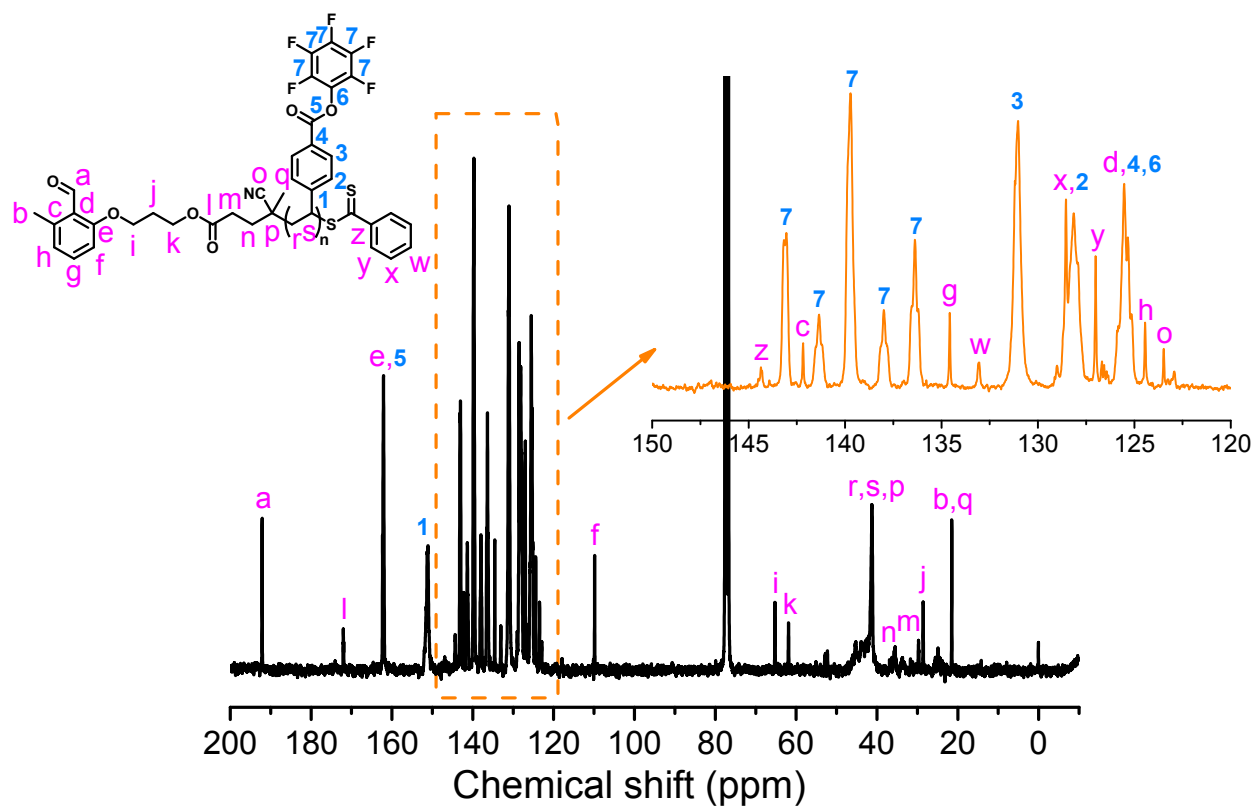
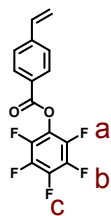


Fig. S2 <sup>13</sup>C NMR (75 MHz) spectrum of linear polymer (*l*-PPF4VB<sub>4.0k</sub>).

(1) PF4VB



(2) *l*-PPF4VB<sub>4.0k</sub>

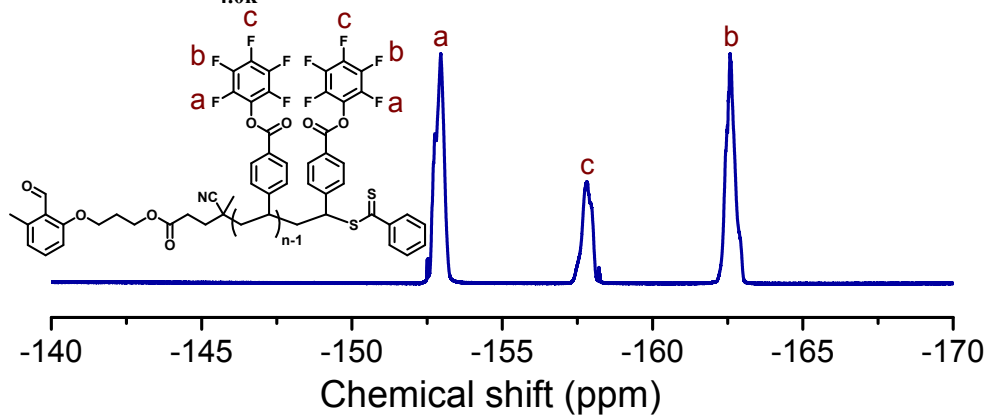
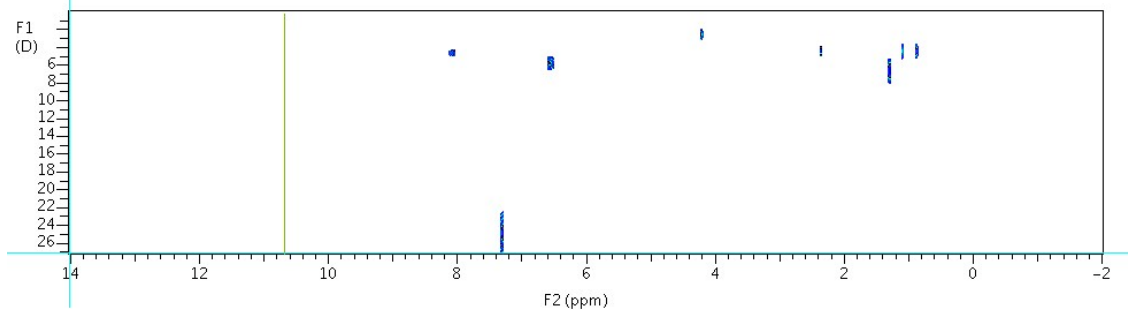


Fig. S3 <sup>19</sup>F NMR (564 MHz) spectrum of monomer (PF4VB) and linear polymer (*l*-PPF4VB<sub>4.0k</sub>).

(1) *l*-PPF4VB<sub>4.0k</sub>



(2) *c*-PPF4VB<sub>4.0k</sub>

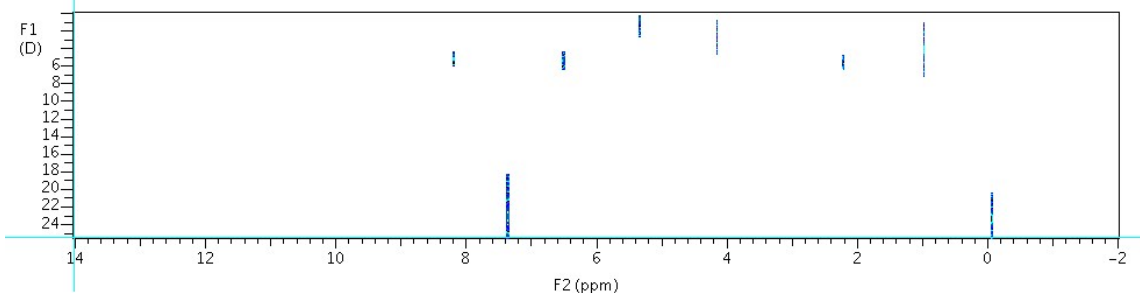


Fig. S4 <sup>1</sup>H DOSY NMR spectrum of linear polymer (*l*-PPF4VB<sub>4.0k</sub>) and cyclic polymer (*c*-PPF4VB<sub>4.0k</sub>).

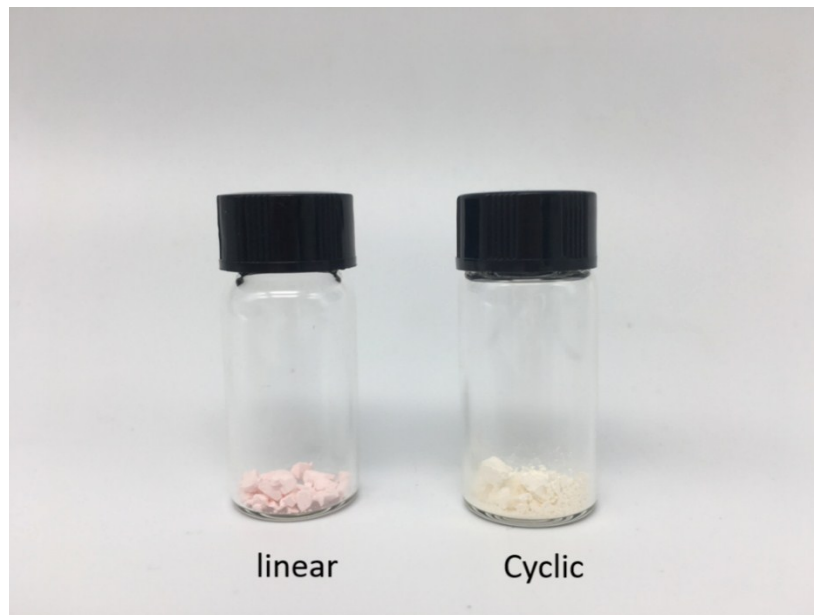


Fig. S5 Pictures of *l*-PPF4VB<sub>4.0k</sub> and *c*-PPF4VB<sub>4.0k</sub>.

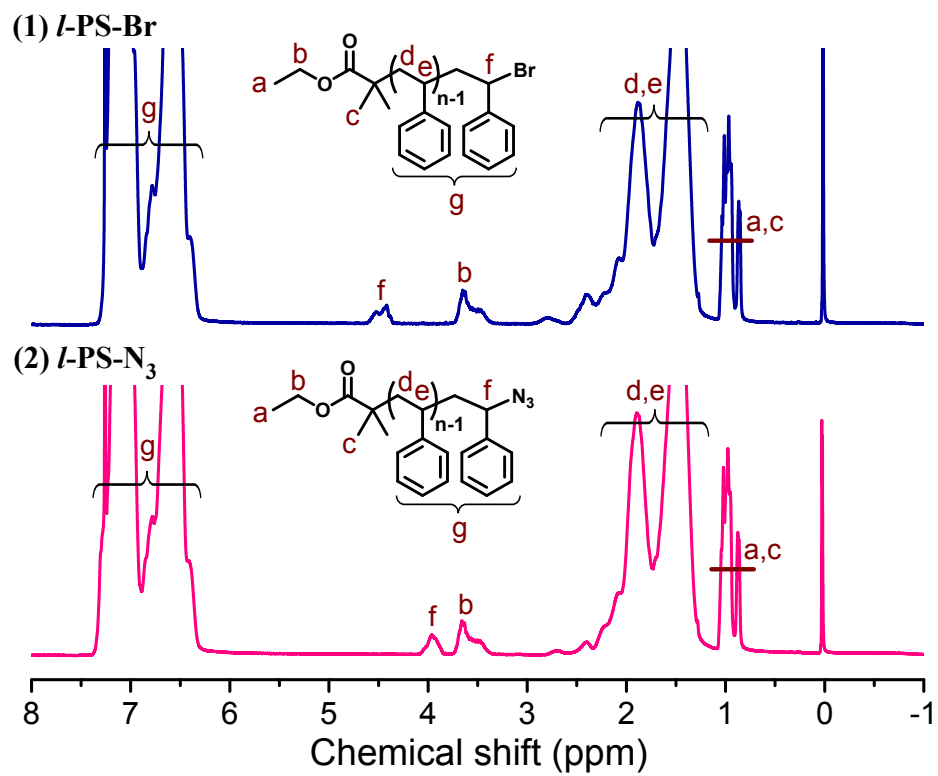


Fig. S6 <sup>1</sup>H NMR (300 MHz) spectrum of *l*-PS-Br and *l*-PS-N<sub>3</sub>.

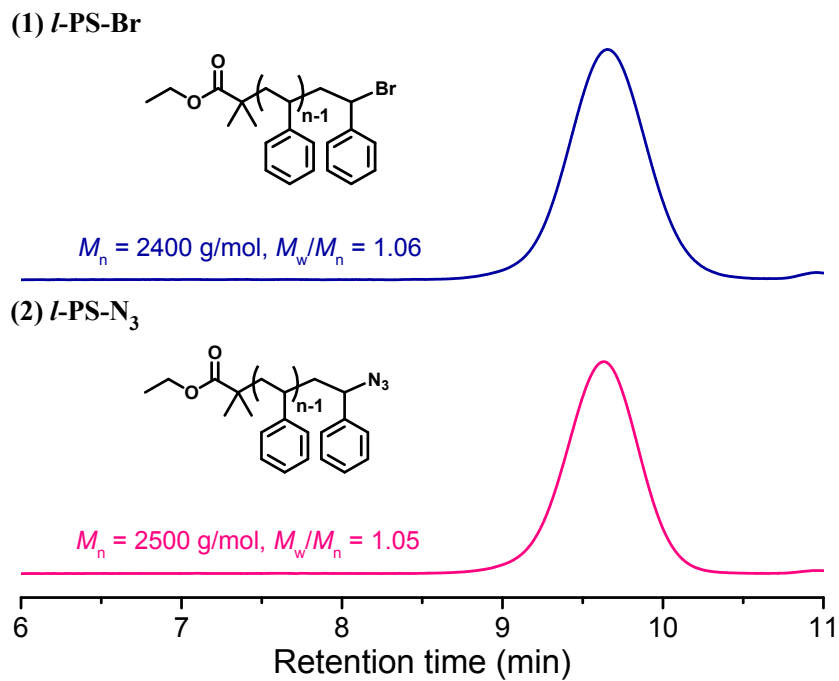


Fig. S7 SEC curves of *l*-PS-Br and *l*-PS-N<sub>3</sub>. THF was used as the eluent and PS standards for the calibration.

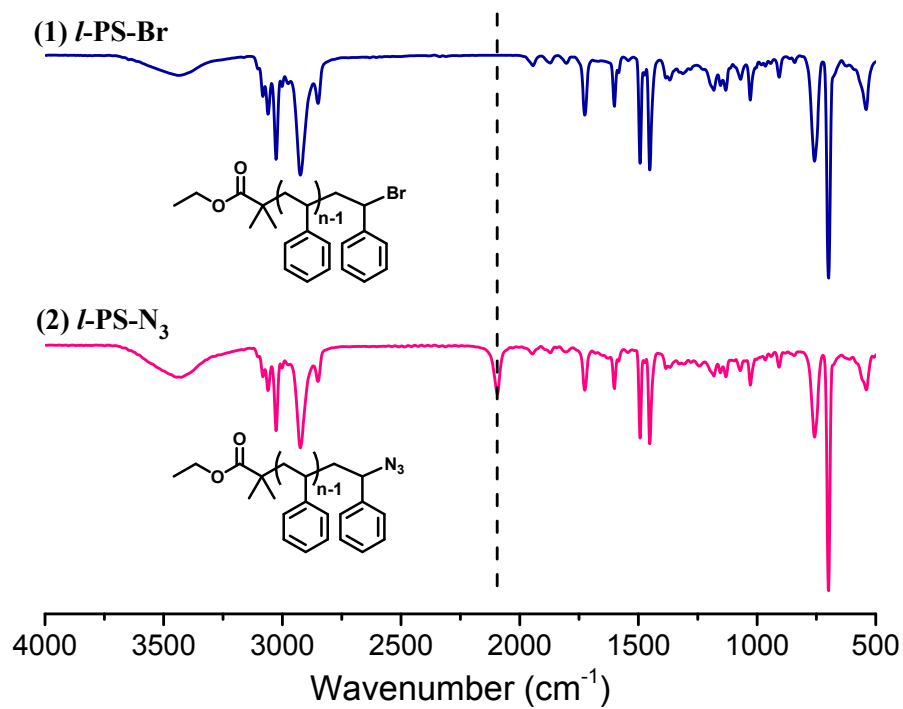


Fig. S8 FT-IR spectrum of *l*-PS-Br and *l*-PS-N<sub>3</sub>.



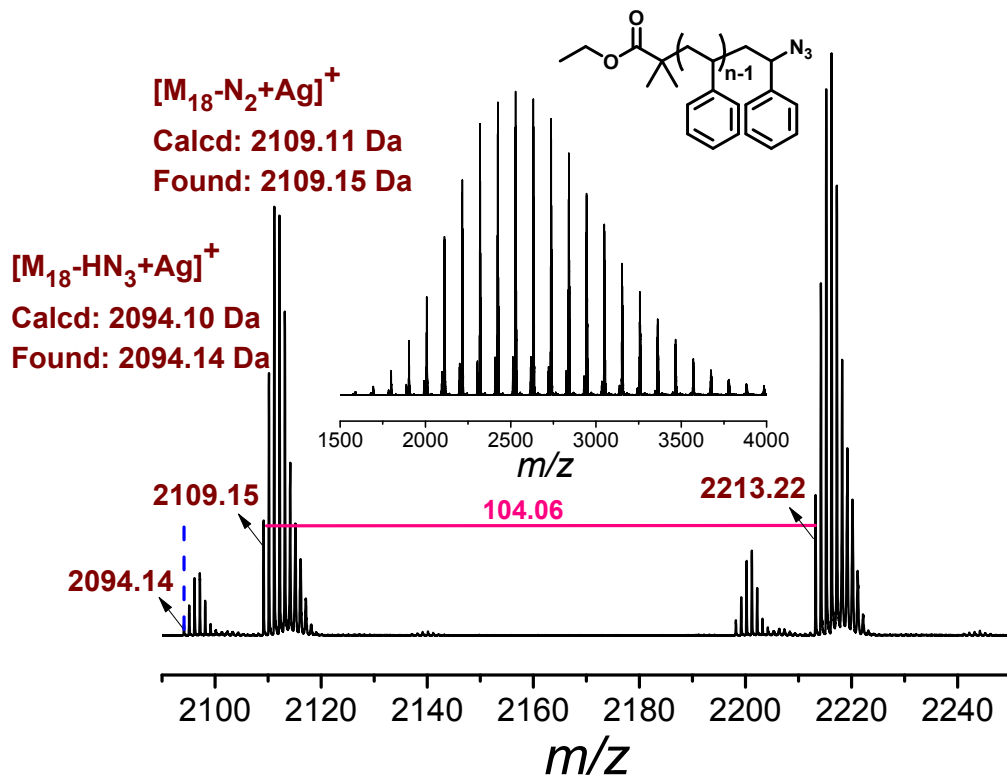


Fig. S9 Expanded MALDI-TOF mass spectrum of *l*-PS-N<sub>3</sub> with the inserted full spectra.

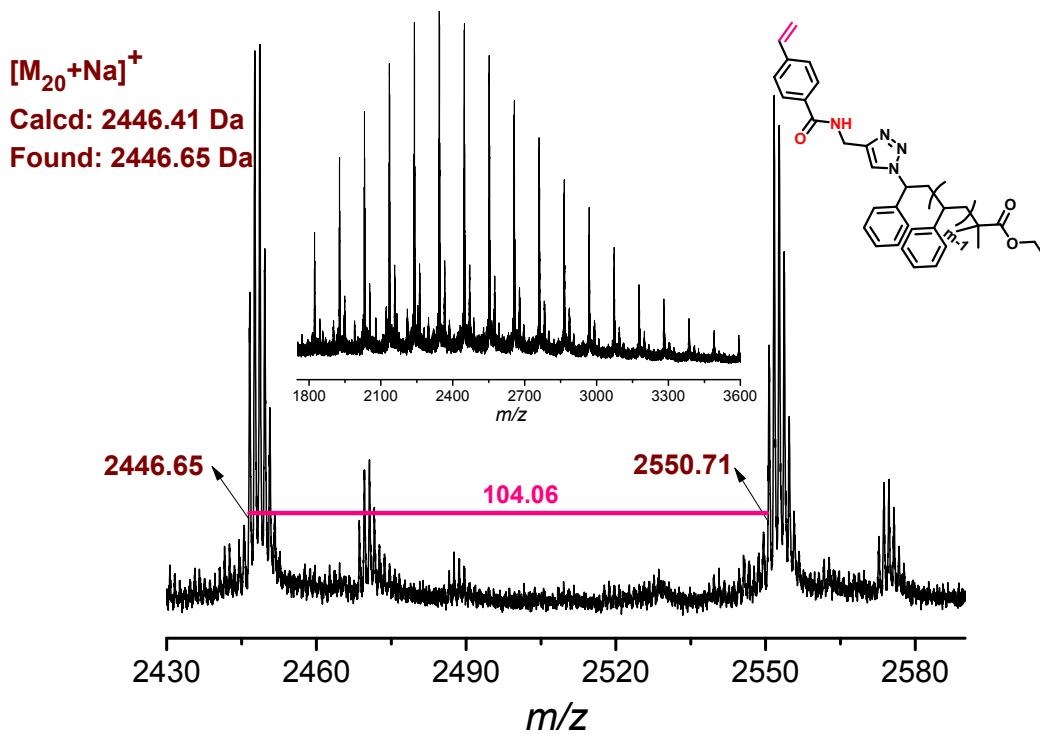


Fig. S10 Expanded MALDI-TOF mass spectrum of *c*-P1-*g*-PS with the inserted full spectra.

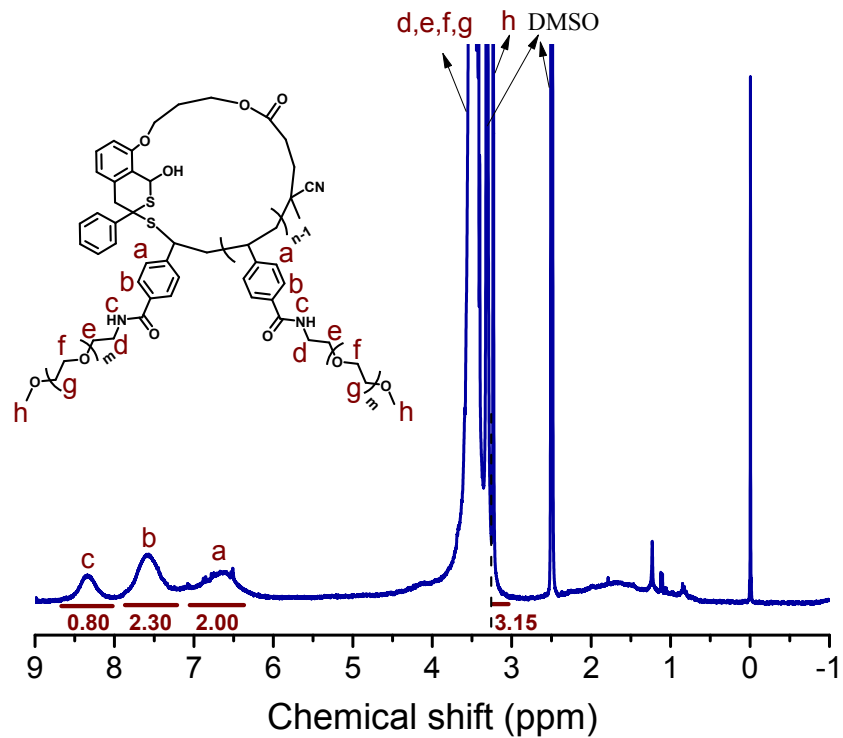


Fig. S11  $^1\text{H}$  NMR (300 MHz) spectrum of *c*-PPF4VB<sub>4.0k</sub>-g-PEG.

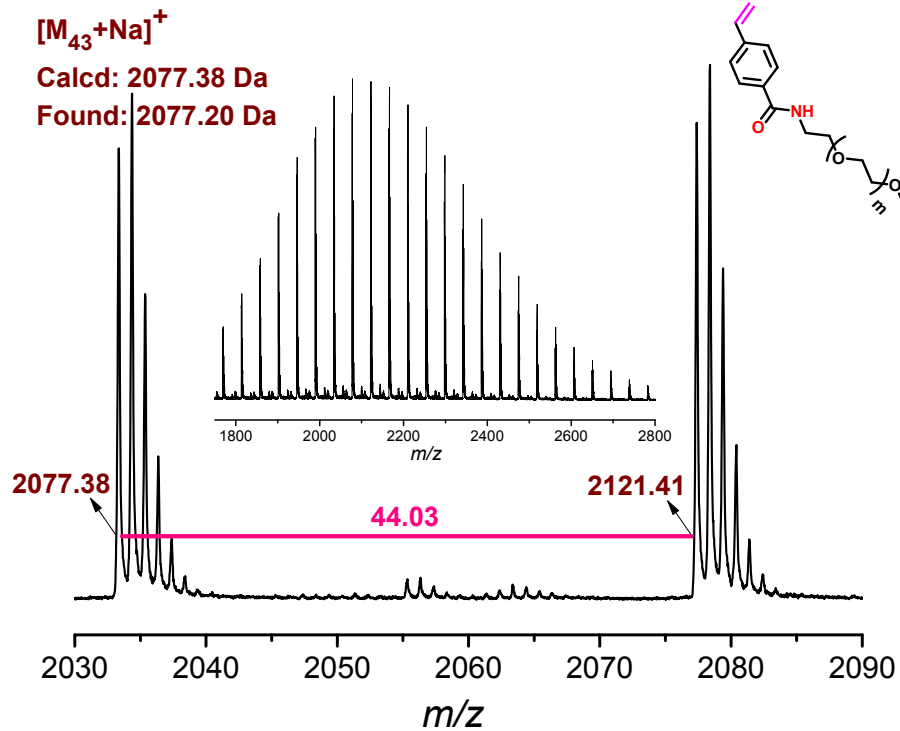


Fig. S12 Expanded MALDI-TOF mass spectrum of *c*-PPF4VB<sub>4.0k</sub>-g-PEG with the inserted full spectra.