Supporting Information

Well-defined Cyclic Polymers via Efficient Etherification-based Bimolecular Ring-Closure Strategy

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Contents

Synthesis of monofunctionalized-OH PS

Anionic polymerization under high vacuum techniques was employed for the synthesis of the PS bearing a terminal –OH group. Specifically, styrene (5 g) was added to 100 mL of benzene, followed by the addition of *sec*-BuLi (1 mmol), and kept for 18 h at room temperature. After completion of polymerization, an aliquot was taken by heat-sealing the proper constriction to verify the molecular characteristics of the synthesized PS. Subsequently, ethylene oxide (~1 mL) was added to the reaction mixture, left for 12 h at room temperature, and the reaction was terminated by the addition of degassed methanol. The resultant reaction mixture was precipitated into a large excess of methanol, and the final polymer was dried in a vacuum oven for 24 h at 40 ^{o}C. The number-average molecular weight and polydispersity index of the synthesized PS were determined by SEC (M_n = 5,100 g/mol and Đ = 1.05).

Characterization results

Table S1. *Ratios between the cyclic and the linear products as calculated by SEC chromatographs of the crude c-PS.*

Sample	Ratio[a] Cyclic : Linear
c-PS-4K-crude	79 : 21
c-PS-7.5K-crude	80 : 20
c-PS-13K-crude	86 : 14
c-PS-23K-crude	82 : 18

[a] Calculated through SEC, by dividing the area of the linear products with the total area (linear and cyclic).

Table S2. . *Ratios between the cyclic and the linear products as calculated by SEC chromatographs of the crude c-PEG.*

Sample	Ratio[a] Cyclic : Linear
c-PEG-2K-crude	84 : 16
c-PEG-6K-crude	81 : 19

[a] Calculated through SEC, by dividing the area of the linear products with the total area (linear and cyclic).

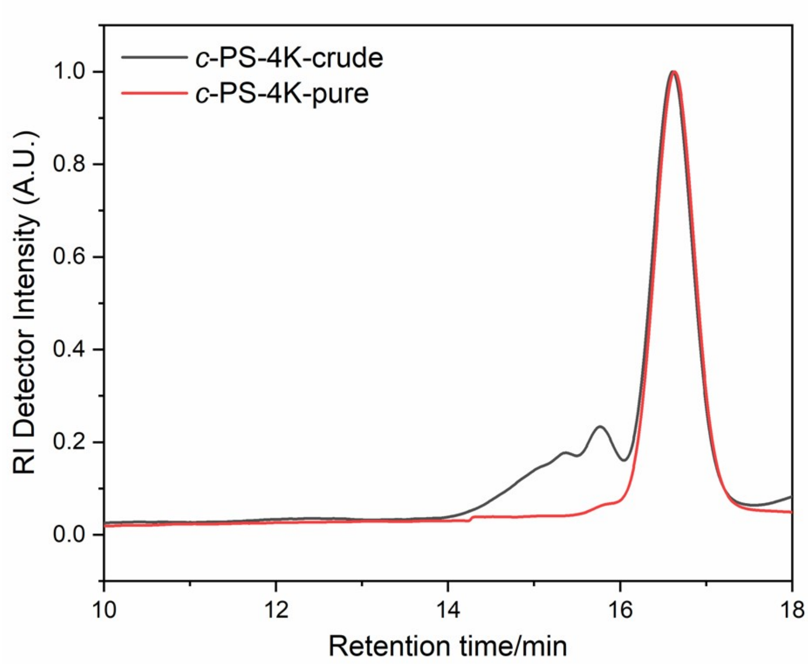

Figure S1. *SEC chromatographs of c-PS-4K before (crude) and after fractionation (pure) (THF, 35 ºC, PS standards).*

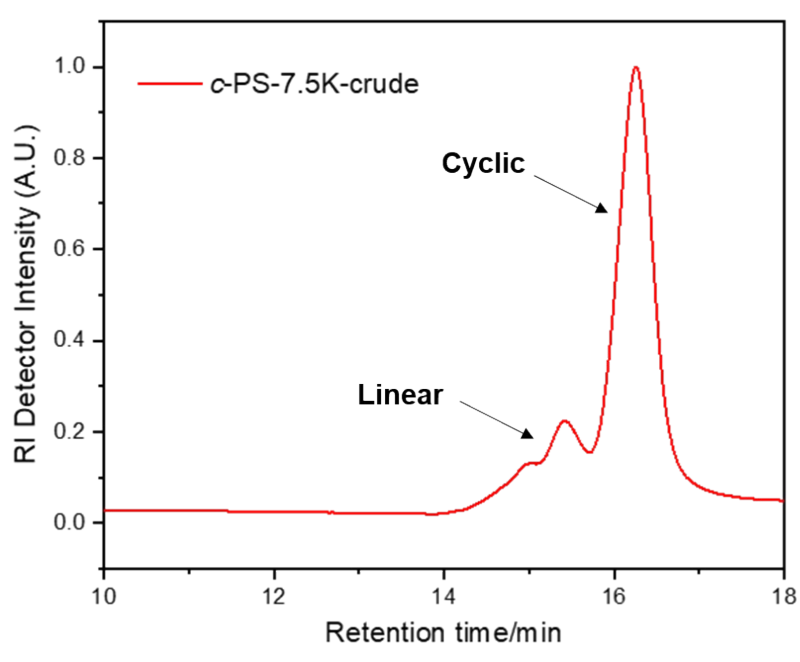

Figure S2. *SEC chromatograph of the c-PS-7.5K crude product (THF, 35 ºC, PS standards).*

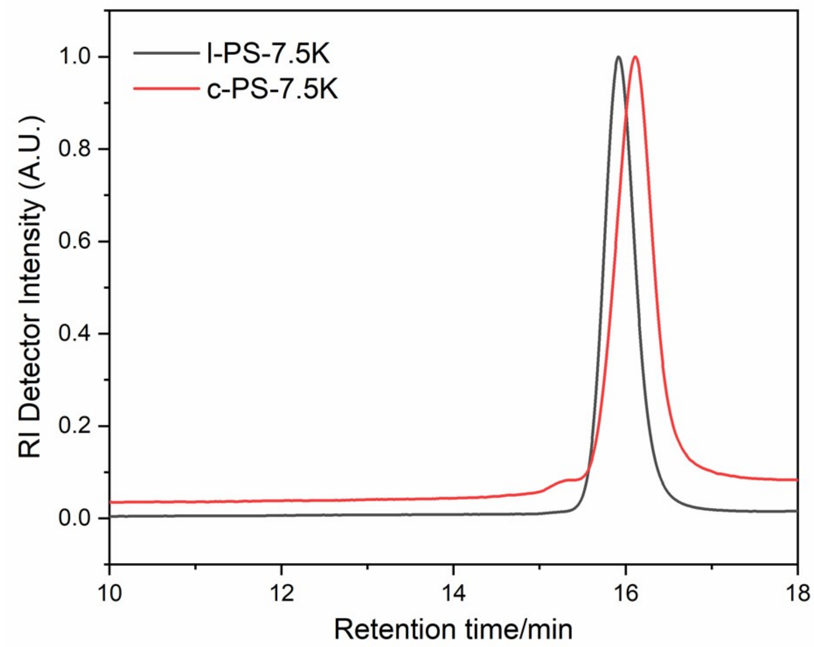

Figure S3. *SEC chromatographs of the l-PS-7.5K and the corresponding purified c-PS-7.5K (THF, 35 ^{o}C, PS standards).*

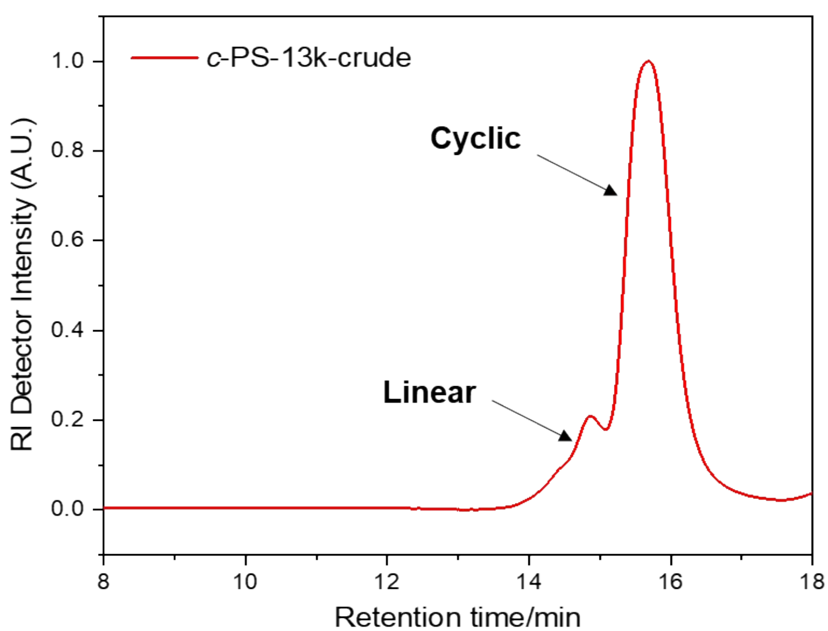

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Figure S4. *SEC chromatograph of the c-PS-13K crude product (THF, 35 ^{o}C, PS standards).*

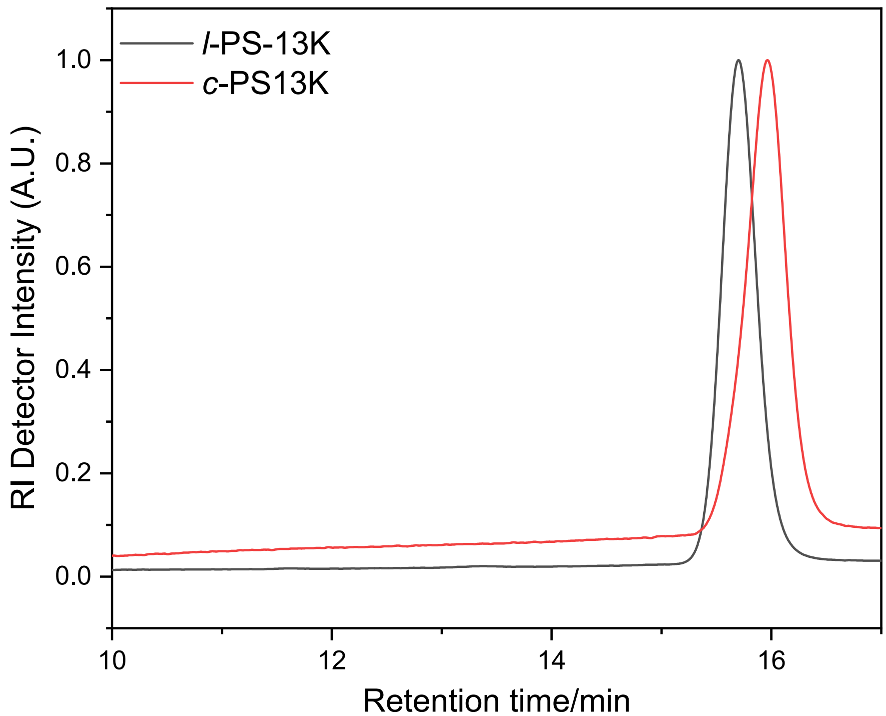

Figure S5. *SEC chromatographs of the l-PS-13K and the corresponding purified c-PS-13K (THF, 35 °C, PS standards).*

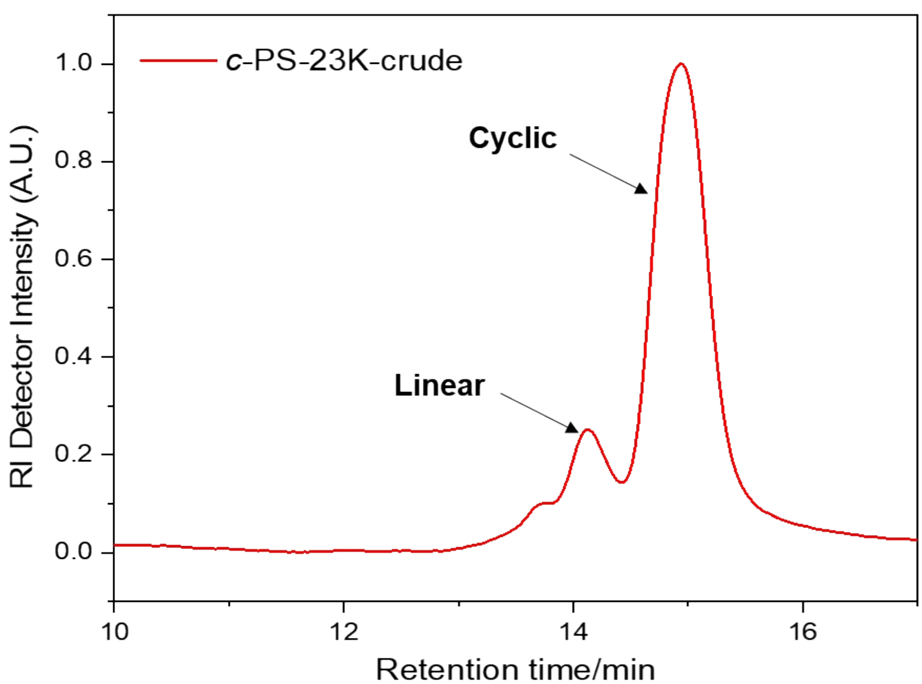

Figure S6. *SEC chromatograph of the c-PS-23K crude product (THF, 35 °C, PS standards).*

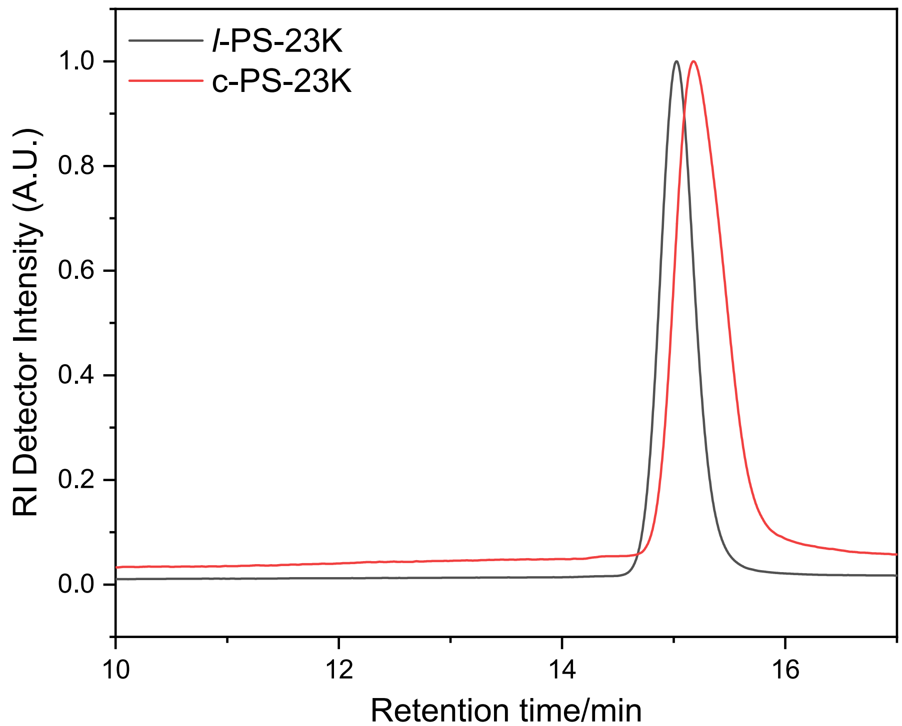

Figure S7. *SEC chromatographs of the l-PS-23K and the corresponding purified c-PS-23K (THF, 35 ᵒC, PS standards).*

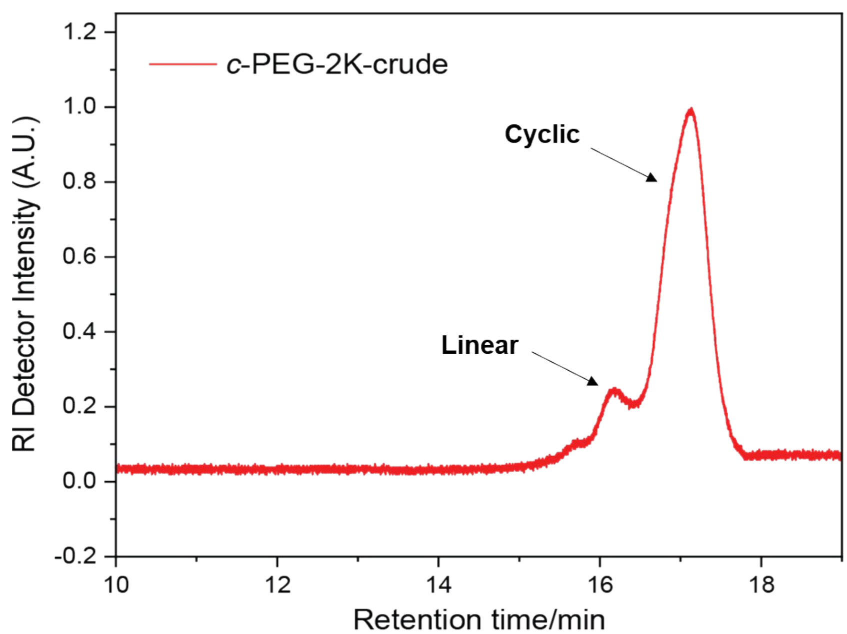

Figure S8. *SEC chromatograph of the c-PEG-2K crude product (THF, 35 ᵒC, PS standards).*

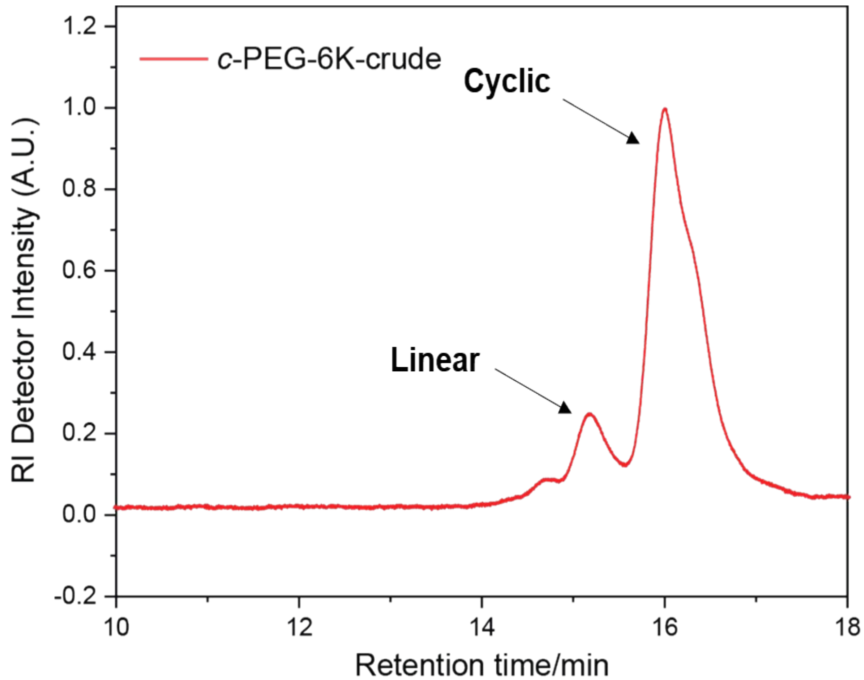

Figure S9. *SEC chromatograph of the c-PEG-6K crude product (THF, 35 °C, PS standards).*

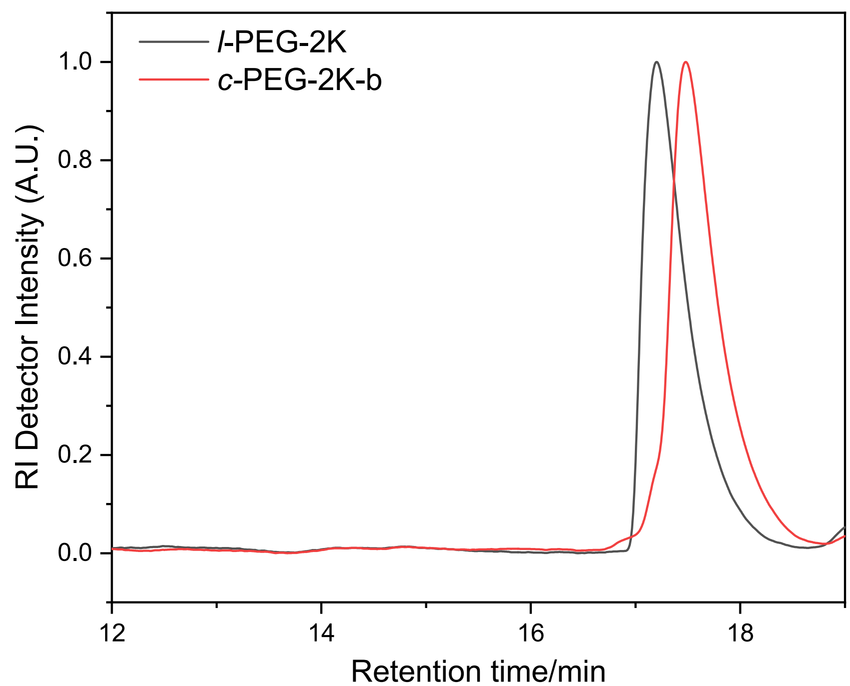

Figure S10. *SEC chromatographs of the l-PEG-2K and the corresponding purified c-PEG-2K-b (THF, 35 °C, PS standards).*

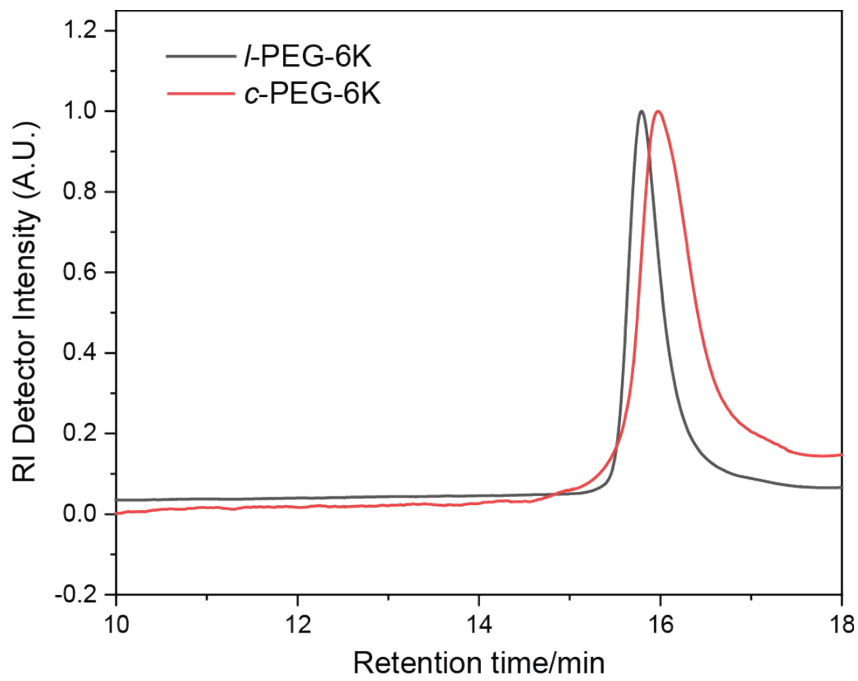

Figure S11. *SEC chromatographs of the l-PEG-6K and the corresponding purified c-PEG-6K (THF, 35 °C, PS standards).*

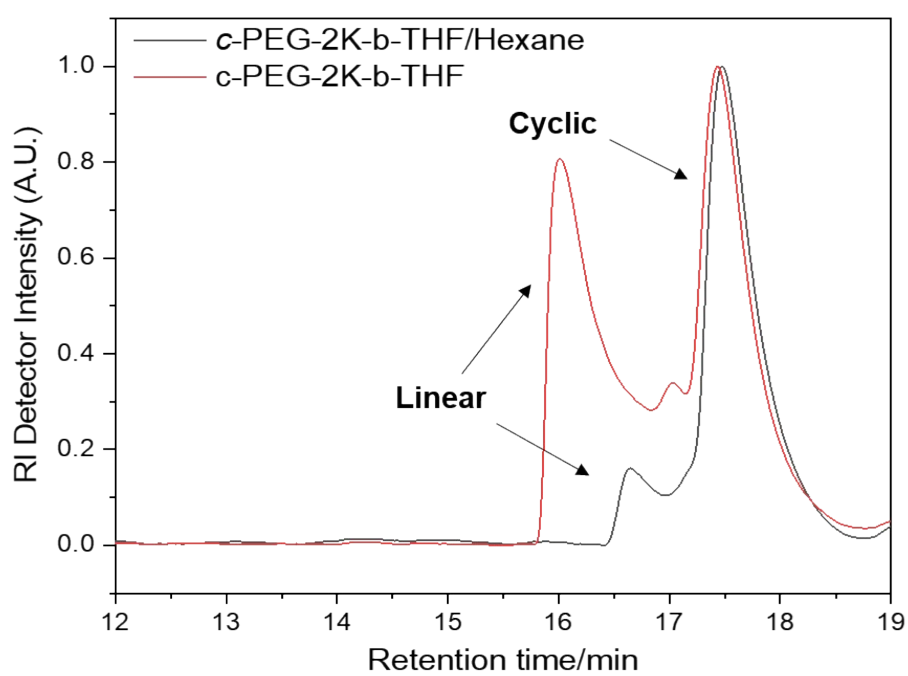

Figure S12. *SEC chromatographs of the c-PEG-2K crude products in THF/hexane and in THF (THF, 35 °C, PS standards).*

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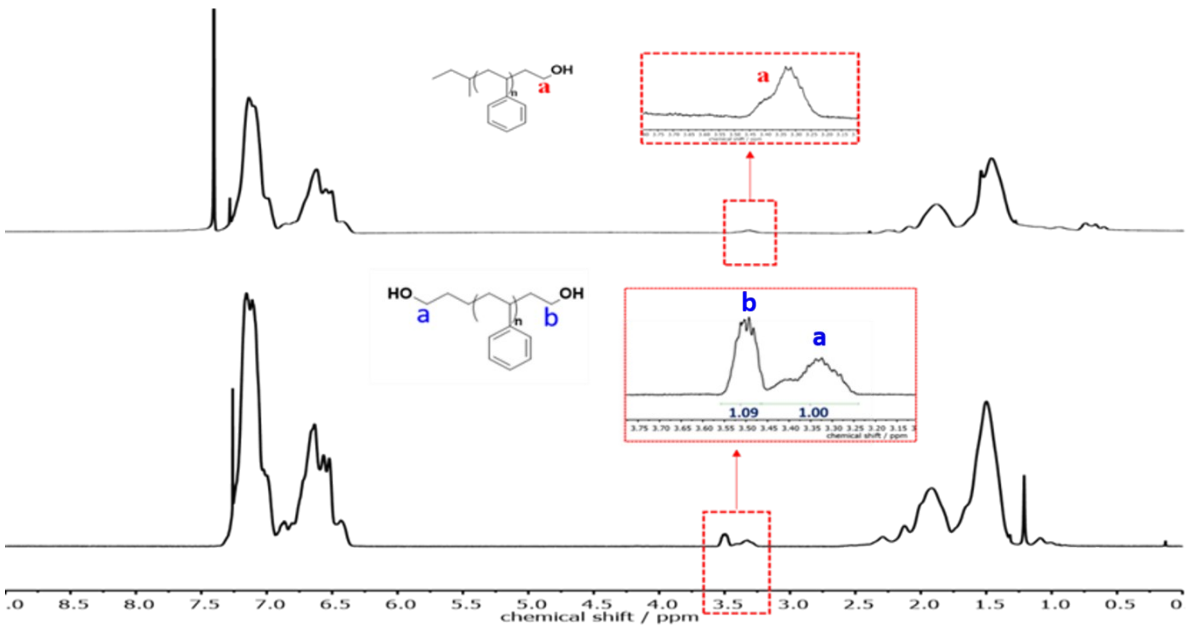

Figure S13. *[1]H NMR spectra of the monofunctionalized-OH PS and the telechelic l-PS-4K polymer ($CDCl_3$, 25 ^oC, 500 MHz).*

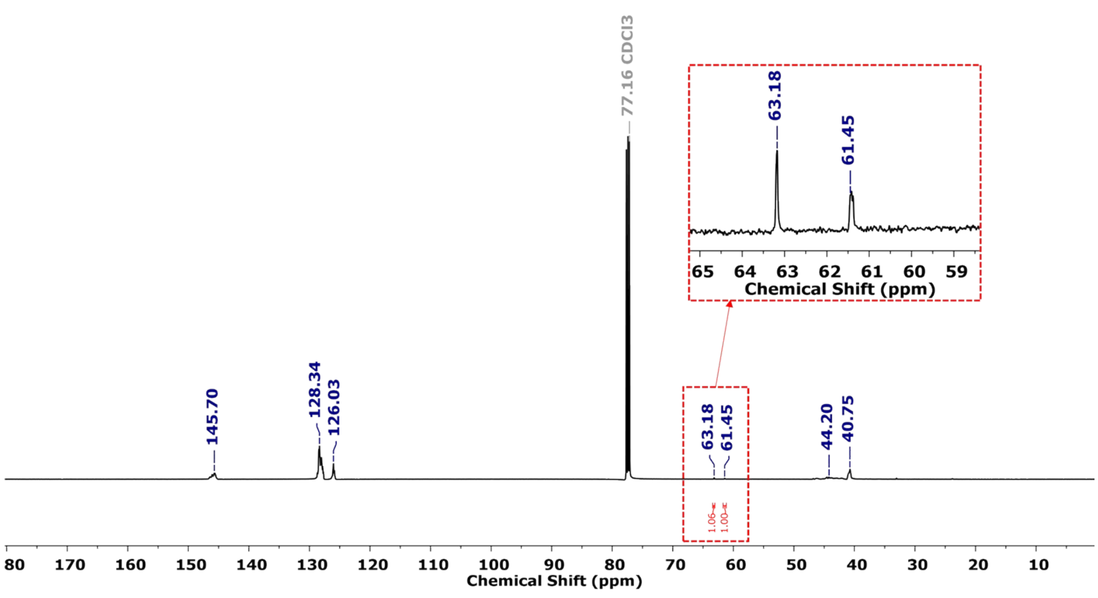

Figure S14. *[13]C-NMR spectrum (quantitative) of l-PS-4K polymer ($CDCl_3$, 25 ^oC, 500 MHz).*

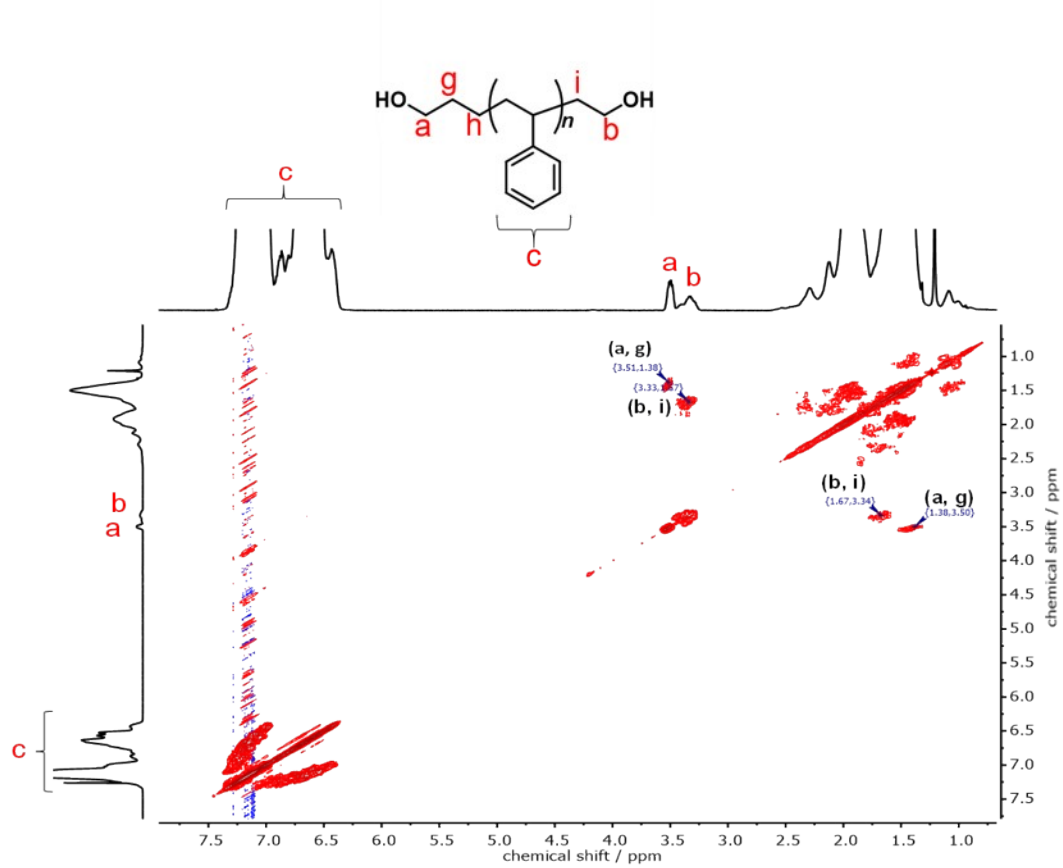

Figure S15. *2D COSY spectrum of l-PS-4K polymer ($CDCl_3$, 25 ^oC, 600 MHz).*

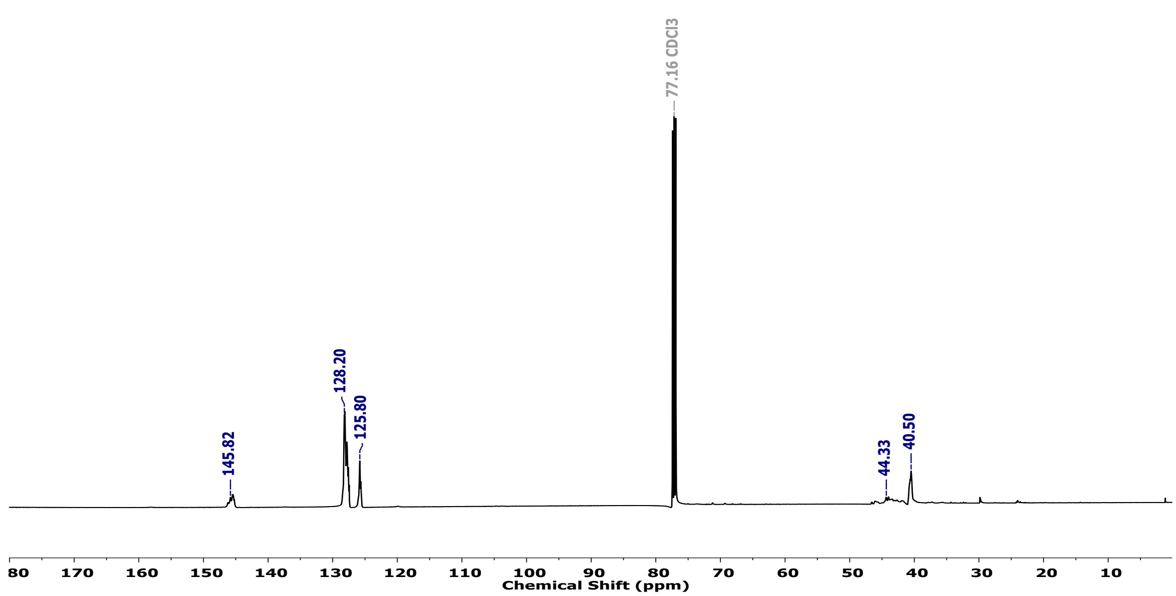

Figure S16. *^{13}C-NMR spectrum (quantitative) of c-PS-4K polymer ($CDCl_3$, 25 ^oC, 500 MHz).*

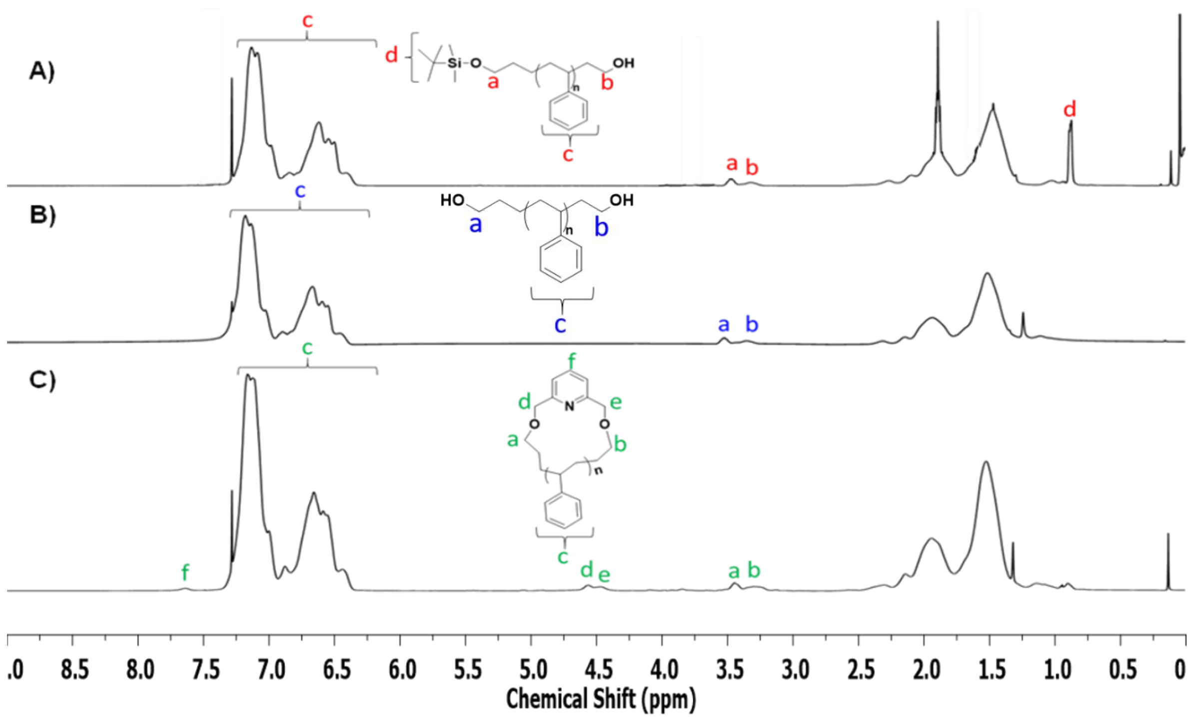

Figure S17. *[1]H-NMR spectra of A) Pr-PS-7.5K, B) l-PS-7.5K, and C) the corresponding purified c-PS-7.5K ($CDCl_3$, 25 °C, 500 MHz).*

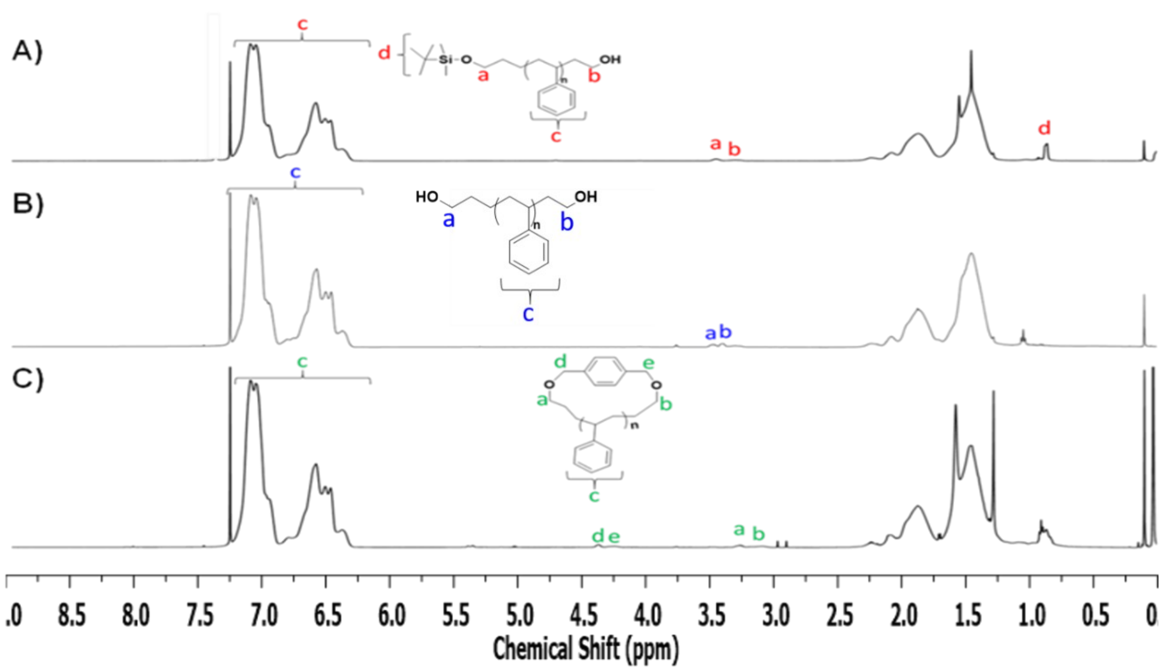

Figure S18. *[1]H-NMR spectra of A) Pr-PS-13K, B) l-PS-13K, and C) the corresponding purified c-PS-13K ($CDCl_3$, 25 °C, 500 MHz).*

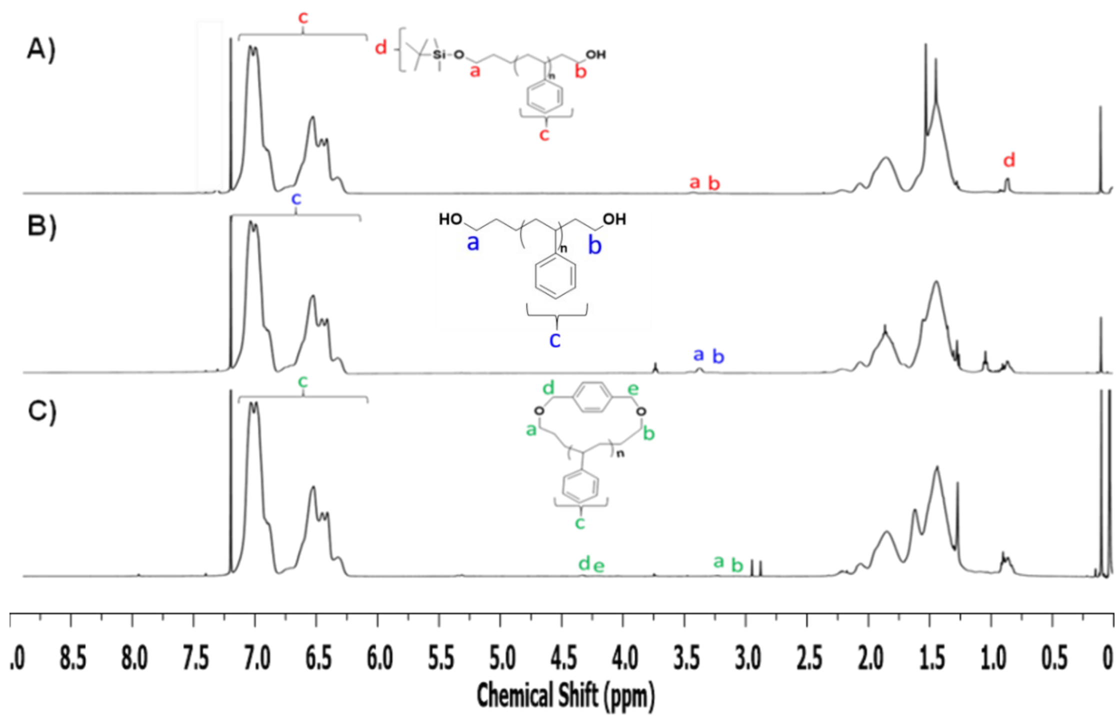

Figure S19. *^{1}H-NMR spectra of A) Pr-PS-23K, B) l-PS-23K, and C) the corresponding purified c-PS-23K (CDCl$_3$, 25 ^{o}C, 500 MHz).*

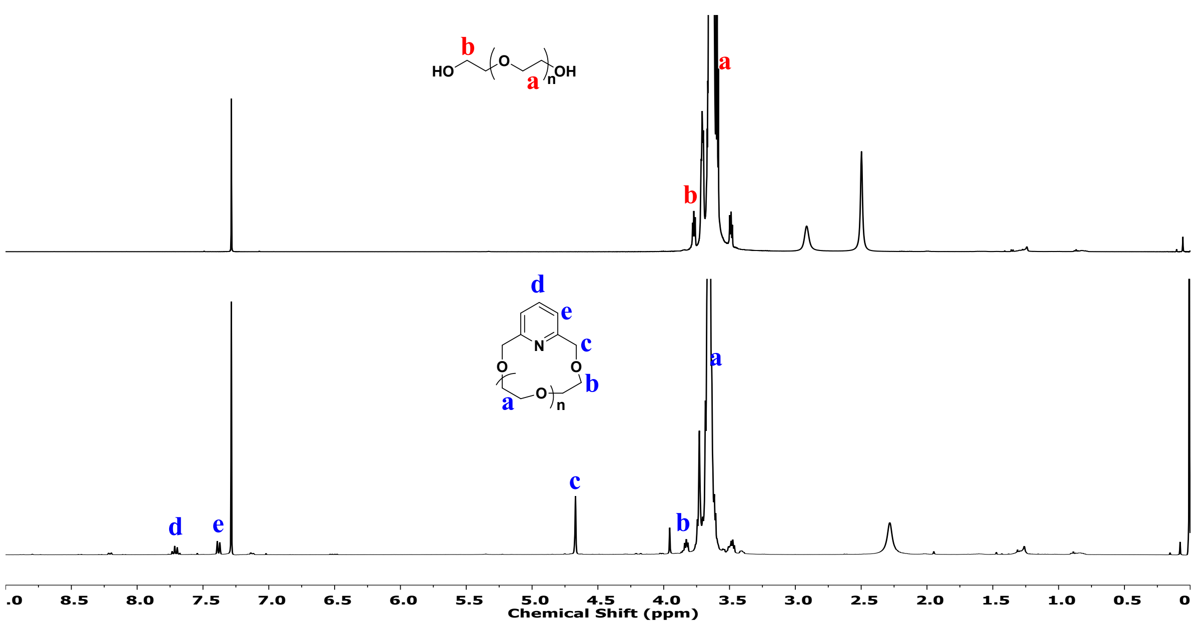

Figure S20. *^{1}H-NMR spectra of PEG-2K and the corresponding purified c-PEG-2K (CDCl$_3$, 25 ^{o}C, 500 MHz).*

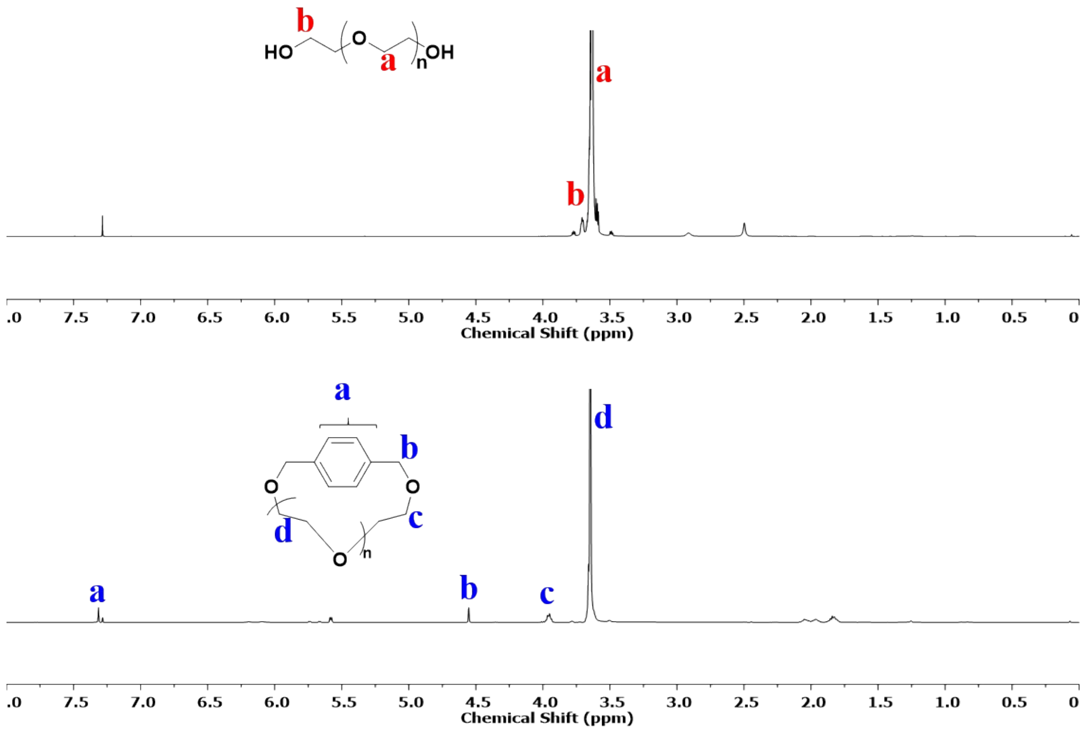

Figure S21. *[1]H-NMR spectra of PEG-2K and the corresponding purified c-PEG-2K-b (CDCl$_3$, 25 ^{o}C, 500 MHz).*

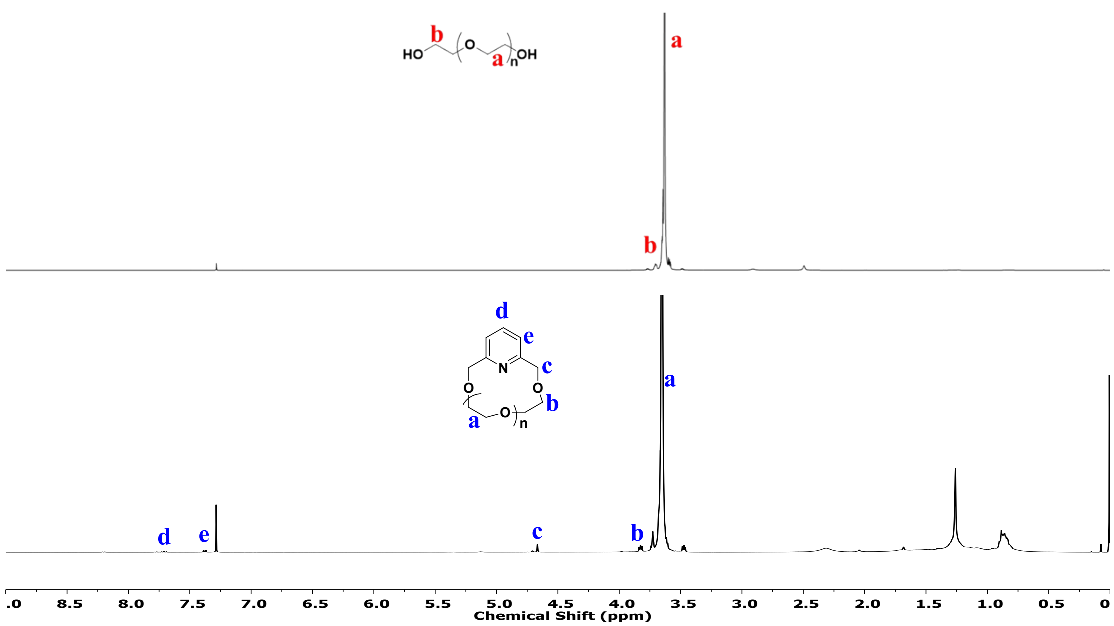

Figure S22. *[1]H-NMR spectra of l-PEG-6K and the corresponding purified c-PEG-6K (CDCl$_3$, 25 ^{o}C, 500 MHz).*

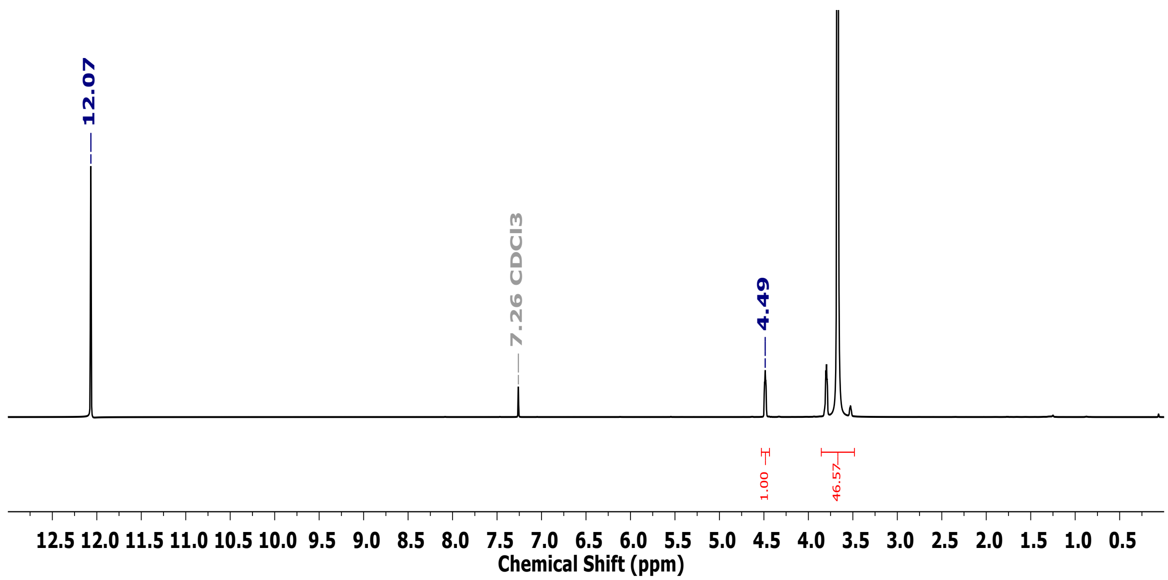

Figure S23. *¹H-NMR spectrum of the l-PEG-2K after addition of TFA ($CDCl_3$, 25 °C, 500 MHz).*

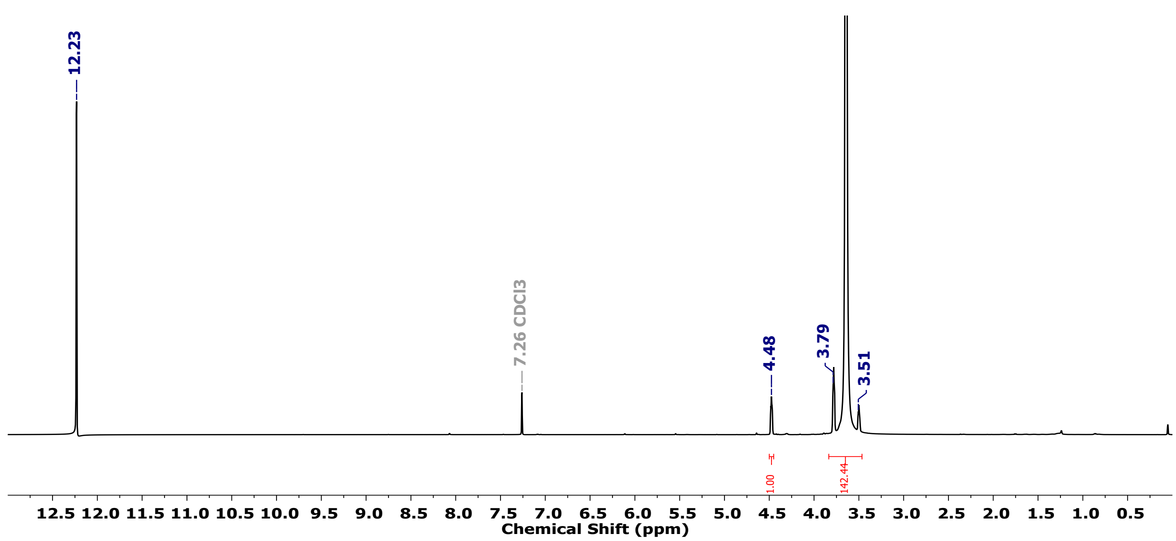

Figure S24. *¹H-NMR spectrum of l-PEG-6K after addition of TFA ($CDCl_3$, 25 °C, 500 MHz).*

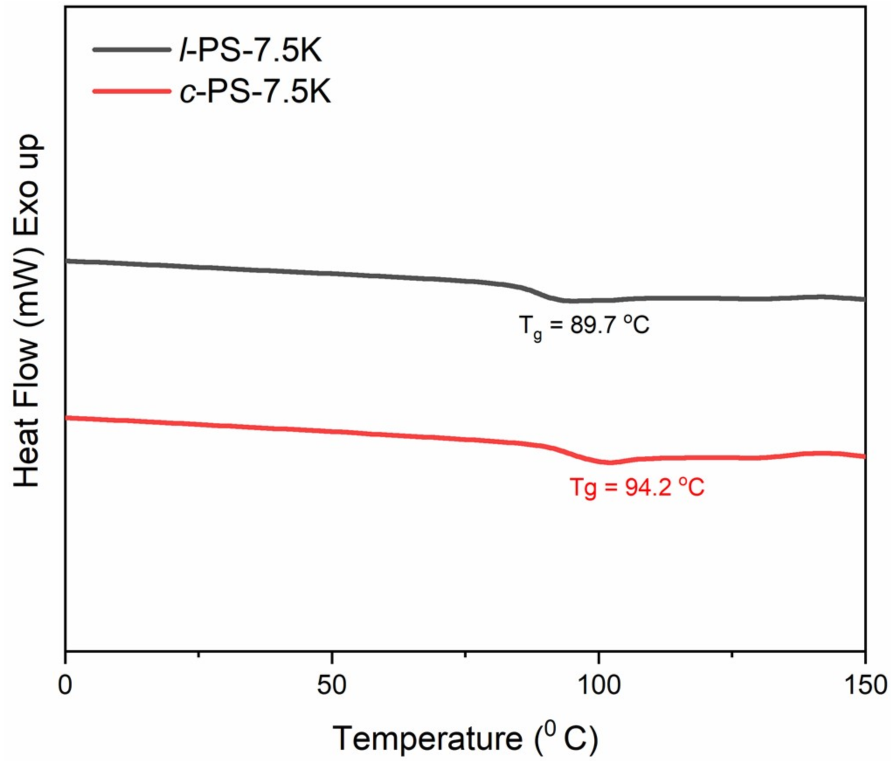

Figure S25. *DSC traces of l-PS-7.5K and the corresponding purified c-PS-7.5K.*

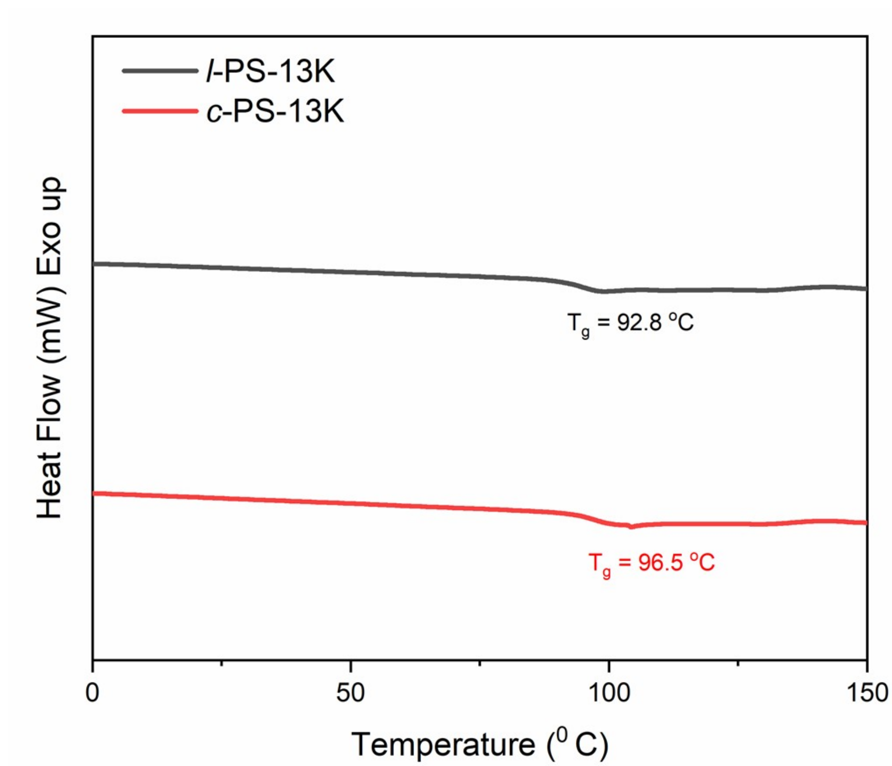

Figure S26. *DSC traces of l-PS-13K and the corresponding purified c-PS-13K.*

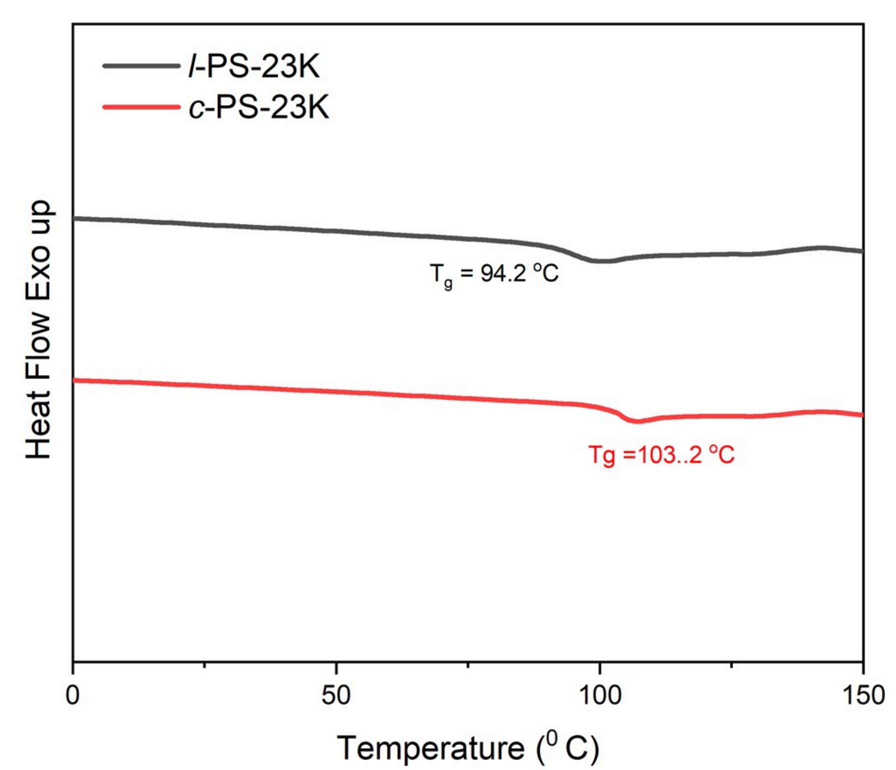

Figure S27. *DSC traces of l-PS-23K and the corresponding purified c-PS-23K.*

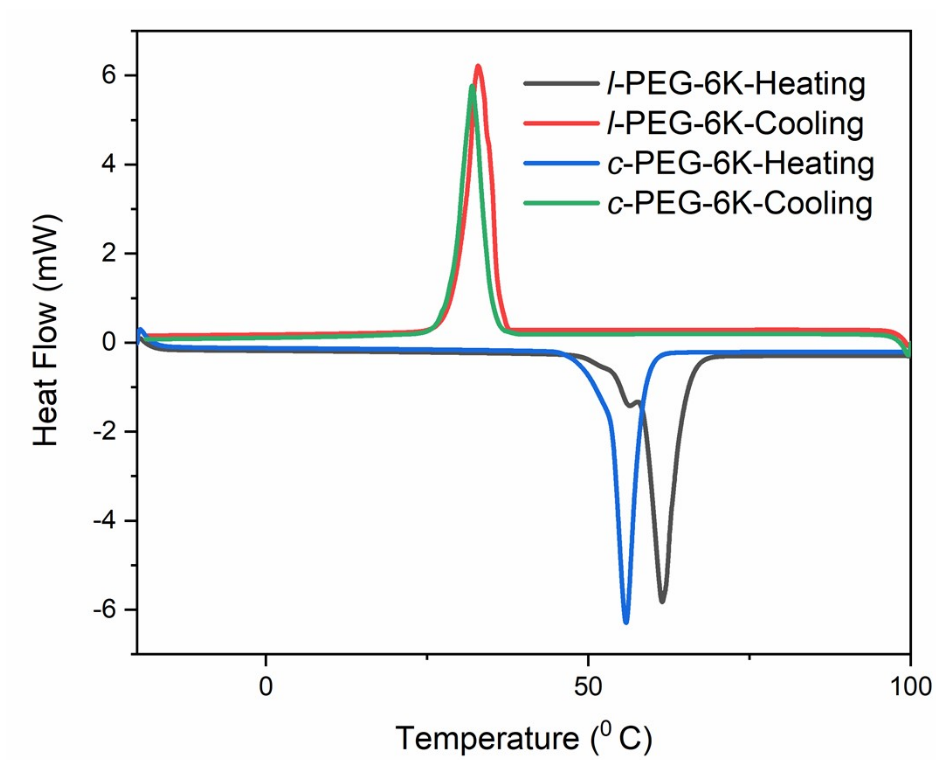

Figure S28. *DSC traces of l-PEG-6K (heating and cooling) and c-PEG-6K (heating and cooling).*