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Supporting information for

## **Direct ionization-driven observational approaches for radical cation formation in solution for pulse radiolysis**

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Figure S1 Transient absorption spectra at time “zero” obtained by fitting of the decay curve.

Figure S2 Time profiles of neat THF and 1.0 mol dm<sup>-3</sup> PS solution of THF at 1200 nm.

Note for NMR analysis and PS purity evaluation

Figure S3 NMR spectra of polystyrene.

Note for GC-MS analysis and PS purity evaluation

Figure S4 Total ion chromatogram for polystyrene by GC-MS analysis.

References

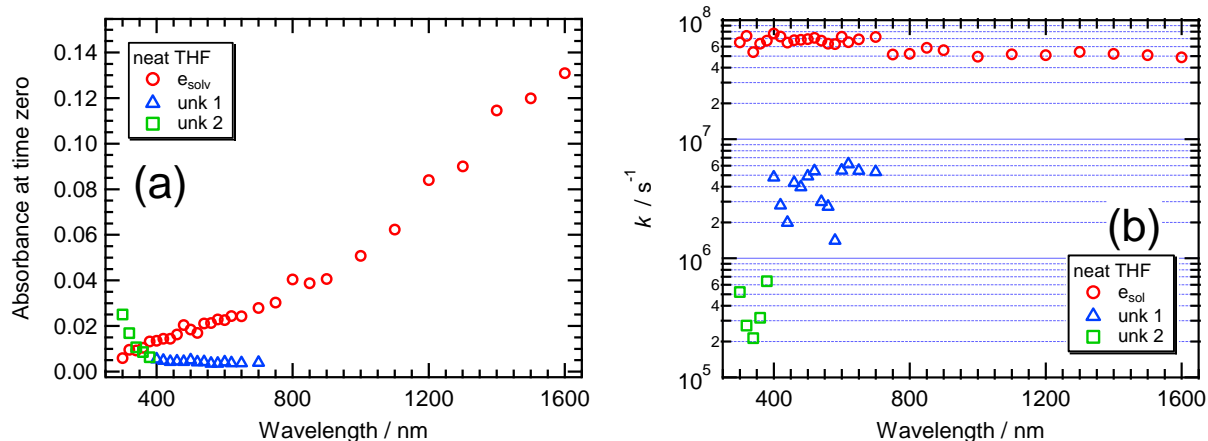


Figure S1 Transient absorption spectra at time “zero” obtained by fitting of the decay curve. (a) The pre-exponential factor of double exponential or single exponential fittings. (b) Spectra of decay rate constants obtained by fitting. Time zero was defined as the maximum intensity time of 8 ns fwhm electron beam pulse.

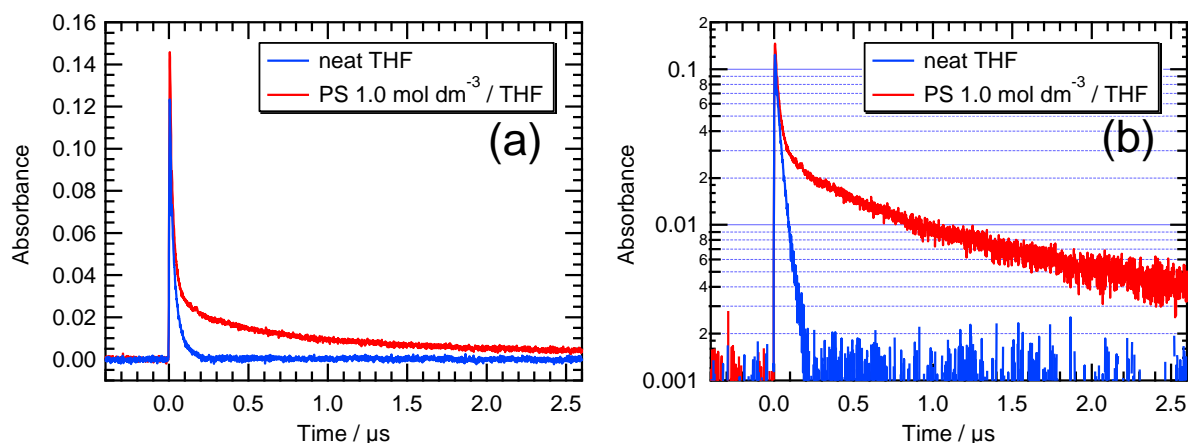


Figure S2 Time profiles of neat THF and 1.0 mol dm<sup>-3</sup> PS solution of THF at 1200 nm. The time profiles were plotted with (a) linear axis and (b) log plot for absorbance.

### Note for NMR measurements and PS purity evaluation

NMR analysis was conducted with a 700 MHz spectrometer (AVANCE III, Bruker) on the comprehensive analysis center at SANKEN, Osaka University. All measurements were conducted on 0.0192 g PS in 0.75×10<sup>-3</sup> dm<sup>-3</sup> of CDCl<sub>3</sub> (0.251 mol/dm<sup>3</sup>) at ambient temperature. Assignment of PS spectra was done according to the literature. According to the literature (Wackerly and Dunne, 2017), observed NMR spectra were well understood as the 24mer polystyrene with -C<sub>2</sub>H<sub>5</sub> end-group for both ends. The integral values were calibrated at the two protons of meta-position because there was no overlapping signal due to water, CHCl<sub>3</sub>, and end-groups.

As seen in Figure S3a, traces of impurity were observed around 3.68, 3.69, 3.71, and 7.37–7.87 ppm for <sup>1</sup>H-NMR. The integral value around 2 ppm was 1.29, which was supposed to be 1, and this may suggest some contribution of impurities. Therefore, the sum of the integral value for these impurities was roughly estimated as 0.31. However, because we could not determine the impurity itself, the number of protons of the impurity was unknown. Therefore, for the estimation, we assumed 8 protons for impurity just as the same number of protons of PS repetitive unit, the impurity concentration estimated as 9.73×10<sup>-3</sup> mol/dm<sup>3</sup> by (0.251×0.31)/8. Therefore, under this assumption, the purity of PS will be evaluated to be 96.1%. Thus, the used PS purity was considered as relatively pure and suitable for the high concentration experiments.

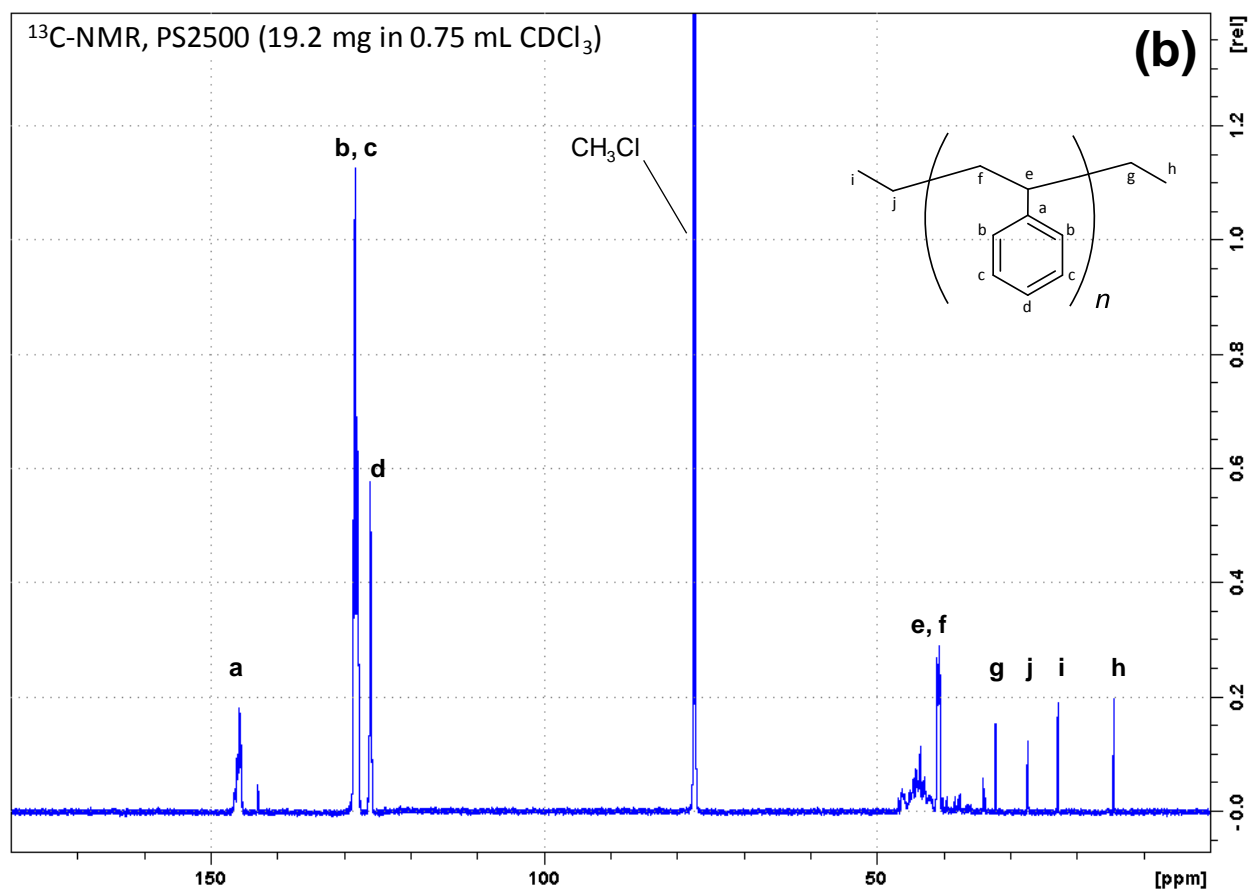
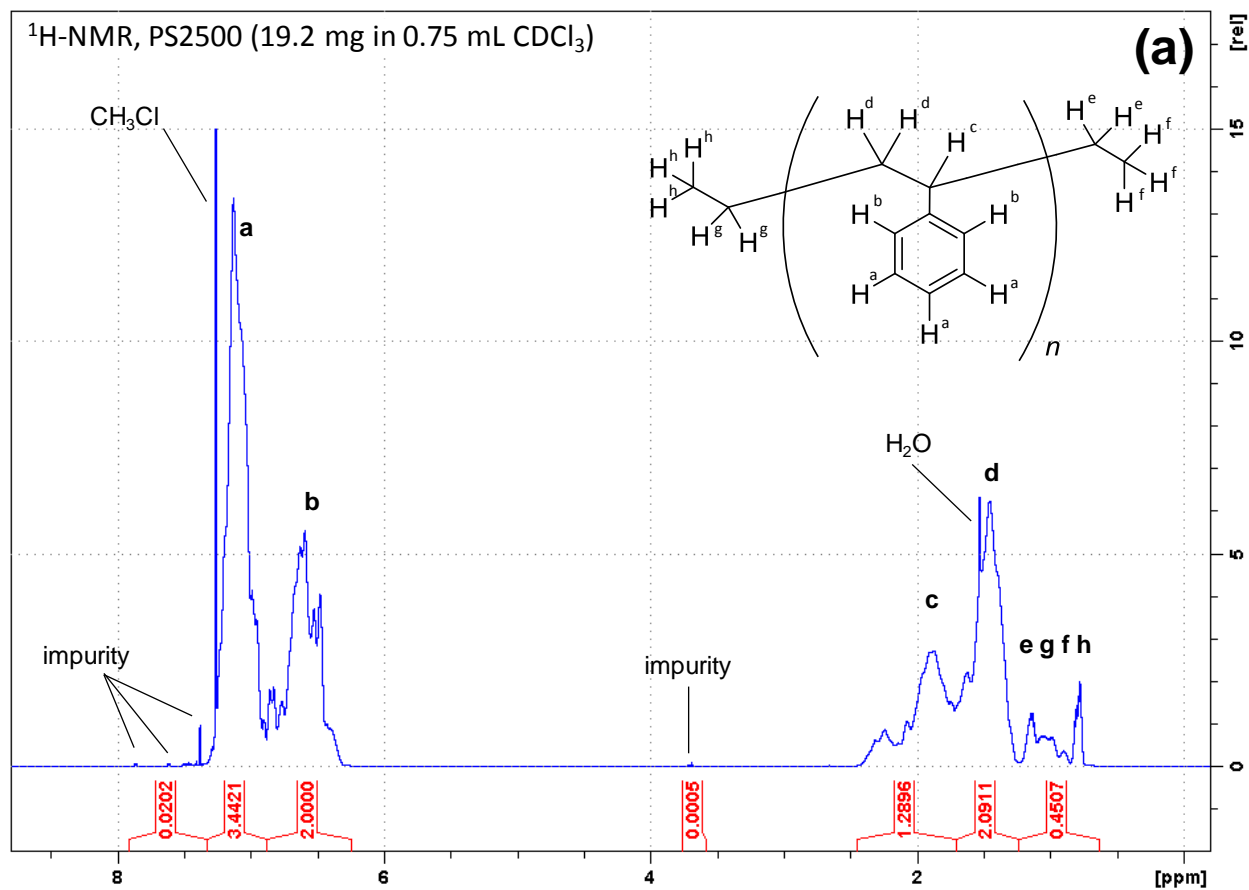


Figure S3 NMR spectra of polystyrene. (a) <sup>1</sup>H-NMR, (b) <sup>13</sup>C-NMR and (c, d) HMQC.

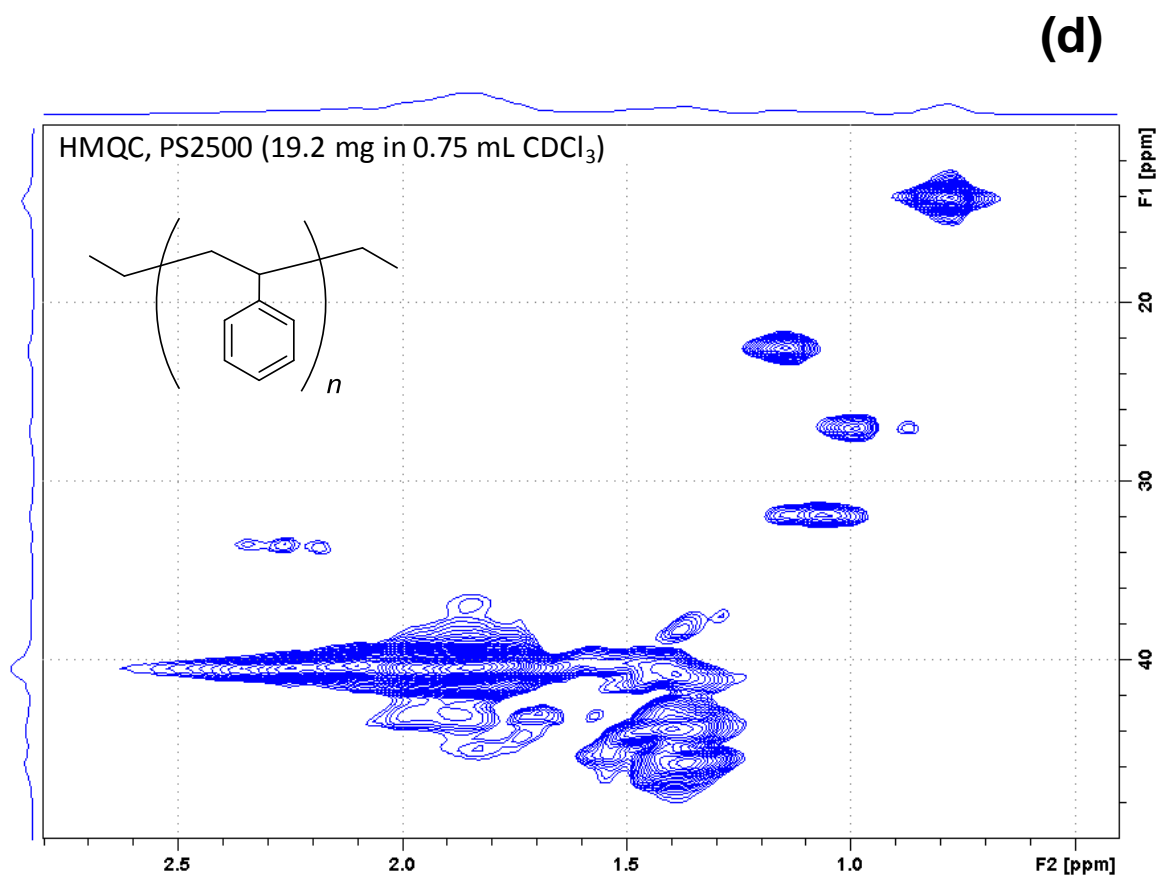
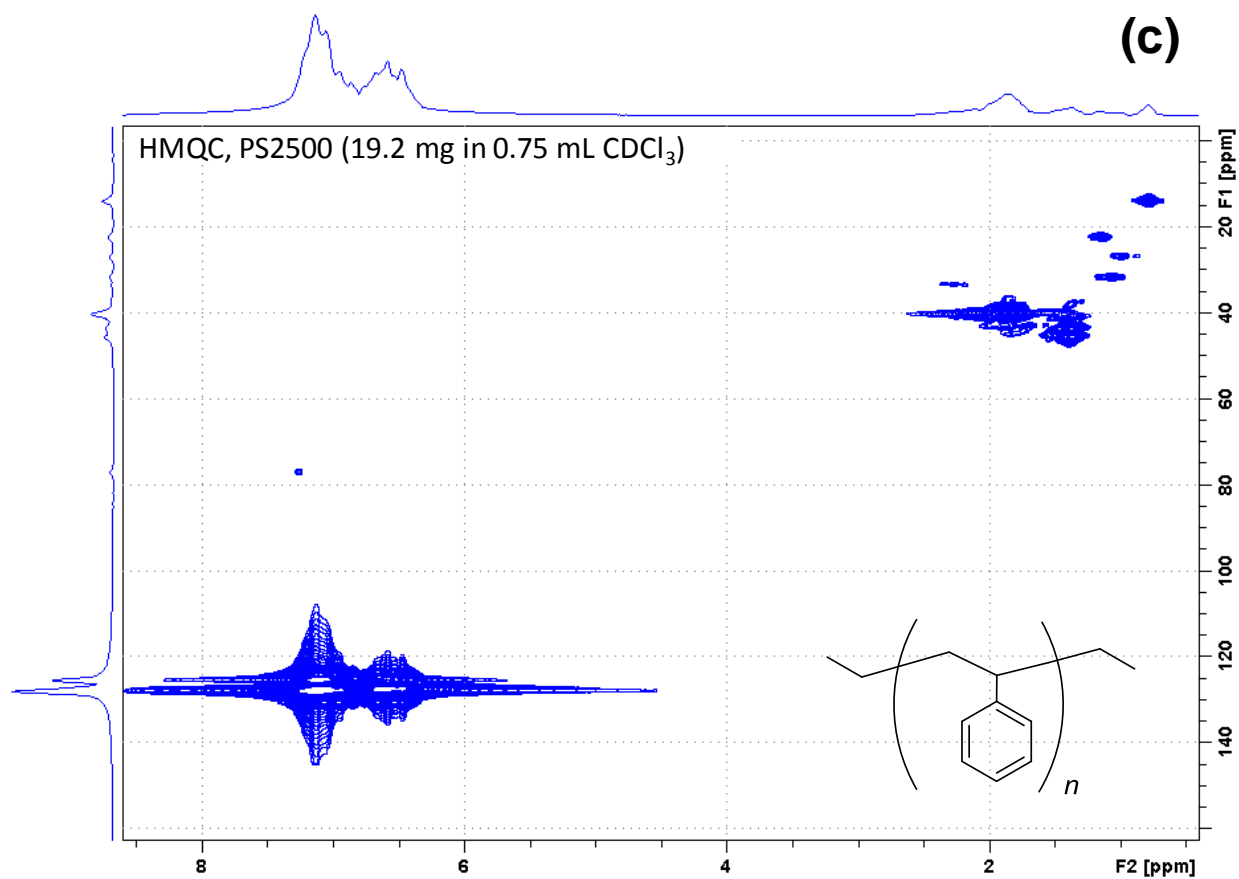


Figure S3 (continued) (c) HMQC spectrum (F1: 0~160 ppm, F2: 0.4~8.6 ppm); (d) HMQC spectrum (F1: 10~50 ppm, F2: 0.2~2.8 ppm)

## Note for GC-MS analysis and PS purity evaluation

GC-MS analysis was performed with GC-17A/QP-5050 (Shimadzu) with nonpolar fused silica capillary columns (Rxi-1ms, 15 m, Restek). The temperature of the injection port was 250 °C. GC temperature was increased from 70 °C to 220 °C with a rate of 20 °C/min. The sample solution was 0.0631 g PS in  $3.0 \times 10^{-3} \text{ dm}^{-3}$  of  $\text{CHCl}_3$ .

As seen in Figure S4, we could find a trace of two volatile impurities at 2.59 min and 4.69 min. Because the intensities were too small to expect mass spectra, we could not identify the impurity. Compared with the internal standard signal, both impurities gave 100 times less intensity. Even though the intensity of total ion chromatography can be different for different compounds, the order of the concentration can be estimated. Thus, the observed impurity was less than  $5 \times 10^{-5} \text{ mol/dm}^3$  beside the PS concentration was  $0.202 \text{ mol/dm}^3$ . Therefore, the purity of PS roughly estimated as  $\{1 - (5 \times 10^{-5} / 0.202)\} \times 100 = 99.9752\%$  ignoring significant figures. Thus, the used PS was considerably clean and had enough purity for the high concentration experiments.

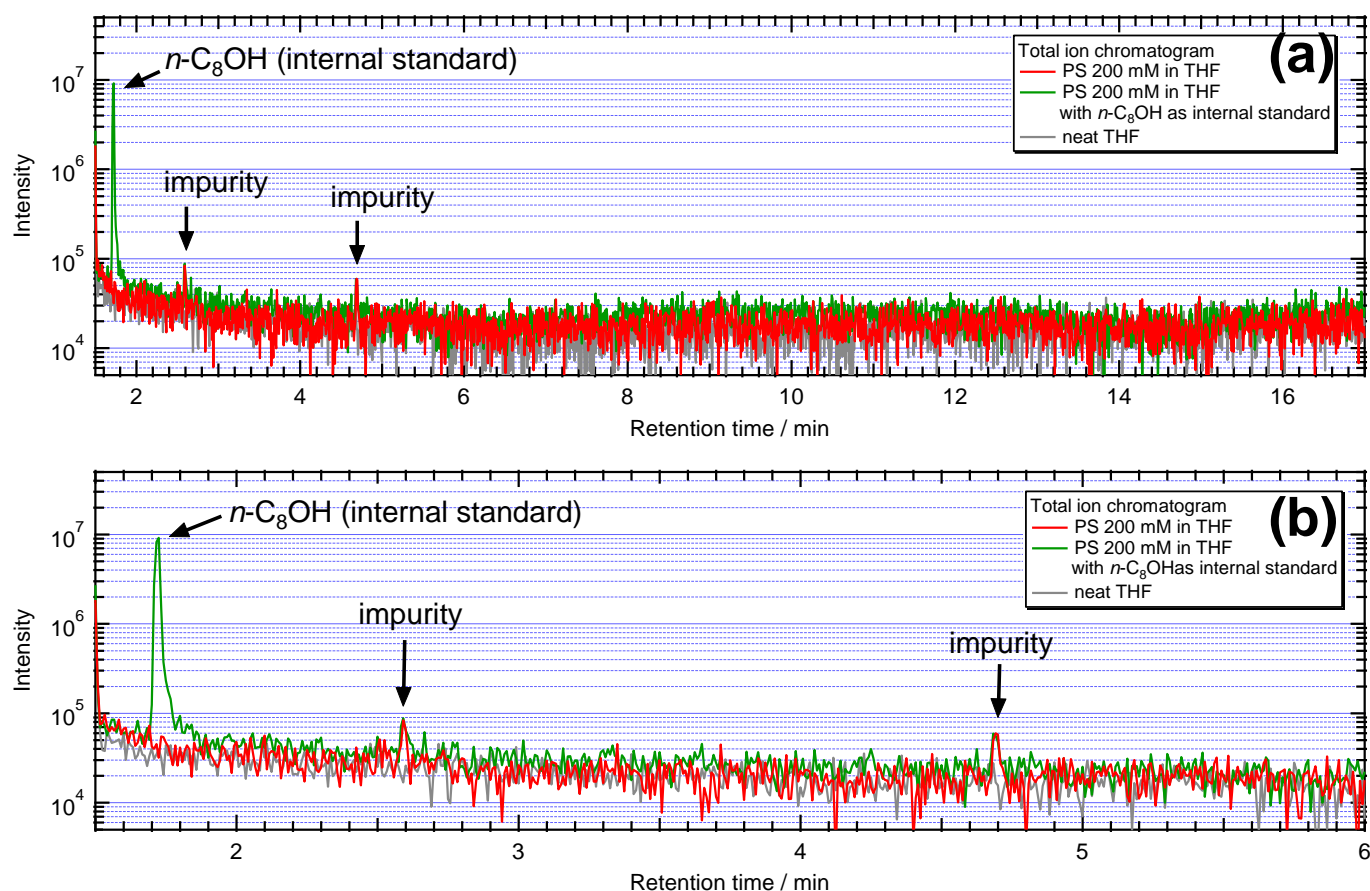


Figure S4 Total ion chromatogram for polystyrene by GC-MS analysis. (a) Full-scale chart and (b) chart of 1.5 to 6 min. *n*-Octanol was used as internal standard material ( $5.0 \text{ mmol/dm}^3$ ).

## References

- J. W. Wackerly and J. F. Dunne, Synthesis of Polystyrene and Molecular Weight Determination by  $^1\text{H}$  NMR End-Group Analysis, J. Chem. Educ., 2017, 94, 1790–1793. doi:10.1021/acs.jchemed.6b00814