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Supporting Information for

Supramolecular complex formation of polysulfide polymers and cyclodextrins

Yuichiro Kobayashi,[1]* Akira Harada,[2]* Hiroyasu Yamaguchi[1]*

[1] Department of Macromolecular Science, Graduate School of Science, Osaka University, Japan.

[2] The Institute of Scientific and Industrial Research, Osaka University, Japan.

* To whom corresponding should be addressed

E-mail: kobayashiy11@chem.sci.osaka-u.ac.jp

harada@chem.sci.osaka-u.ac.jp

hiroyasu@chem.sci.osaka-u.ac.jp

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General information

Materials.

All of the reagents and chemicals used were obtained from commercial sources, unless otherwise noted. Sulfur was recrystallized from carbon disulfide solution. Permethylated α-cyclodextrin (TMαCD) were prepared by previously described method.[1]

Measurements.

The NMR spectra were obtained using a JEOL JNM-ECS 400, 500, and 600 MHz NMR spectrometer. MALDI–TOF MS spectra were recorded in the linear positive mode on a mass spectrometer (BRUKER DALTONICS, Ultraflex III and autoflex maX). 2,5-Dihydroxybenzoic acid was used as a matrix. The molecular weights of the polymers were measured by gel permeation chromatography (GPC) in chloroform at 40 ºC with polystyrene columns [TSKgel GMHHR-M × 2; flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive-index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 PSt standards (Tosoh; $M_n = 577–1.09 \times 10^6$, $M_w/M_n < 1.1$). The TG analysis was carried out from 25 to 500 ºC at a heating rate of 10 ºC min^{-1} using a PerkinElmer STA 6000 under N_2. Differential scanning calorimetry (DSC) was carried out with Hitachi High-Tech DSC 7020 under a N_2 atmosphere and 10 K min^{-1} heating rate.

1. Optimization of the molar ratio of sulfur to styrene in polymerization molten

We investigate the optimum molar ratio of sulfur to styrene (St) in the polymerization. Sulfur (1.0 g, 3.9 mmol) was stirred at 160 °C for 6 h under N_2. At this time, the sulfur was molten. St was added to the molten sulfur, which was stirred at 160 °C for 3 h under N_2 (Table S1). We performed GPC measurements of the resulting products (Fig. S1). When the molar ratio of sulfur to styrene was 5:1 (Table S1, Entry 3), there were no peaks of sulfur and styrene in GPC results. From these results, the molar ratio of St to sulfur was set to 5: 1 in this paper.

Table S1. Copolymerization of St and sulfur

Entry	St g/mmol	Sulfur g/mmol	Molar ratio of St : sulfur
1	4.0 / 39	1.0 / 3.9	10:1
2	2.8 / 27		7:1
3	2.0 / 20		5:1
4	10.41 / 3.9		1:1

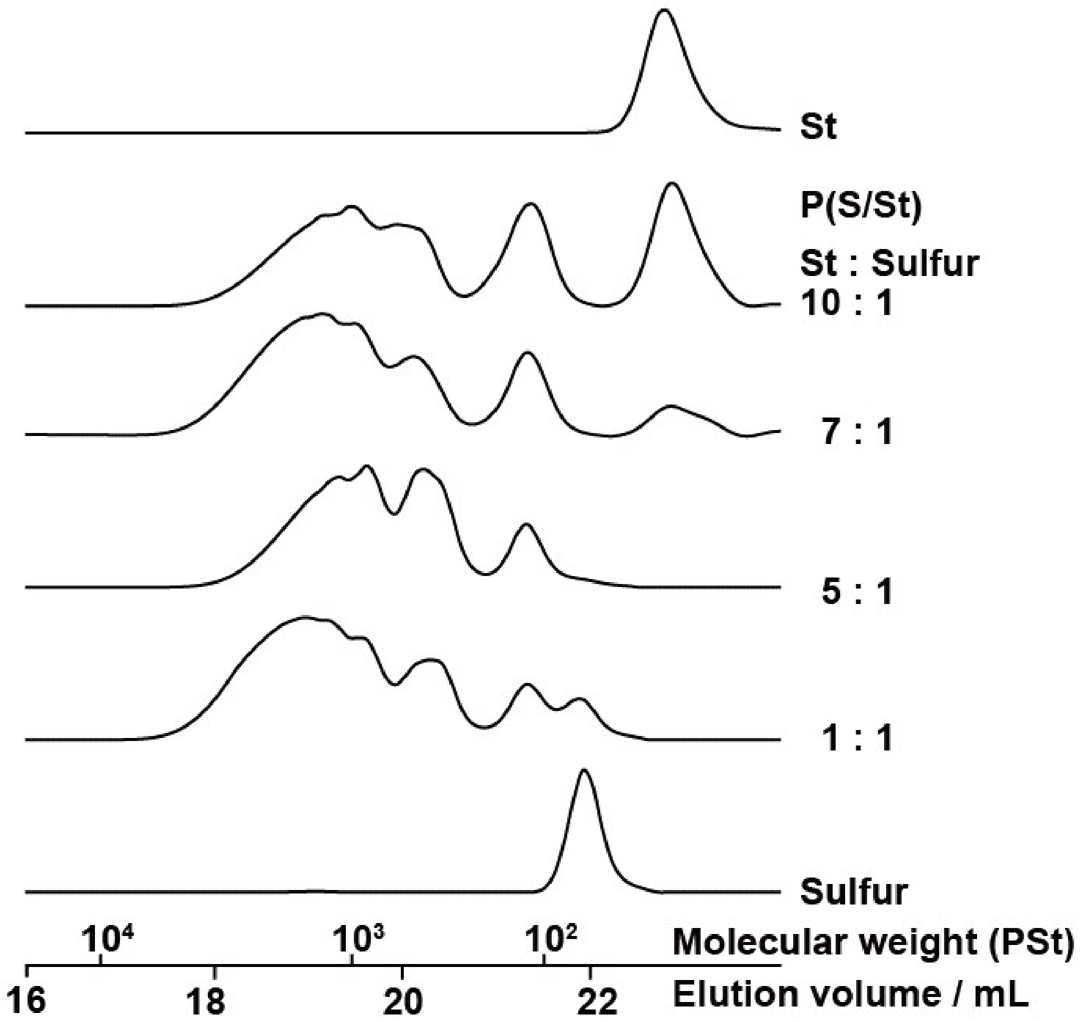

Figure S1. GPC profiles of St, the resulting product of copolymerization of St and sulfur [monomer (St: sulfur) molar ratio = 10:1, 7:1, 5:1, and 1:1], and sulfur. Molecular weights are based on the calibration of PSt

2. Copolymerization of sulfur and styrene in the presence of α-cyclodextrins

α-Cyclodextrin (αCD) (38 mg, 39 μmol) was dried by heating at 100 °C under vacuum for 4 h. The dried αCD and sulfur (S_8) (1.0 g, 3.9 mmol) was mixed at 160 °C for 6 h under N_2. At this time,αCD did not dissolved in the molten sulfur. Styrene (2.0 g, 20 mmol) was added to the heterogeneous molten sulfur, which was stirred at 160 °C for 10 h under N_2. The product did not contain any polymeric products, as was evidenced by matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI–TOF MS) measurement. In the MALDI-TOF MS measurements, peaks for polymer with the repeating unit of sulfur (*m*/*z* 32) were not detected in a region of a molecular weight higher than αCD (*m*/*z* >972).

3. Preparation of SPRx

3-1. Preparation of SPRx

TMαCD (48 mg, 39 μmol) was dried by heating at 130 °C under vacuum for 4 h. The dried TMαCD and sulfur (S_8) (1.0 g, 3.9 mmol) was stirred at 160 °C for 6 h under N_2. Styrene (2.0 g, 20 mmol) was added to the TMαCD dissolved molten sulfur, which was stirred at 160 °C for 3 h under N_2. The resulting product was purified on a flash column chromatography using EtOAc/Hex (1/1) as eluent (15 % yield based on the total weight of the compound used).

3-2. Preparation of P(S/St).

Sulfur (1.0 g, 3.9 mmol) was stirred at 160 °C for 6 h under N_2. At this time, the sulfur was molten. St (2.0 g, 20 mmol) was added to the molten sulfur, which was stirred at 160 °C for 3 h under N_2. The resulting product was stirred in $CHCl_3$ (5 ml). The obtained clear solution was added to MeOH (50 mL) to give a precipitate that was washed several times with MeOH and dried under reduced pressure at room temperature (90 % yield based on the total weight of the compound used).

4. Characterization of SPRx

4-1. ^{1}H NMR

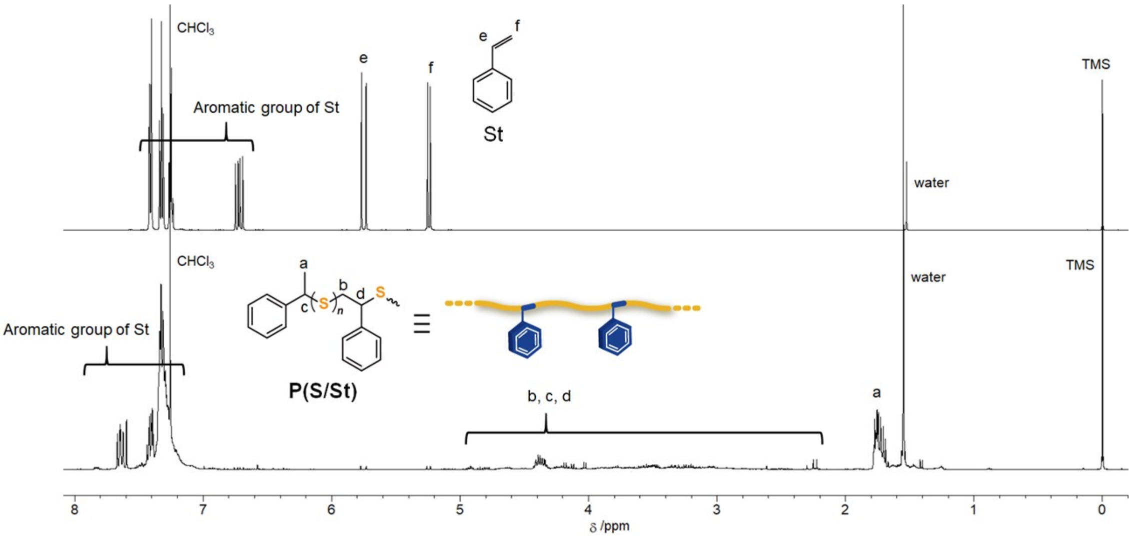

Figure S2. ^{1}H NMR spectra of St and P(S/St) ($CDCl_3$, 25 °C). Assignment was based on literature[2].

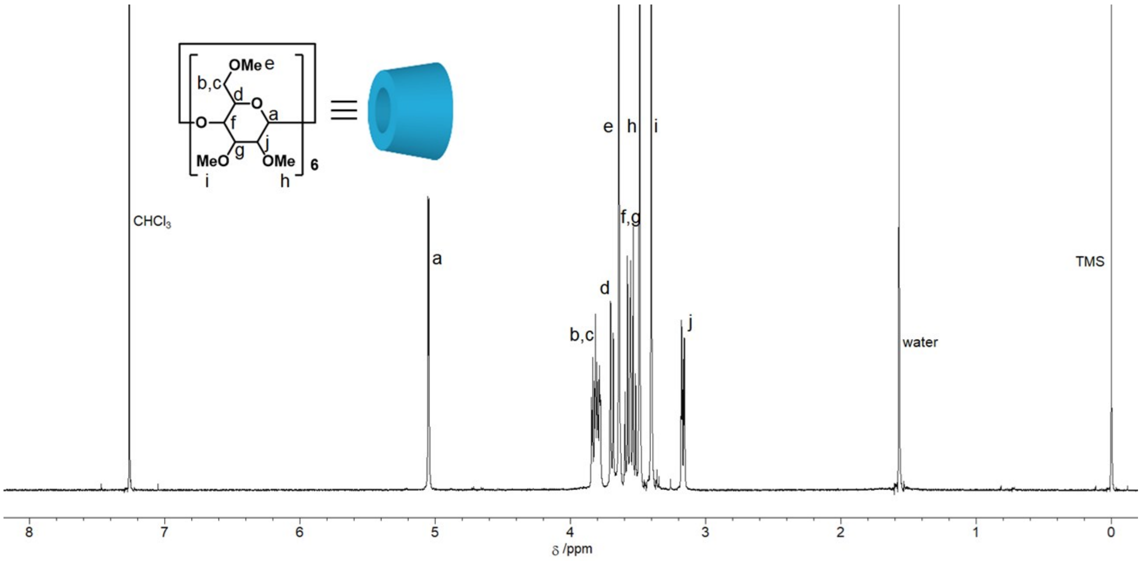

Figure S3. ^{1}H NMR spectra of St and TMαCD (CDCl$_3$, 25 °C). Assignment was based on literature**.**

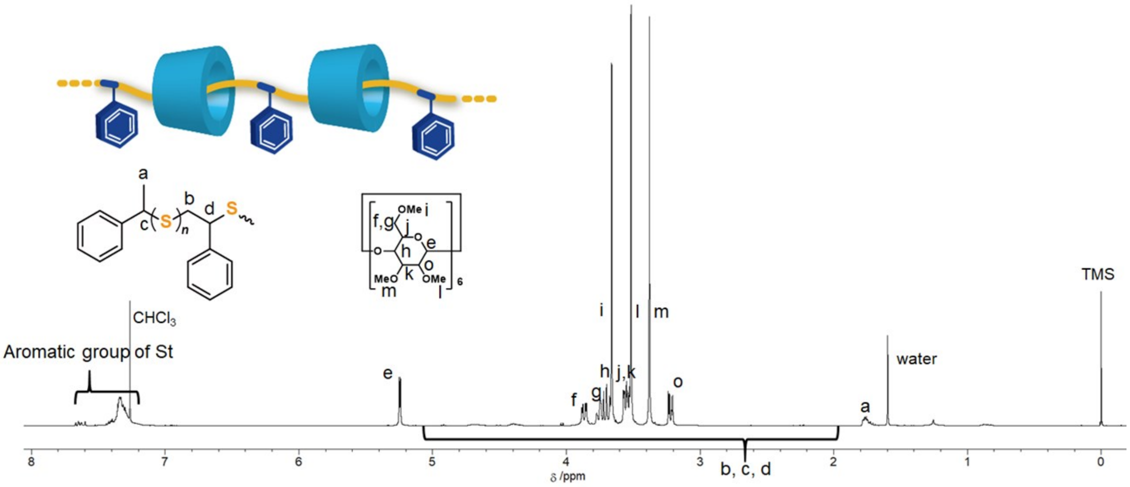

Figure S4. ^{1}H NMR spectrum of SPRx (CDCl$_3$, 25 °C).

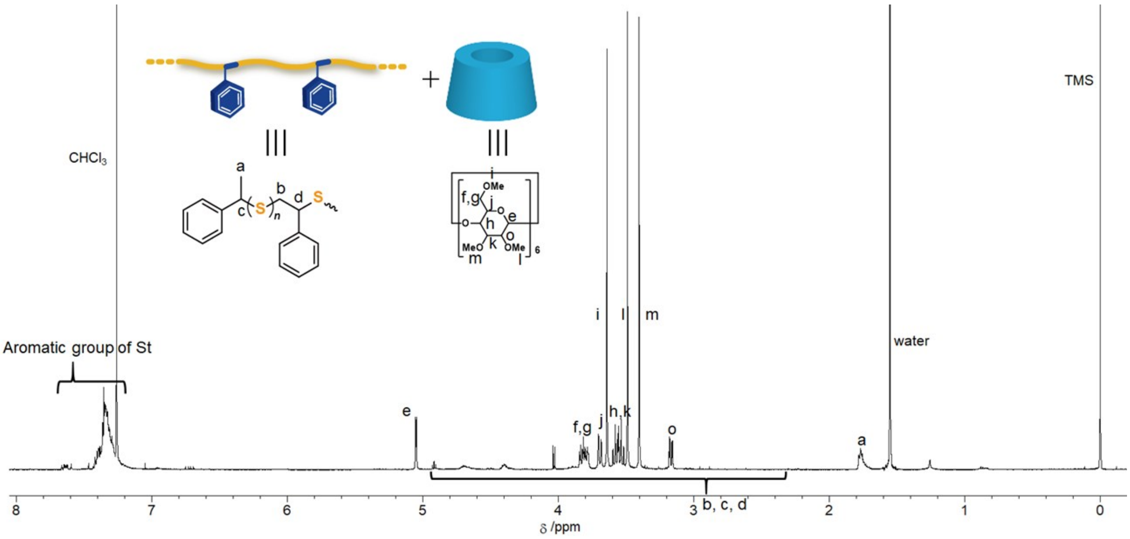

Figure S5. ^{1}H NMR spectrum of mixture of P(S/St) and TMαCD (CDCl$_3$, 25 °C).

4-2. ^{1}H relaxation measurements

Table S2. T_1(^{1}H)s of TMαCD.

Protons of TMαCD	T_1(^{1}H) [s]		
	Free TMαCD	Mixture of P(S/St) and TMαCD	SPRx
H1	0.7409	0.7511	0.9812
H2	0.7701	0.7601	0.9744
H3	0.4000	0.4109	0.9924
H4	0.7793	0.7591	0.9454
H5	0.4936	0.4120	0.9914
H6	0.6756	0.6855	0.9547
H6’	0.6766	0.6451	0.9912
OMe(2)	0.8102	0.8122	1.051
OMe(3)	0.8718	0.8815	1.002
OMe(6)	0.9577	0.9611	1.178

4-3. MALDI-TOF MS

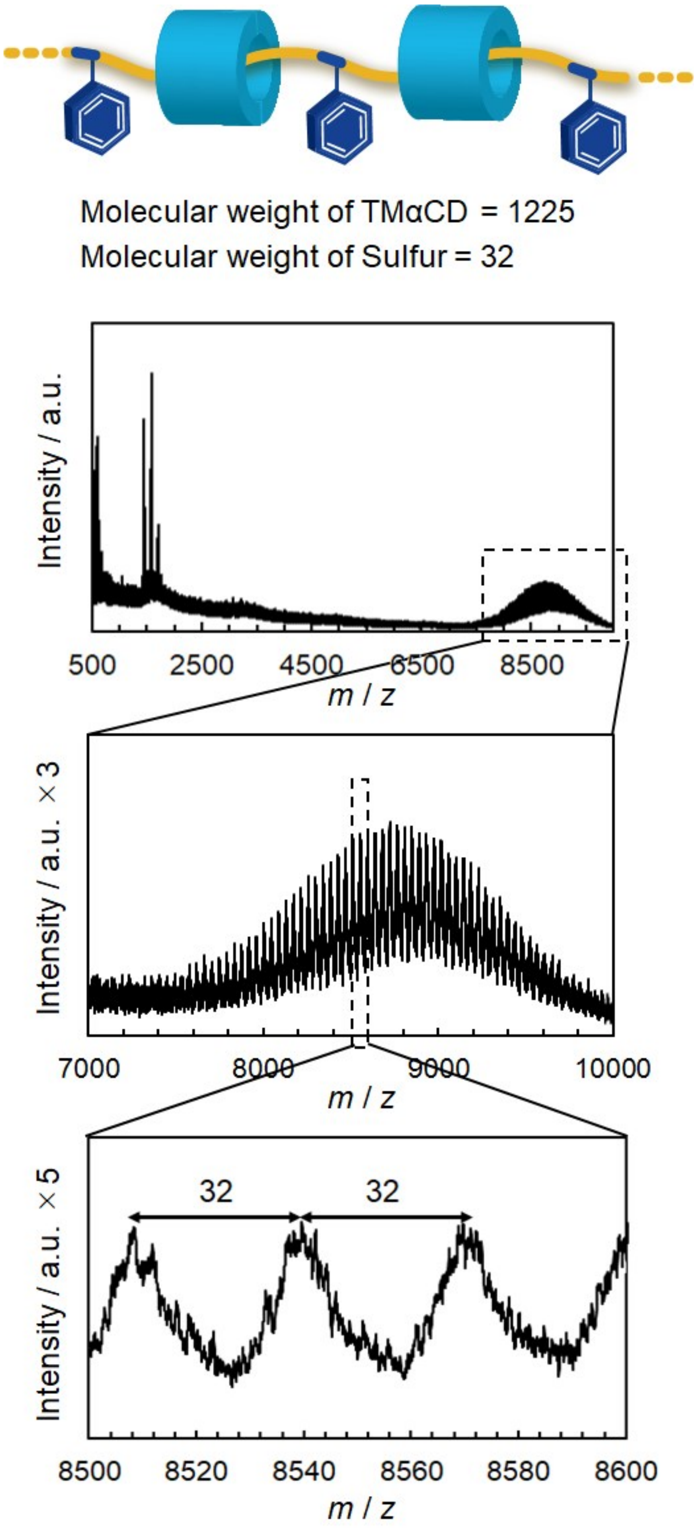

Figure S6. MALDI–TOF MS spectrum of SPRx. Peaks for polymers with the repeating unit of sulfur (*m*/*z* 32) could be detected.

4-3. DOSY NMR

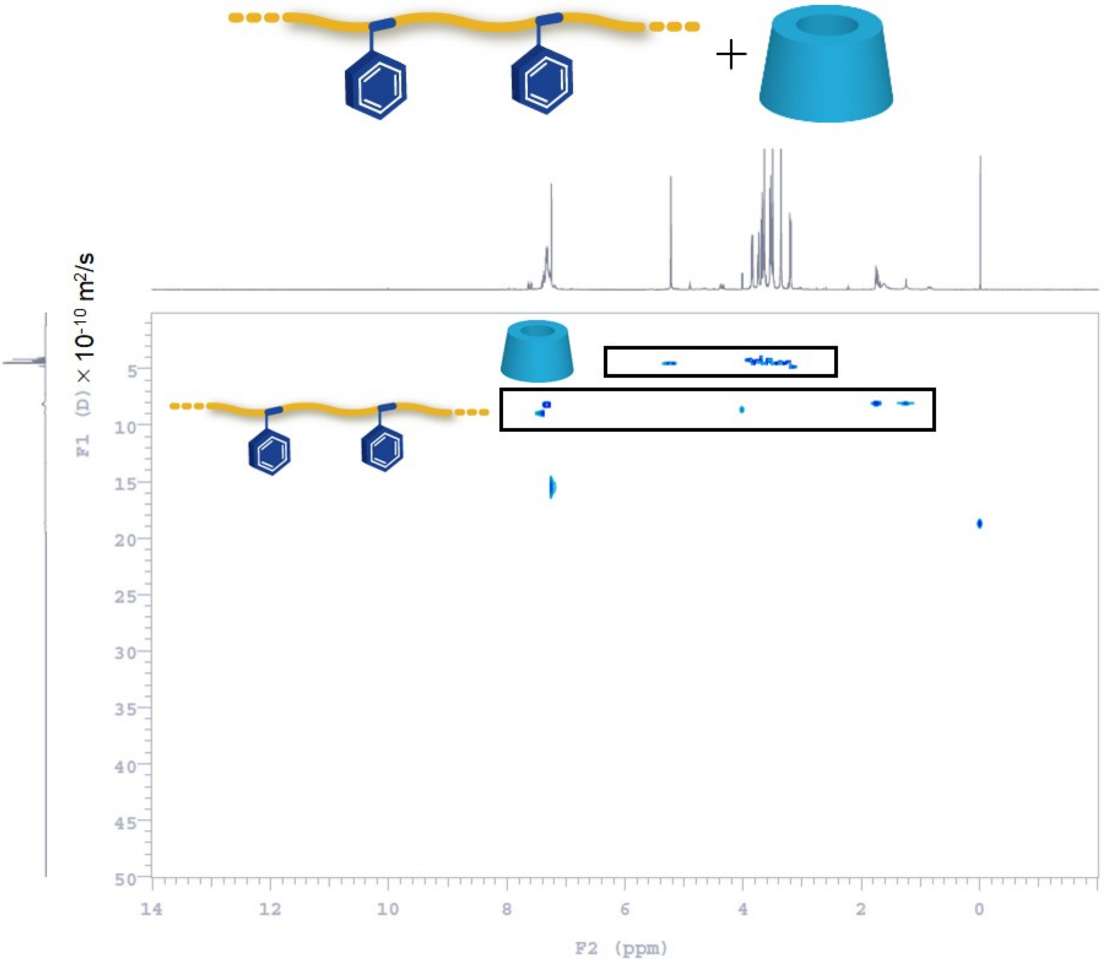

Figure S7. ^{1}H DOSY NMR spectrum of mixture of P(S/St) and TMαCD ($CDCl_3$, 25 °C).

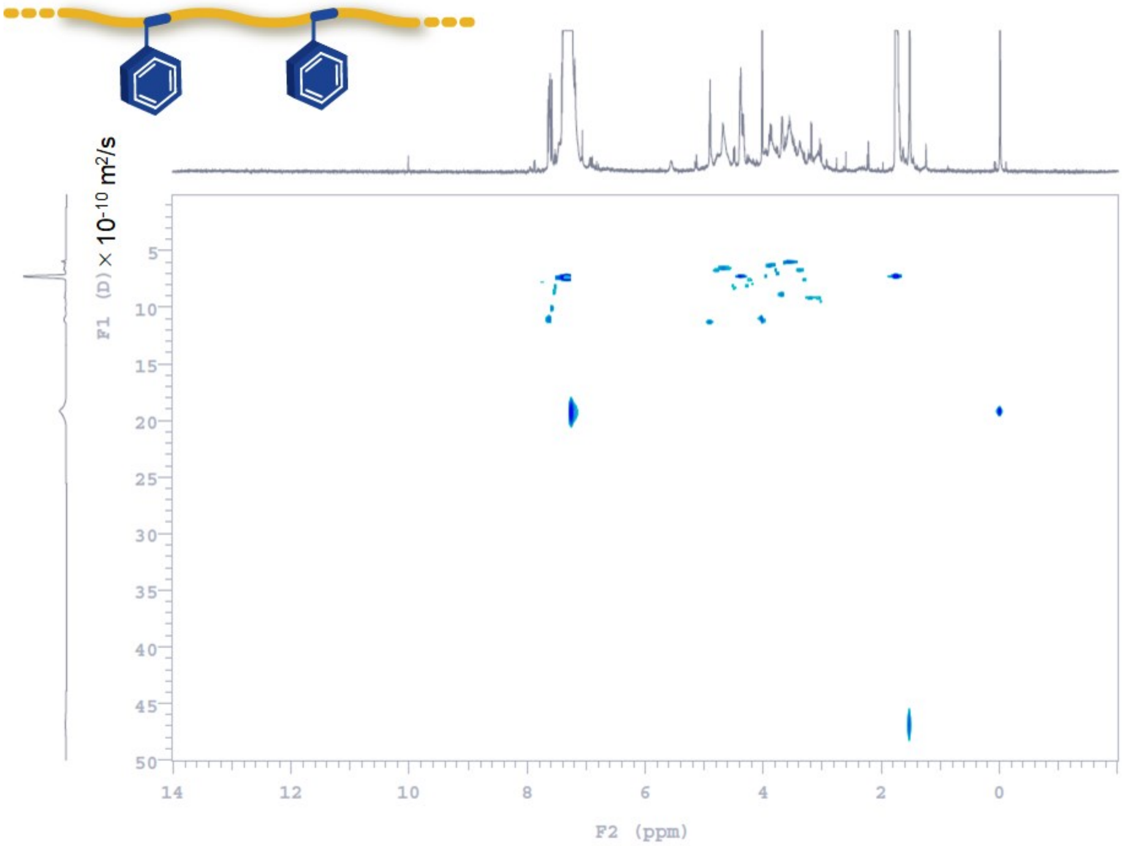

Figure S8. ^{1}H DOSY NMR spectrum of P(S/St) ($CDCl_3$, 25 °C).

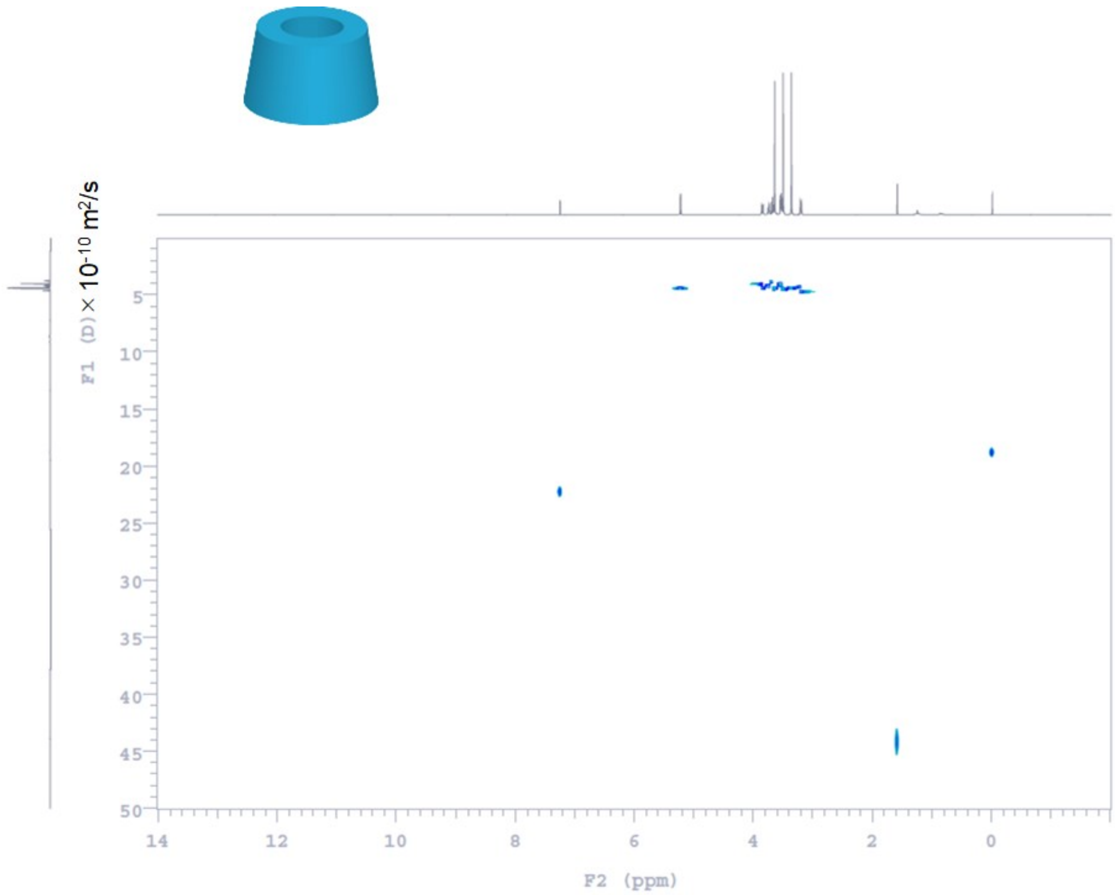

Figure S9. ^{1}H DOSY NMR spectrum of TMαCD (CDCl$_3$, 25 °C).

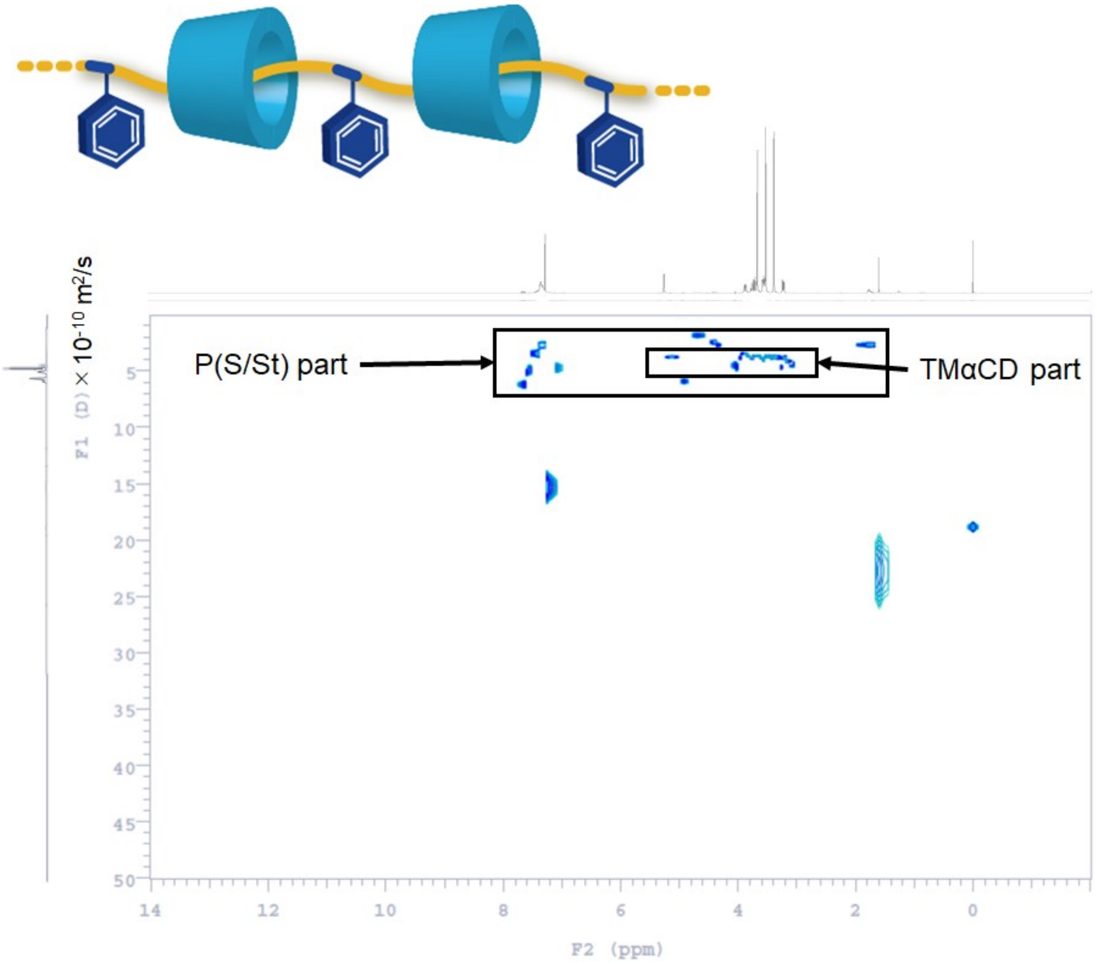

Figure S10. ^{1}H DOSY NMR spectrum of SPRx ($CDCl_3$, 25 °C).

4-5. GPC

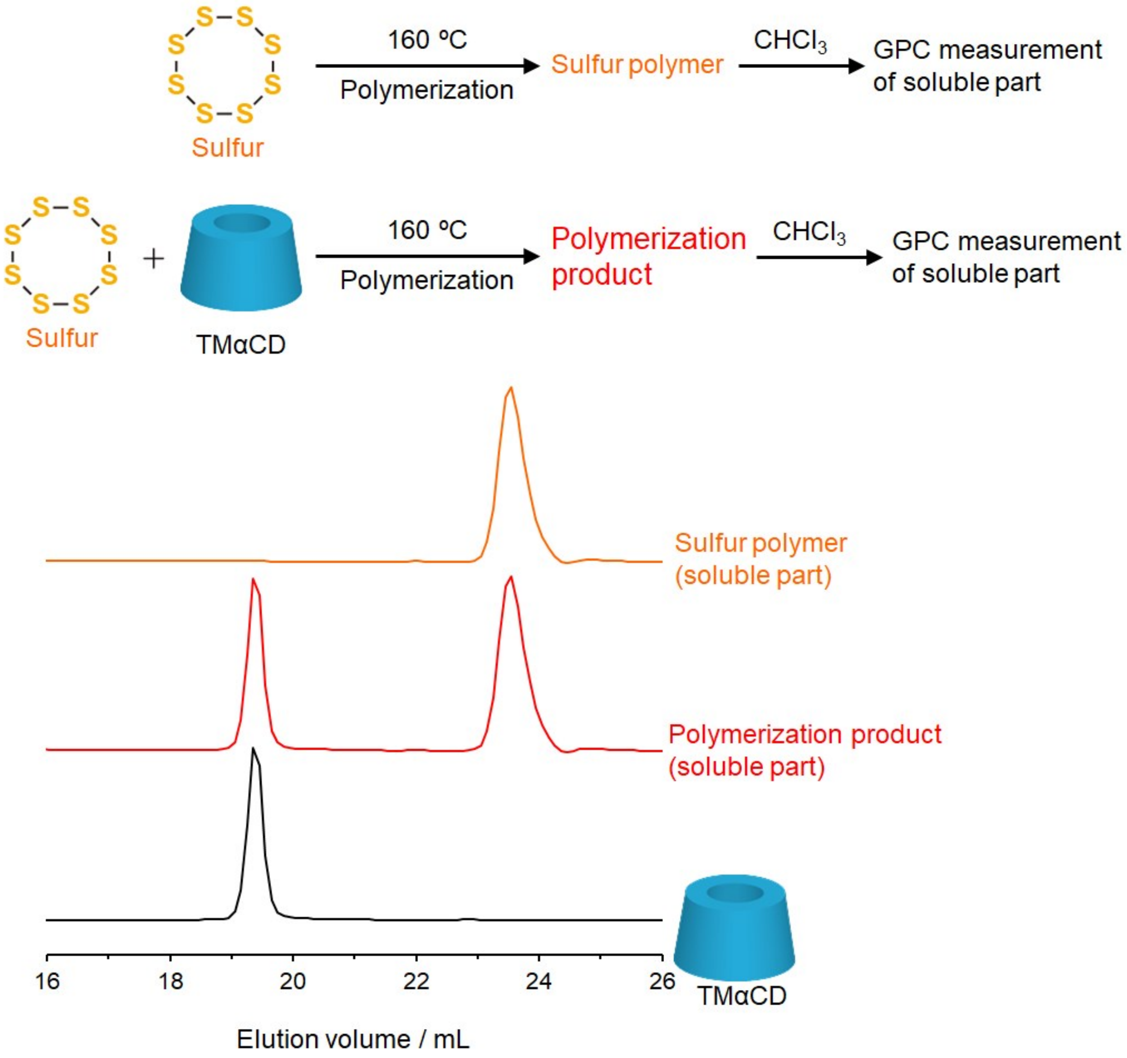

Figure S11. GPC profiles of sulfur polymer (upper), the polymerization product that sulfur was polymerized in the presence of the TMαCD, (middle), and TMαCD (lower).

To confirm the SPRx structure, we performed reductive degradation of SPRx (0.20 g, 40 μmol) by treatment of the SPRx with $LiAlH_4$ (LAH) (156 mg, 4.1 mmol) in dry THF (5 mL) solution (Fig. S12). After LAH reduction, molecular weight of SPRx was reduced from 5,000 g/mol to 600 g/mol and a peak was observed at the same elution volume as TMαCD. In addition, the diffusion coefficients of P(S/St) and TMαCD in SPRx was increased after LAH reduction (Fig. S12b). These result indicate the resultant sample contain TMαCD and oligomers (Fig. S12c).

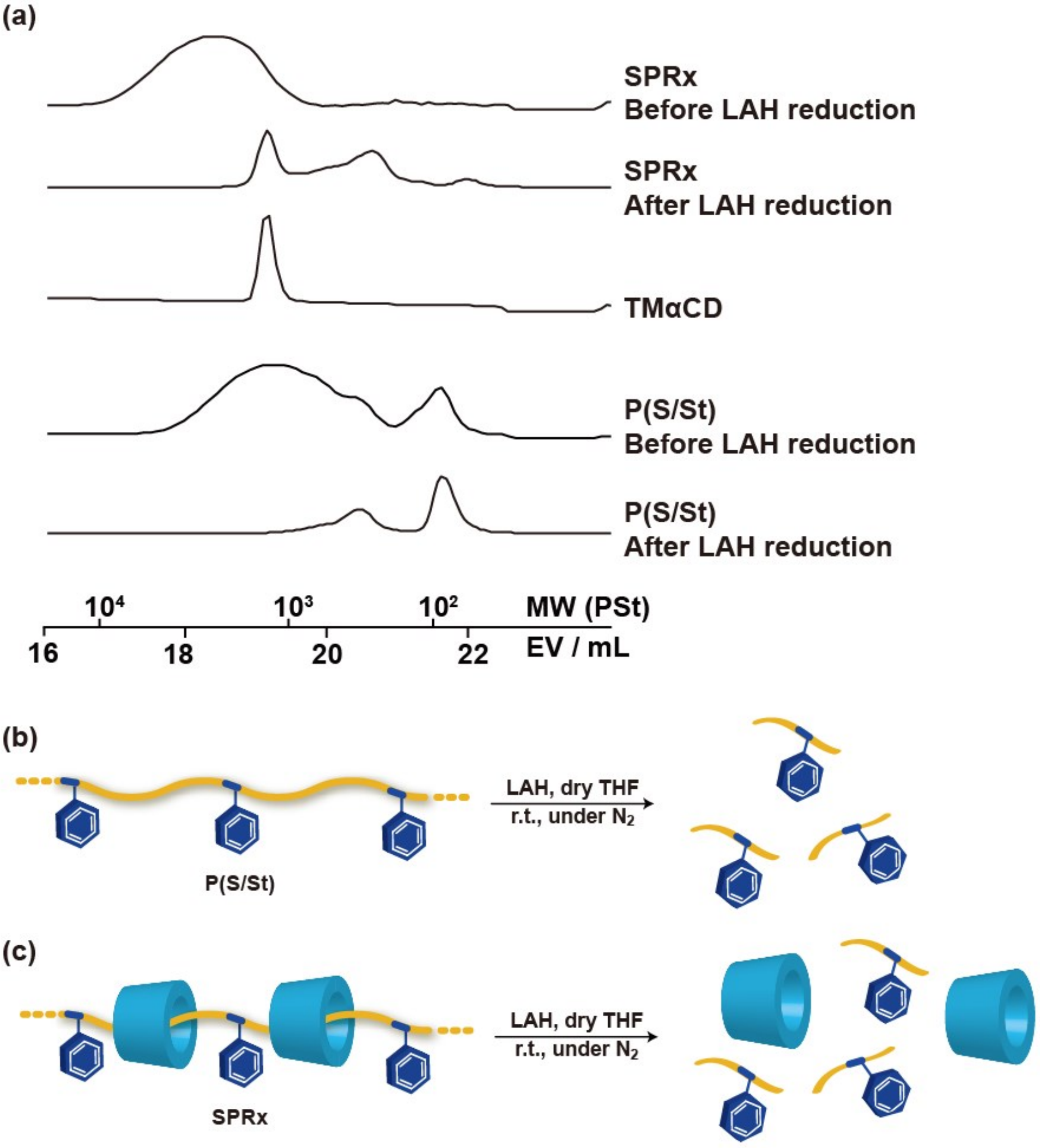

Figure S12. (a) GPC profiles of SPRx before and after LAH reduction, TMαCD, and P(S/St) before and after LAH reduction. (b) ^1H DOSY NMR spectrum of SPRx before and after LAH reduction ($CDCl_3$, 25 °C). (c) Schematic illustration of LAH reduction of SPRx.

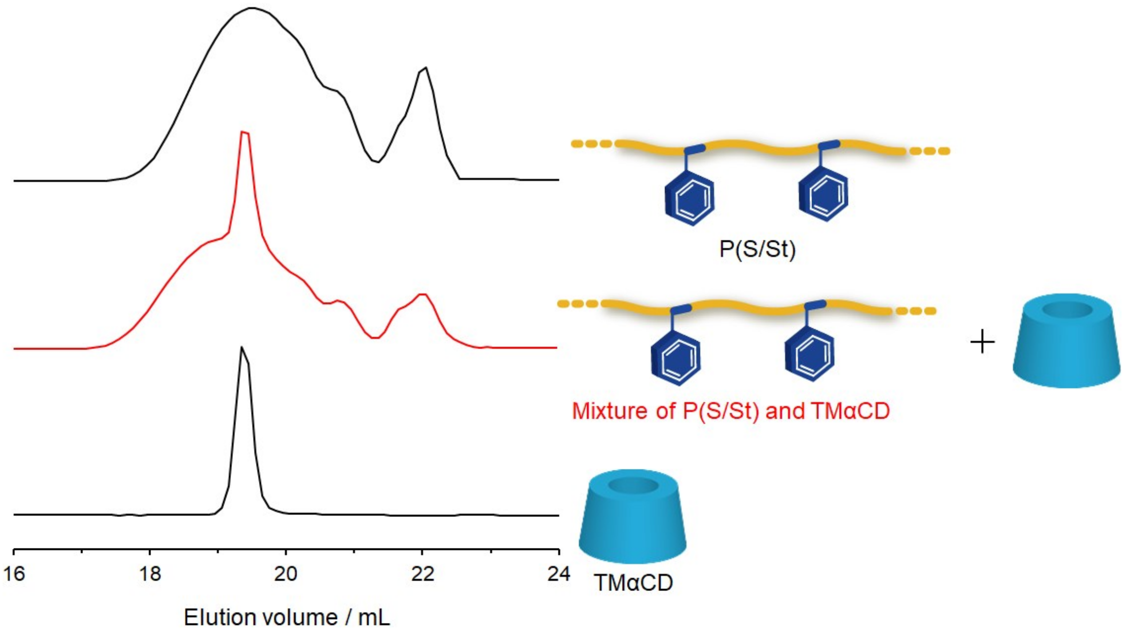

Figure S13. GPC profiles of P(S/St) (upper), the mixture of P(S/St) and TMαCD (middle), and TMαCD (lower).

4-6. MALDI-MS/MS

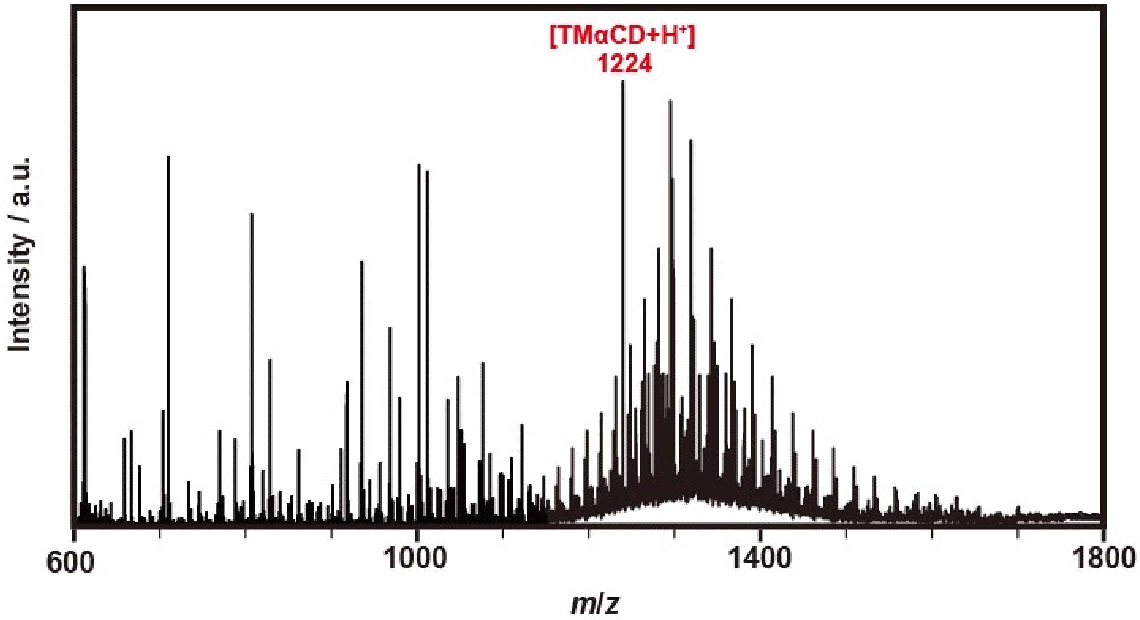

Figure S14. MALDI–TOF MS/MS spectrum of SPRx (the precursor ion = 8539 ± 10 *m*/*z*, CID 15 kV). Peaks for TMαCD (*m*/*z* 1224) could be detected.

4-7. Elemental analysis

Table S2. Elemental analysis of P(S/St) and SPRx

Samples	C (%)	H (%)	S (%)
P(S/St)	57.45	4.74	37.64
SPRx	31.36	3.96	55.25

5. Stability of SPRx

5-1. Environmental stability of SPRx

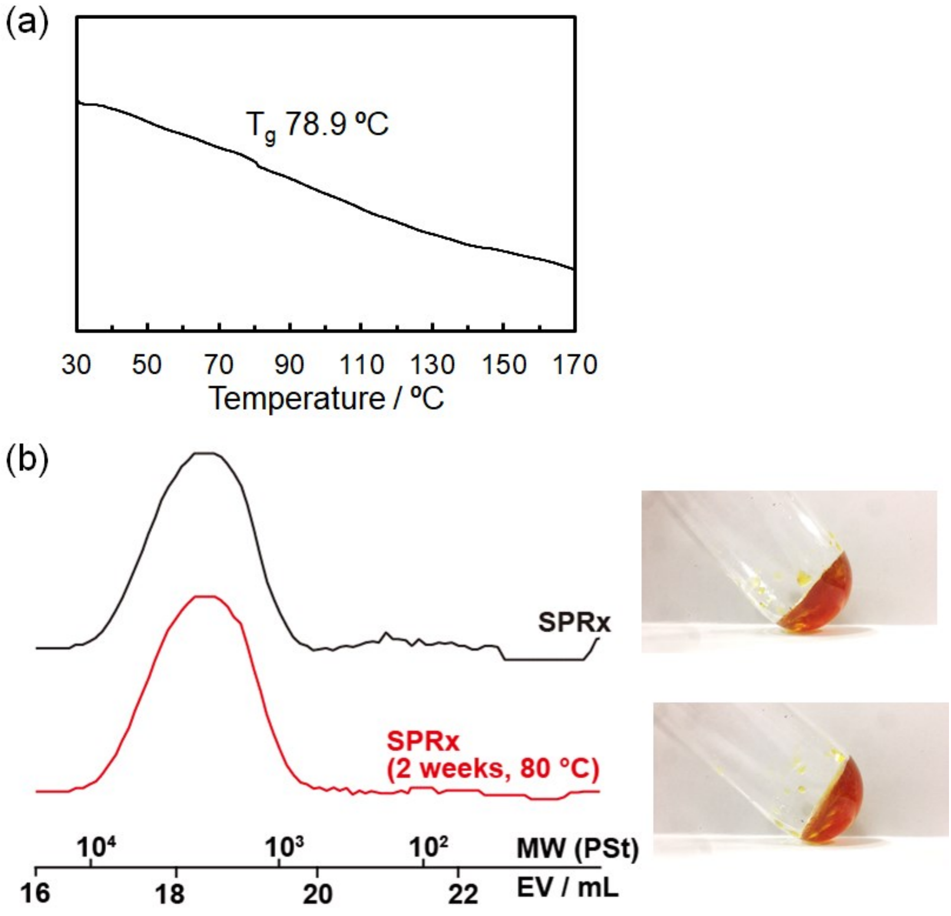

Figure S15. (a) DSC profiles of SPRx. To remove thermal history of SPRx, SPRx was heated at 100 °C before DSC measurement and the second scan is shown. (b) GPC profiles of (a) SPRx and (b) SPRx left for 2 weeks at 80 °C. Inset pictures are photographs of SPRx in each state.

P(S/St) and SPRx (1.0 g) was allowed to stand at r.t. under atmospheric conditions. In the ^{1}H NMR spectrum of P(S/St), the intensity of the peaks (4.02 and 7.65 ppm) changed after 2 weeks (Fig. S16). In contrast, SPRx was almost the same after 6 months (Fig. S17).

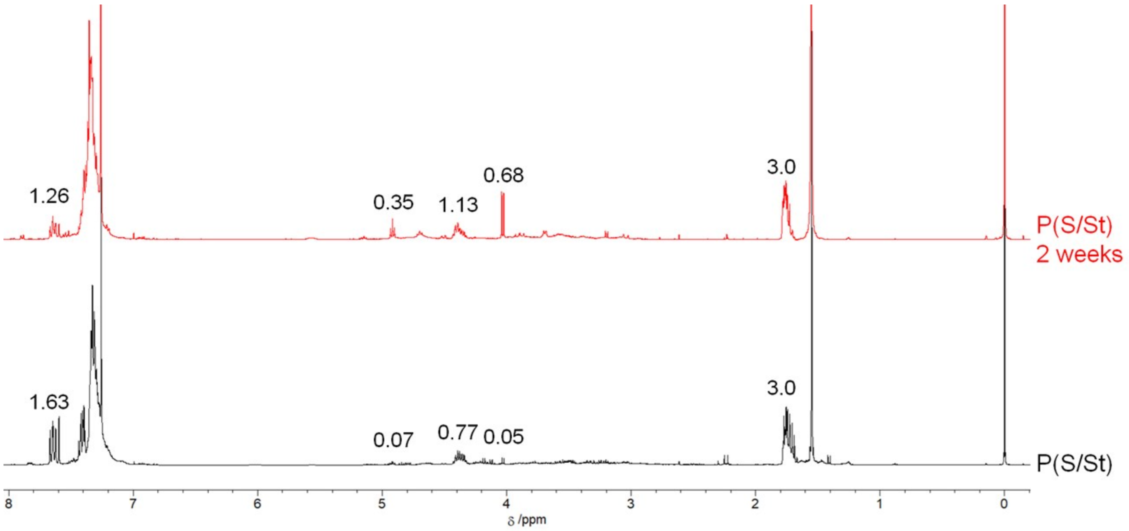

Figure S16. ^{1}H NMR spectra of P(S/St) (immediately; black, 2 weeks; red) ($CDCl_3$, 25 °C).

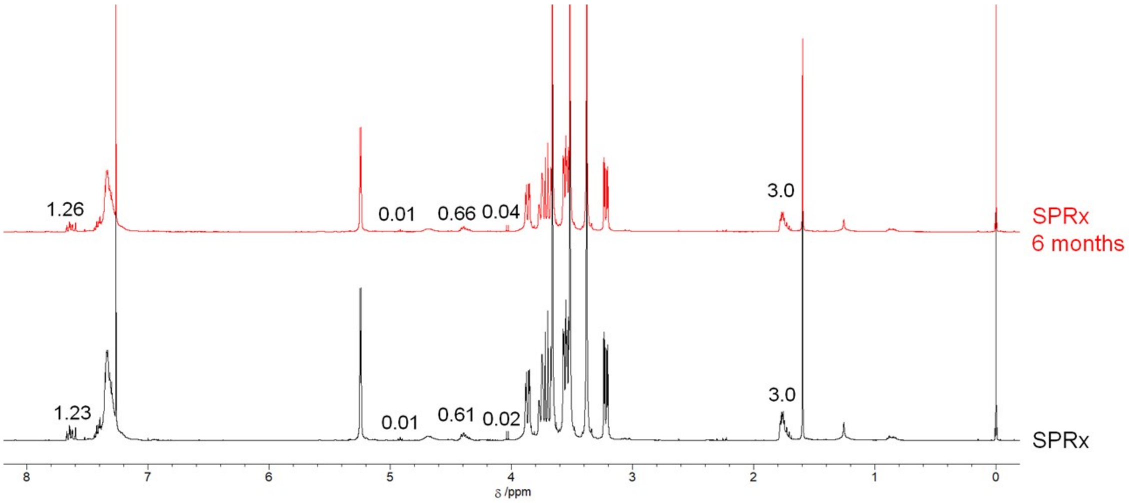

Figure S17. ^{1}H NMR spectra of SPRx (immediately; black, 6 months; red) ($CDCl_3$, 25 °C).

5-2. Thermal stability of SPRx

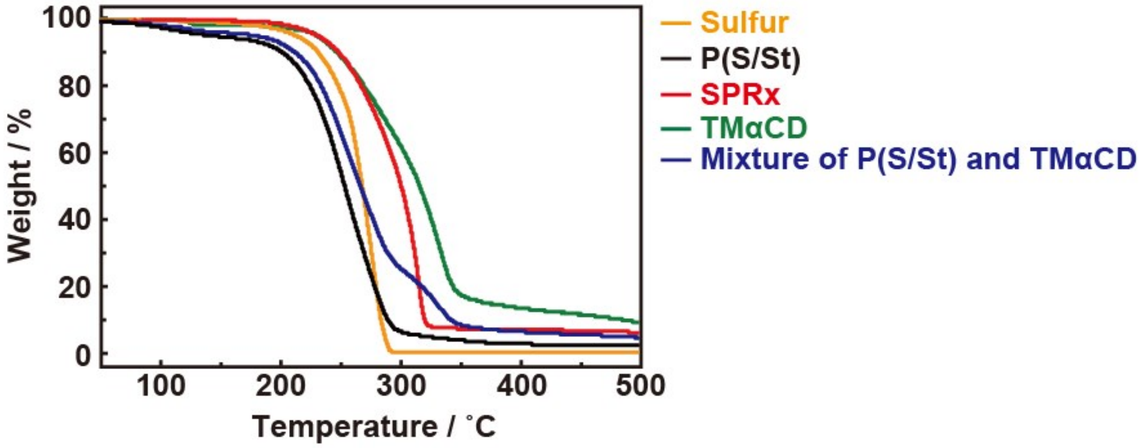

Figure S18. TGA profiles of sulfur (yellow), P(S/St) (black), SPRx (red), TMαCD (green) and mixture of P(S/St) and TMαCD.

References

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2. Y. Y. Zhang, K. M. Konopka, R. S. Glass, K. Char and J. Pyun, *Polym. Chem.*, 2017, **8**, 5167.