

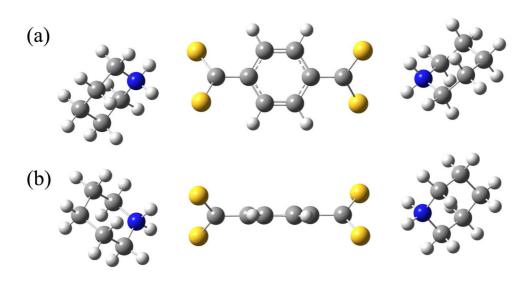
## Chemistry of aromatic polythioesters and polydithioesters

## Daisuke Abe, Yuichiro Fukuda and Yuji Sasanuma\*

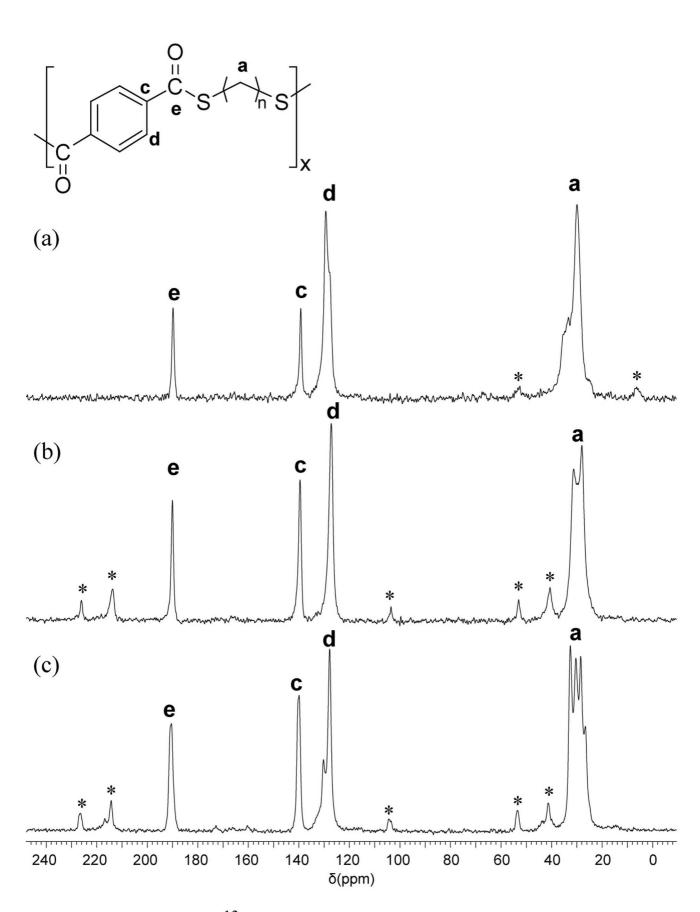
Department of Applied Chemistry and Biotechnology, Graduate School and Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

E-mail: sasanuma@faculty.chiba-u.jp; Tel and Fax: +81 43 290 3394.

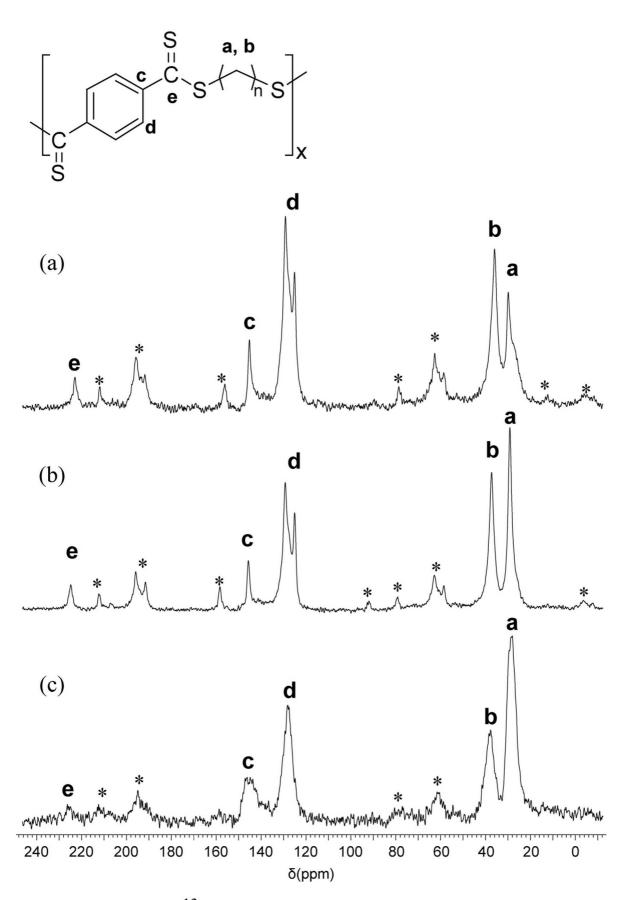
<sup>\*</sup>Corresponding author



**Fig. S1** The optimized structure of the S<sub>4</sub>TPA-Pip complex:
(a) top and (b) side views with respect to the benzene ring.
The H-N-H and S-C-S triangles lie in a plane, the N-H and C-S lengths and the N-H...S-C distance are, respectively, 1.04, 1.71, and 2.32 Å, the N-N-H and S-C-S angles are, respectively, 100.1 and 125.1°, and the two S-C-S triangles make an angle of 78°.



**Fig. S2** Solid state <sup>13</sup>C CP/MAS NMR spectra: (a) P3TS<sub>2</sub>; (b) P4TS<sub>2</sub>; (c) P5TS<sub>2</sub>. The peaks were assigned as indicated. The asterisks represent spinning side bands.



**Fig. S3** Solid state <sup>13</sup>C CP/MAS NMR spectra: (a) P3TS<sub>4</sub>; (b) P4TS<sub>4</sub>; (c) P5TS<sub>4</sub>. The peaks were assigned as indicated. The asterisks represent spinning side bands.

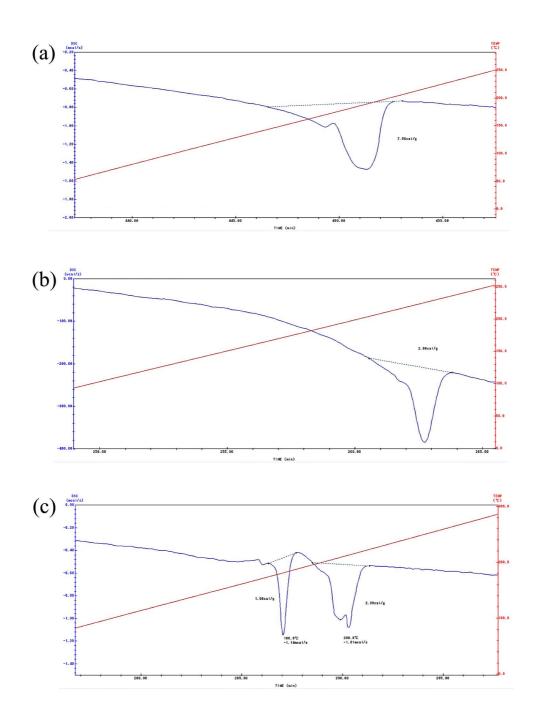
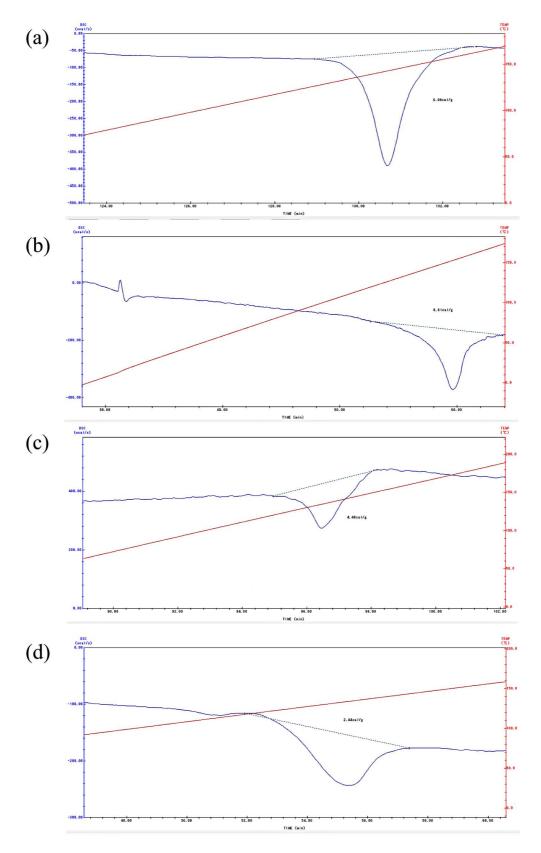
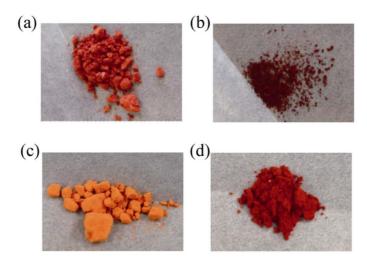


Fig. S4 DSC charts of  $P_y$ TS<sub>2</sub>: (a) P3TS<sub>2</sub>; (b) P4TS<sub>2</sub>; (c) P5TS<sub>2</sub>.



**Fig. S5** DSC charts of PyTS<sub>4</sub>: (a) P3TS<sub>4</sub> (DMF); (b) P3TS<sub>4</sub> (DMSO); (c) P4TS<sub>4</sub> (DMF); (d) P4TS<sub>4</sub> (DMSO). The polymerization solvent is written in the parenthesis.



**Fig. S6** P3TS<sub>4</sub> and P4TS<sub>4</sub>: (a) as-precipitated P3TS<sub>4</sub>; (b) annealed P3TS<sub>4</sub>; (c) as-precipitated P4TS<sub>4</sub>; (d) annealed P4TS<sub>4</sub>. The annealing was carried out at 150  $^{\circ}$ C for 2 h.