

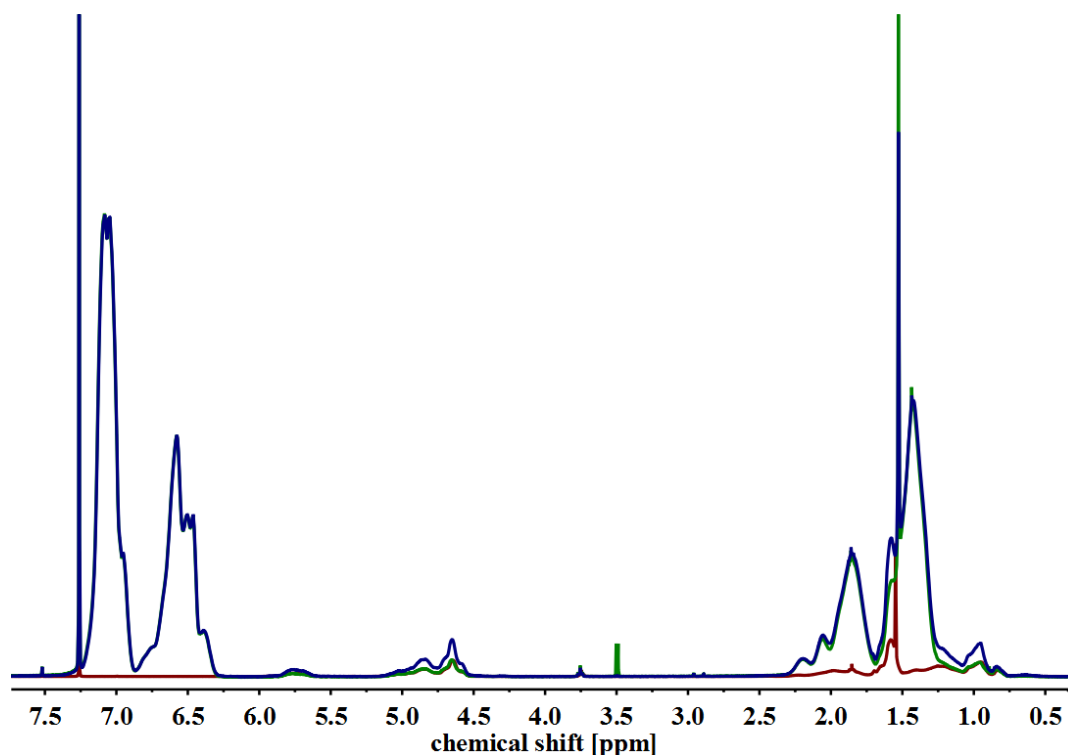
# Supramolecular Networks from Block Copolymers Based on Styrene and Isoprene Using Hydrogen Bonding Motifs – Part 1: Synthesis and Characterization

Elaine Rahmstorf <sup>1</sup>, Volker Abetz <sup>1,2,\*</sup>

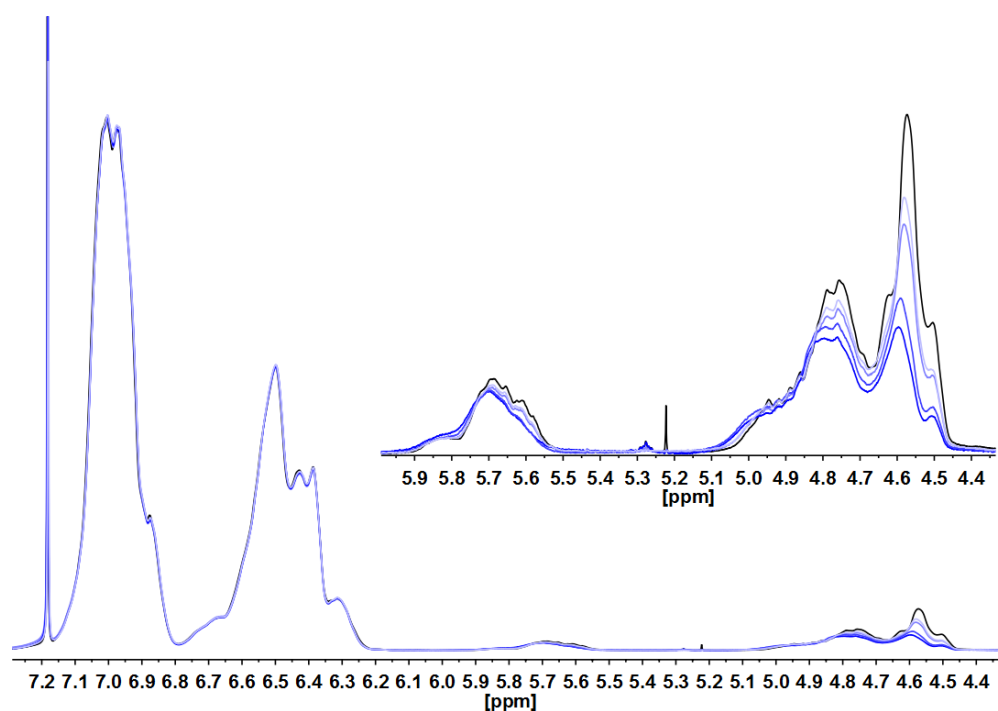
<sup>1</sup> Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg, Germany; elaine.rahmstorf@chemie.uni-hamburg.de

<sup>2</sup> Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Straße 1, 21502 Geesthacht, Germany; volker.abetz@hzg.de

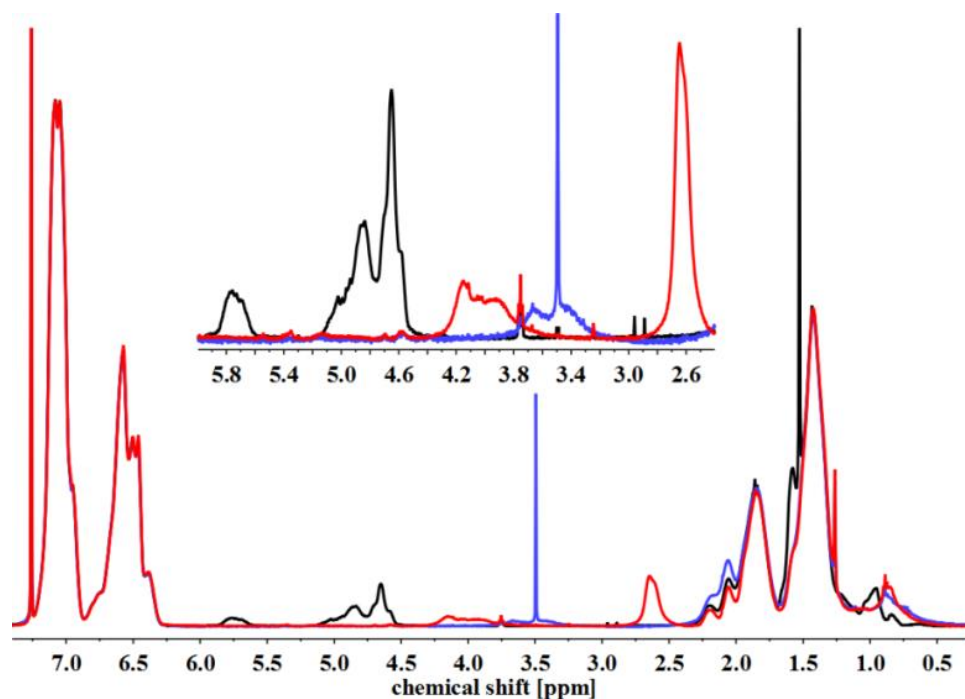
\* Correspondence: volker.abetz@hzg.de; Tel.: +49 40 42838-3460



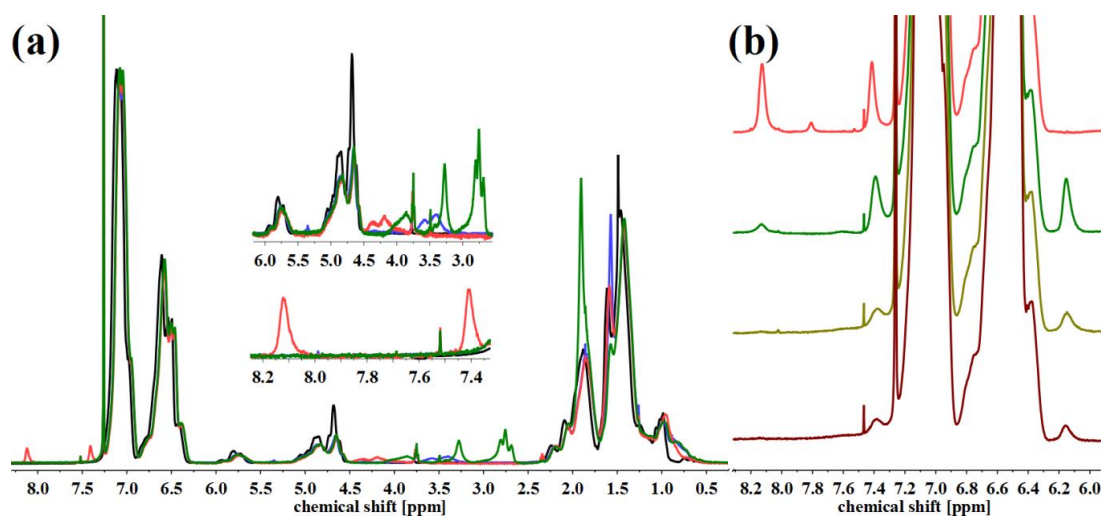
**Figure S1:** <sup>1</sup>H NMR spectra of PI-Precursor (red), PI-*b*-PS-Precursor (green) and IsS<sub>90</sub>Is<sup>62</sup> (blue) in CDCl<sub>3</sub>. Spectra of PI-Precursor and PI-*b*-PS-Precursor were normalized to PI signals. Spectra of PI-*b*-PS-Precursor and IsS<sub>90</sub>Is<sup>62</sup> were normalized to aromatic protons of polystyrene (6.2–7.2 ppm, 5H).



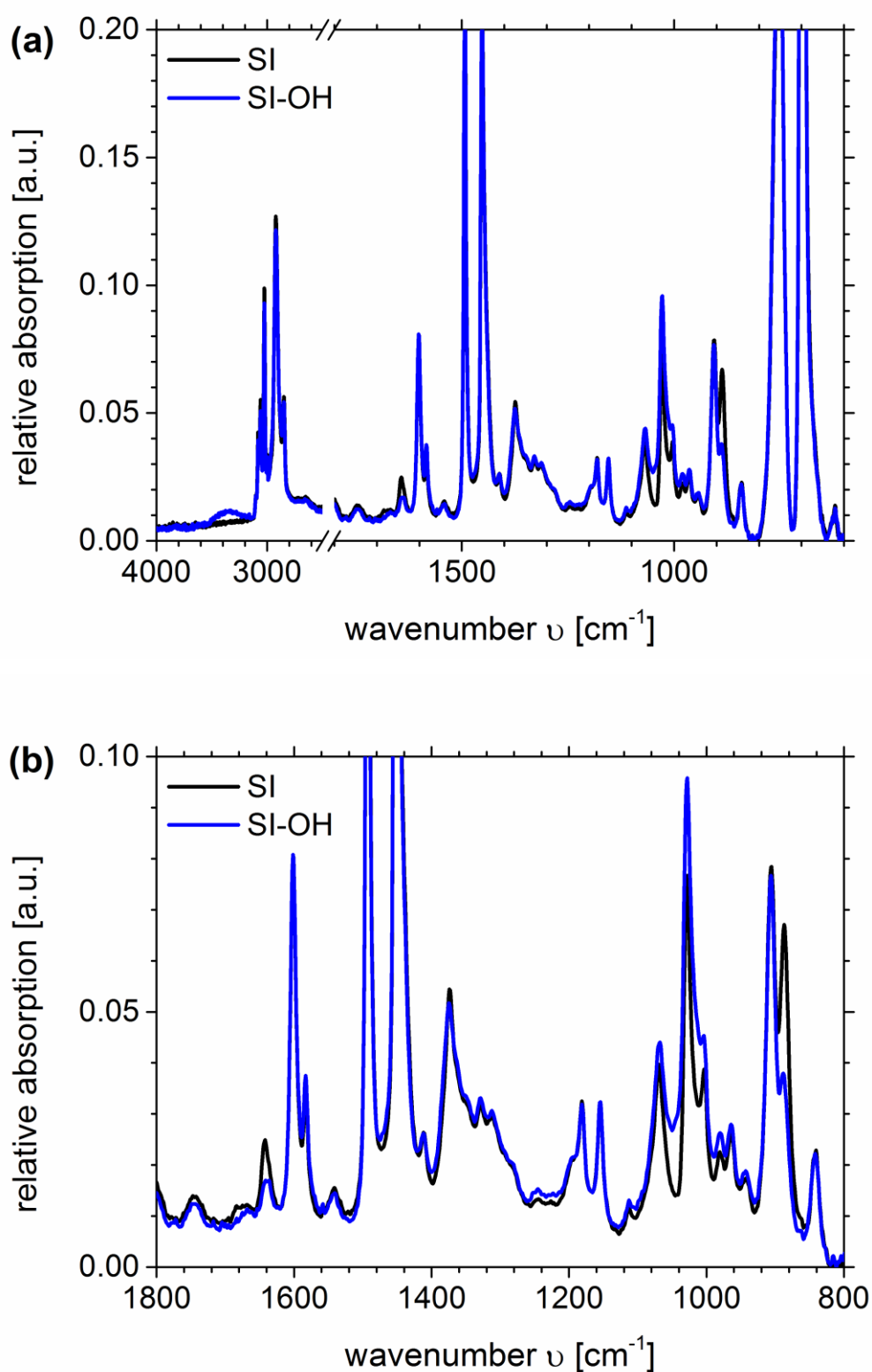
**Figure S2:**  $^1\text{H}$  NMR spectra of  $\text{S}_{91}\text{I}_{967}$  (black), and after hydroxylation with different degree of modification (0%, 13%, 18%, 29%, and 35%) in  $\text{CDCl}_3$ . Hydroxylation of 3,4-PI (signal at 4.45–4.65 ppm) is favoured. Spectra were normalized to aromatic protons of polystyrene (6.2–7.2 ppm, 5H).



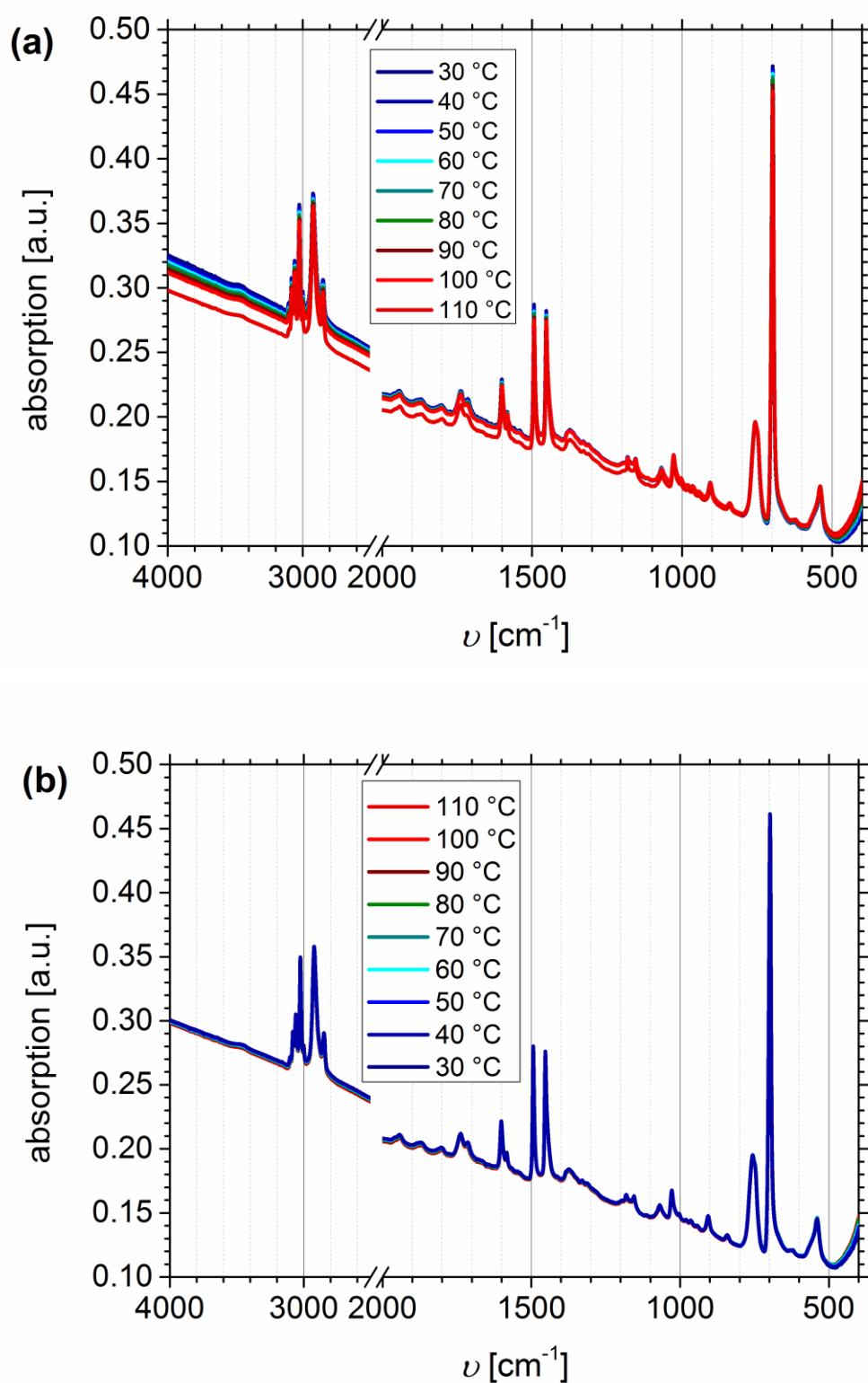
**Figure S3:**  $^1\text{H}$  NMR spectra of unfunctionalized (black), hydroxylated (blue) and with succinic anhydride carboxylated (red)  $\text{I}_{5\text{S}_{90}}\text{I}_{562}$  in  $\text{CDCl}_3$ . Spectra were normalized to aromatic protons of PS (6.2–7.2 ppm, 5H).



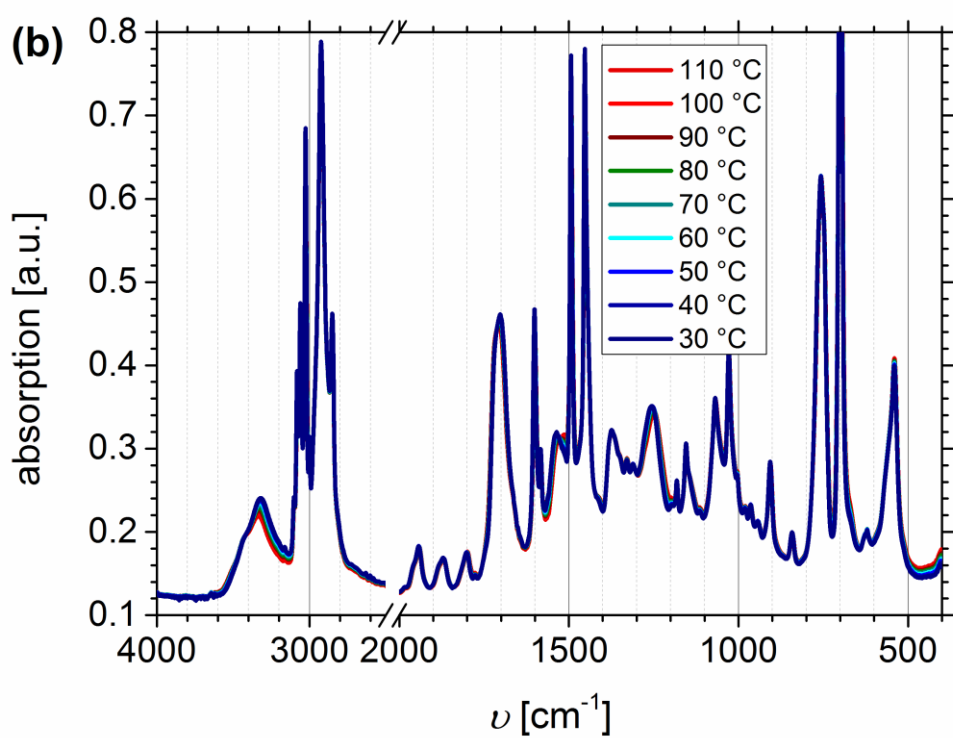
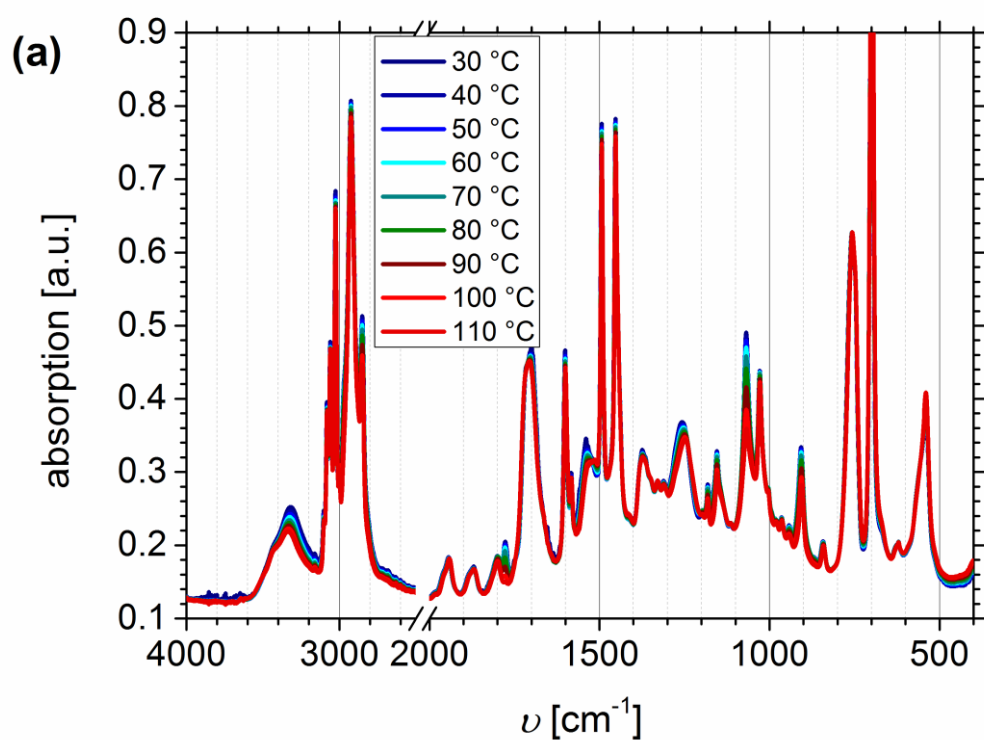
**Figure S4:** (a)  $^1\text{H}$  NMR spectra of  $\text{S}_{85}\text{I}_{15}^{51}$  (black), after hydroxylation (blue), and after reaction with CDI (orange) and DETA (green) in  $\text{CDCl}_3$ . (b)  $^1\text{H}$  NMR spectra of CDI-functionalized  $\text{S}_{85}\text{I}_{15}^{51}$  (top), and after addition of DAP with reaction times of 7 h, 3 d and 4 d (from top to the bottom) in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR spectra were normalized to aromatic protons of PS (6.2–7.2 ppm, 5H).



**Figure S5:** ATR-FTIR spectra of  $S_{91}I_{967}$  before (black) and after (blue) hydroxylation ( $D_f = 30\%$ ). Characteristic decrease of PI related bands can be observed, for example, at 1645 and 890  $\text{cm}^{-1}$ . Both bands can be assigned to the main 3,4-addition product of PI. (a) Complete spectra and (b) enlarged area of (a) at 1800–800  $\text{cm}^{-1}$ .



**Figure S6:** Full range temperature dependent FTIR spectra of I<sub>1.5</sub>S<sub>96.1</sub>I<sub>2.4</sub><sup>82</sup>-SA ( $D_f = 33\%$ ). Temperature range was 30 to 110 (a) and to 30 °C (b) with 10 °C steps, and a 15 min isothermal hold at each temperature.



**Figure S7:** Full range temperature dependent FTIR spectra of I<sub>5</sub>S<sub>90</sub>I<sub>5</sub><sup>62</sup>-DETA (*D<sub>f</sub>* = 32%). Temperature range was 30 to 110 (a) and to 30 °C (b) with 10 °C steps, and a 15 min isothermal hold at each temperature.