

Supporting Information

Crosslinked nanoporous materials from reactive and multifunctional block polymers

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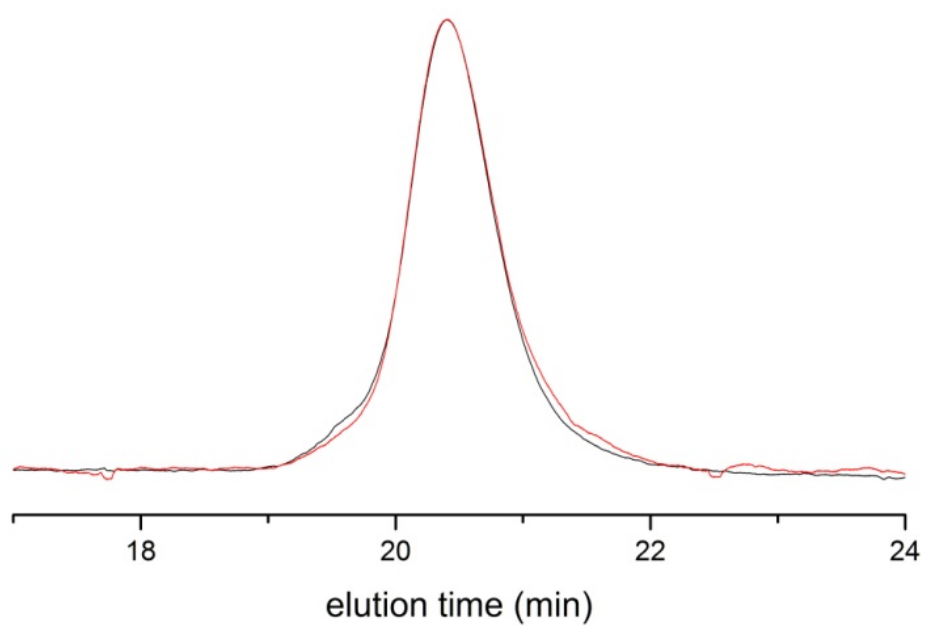


Figure S1. SEC profiles of PLA-OH (black, $M_{n, SEC} = 37$ kDa, PDI = 1.10 based on PS standard) and PLA-CTA (red, $M_{n, SEC} = 37$ kDa, PDI = 1.10).

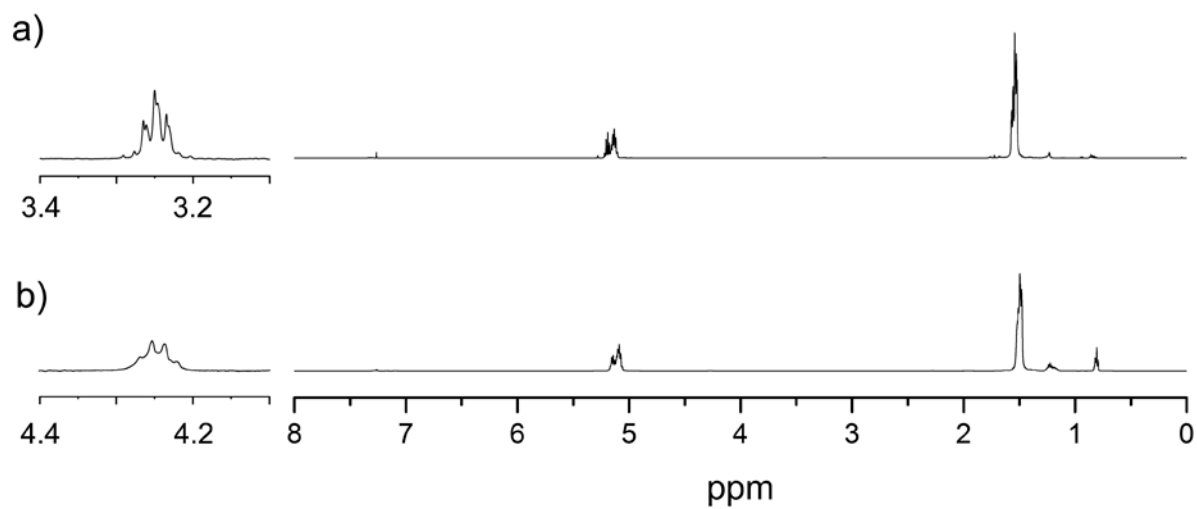


Figure S2. ^1H NMR spectra of a) PLA-OH and b) PLA-CTA (CDCl_3 , 500 MHz, 20 °C).

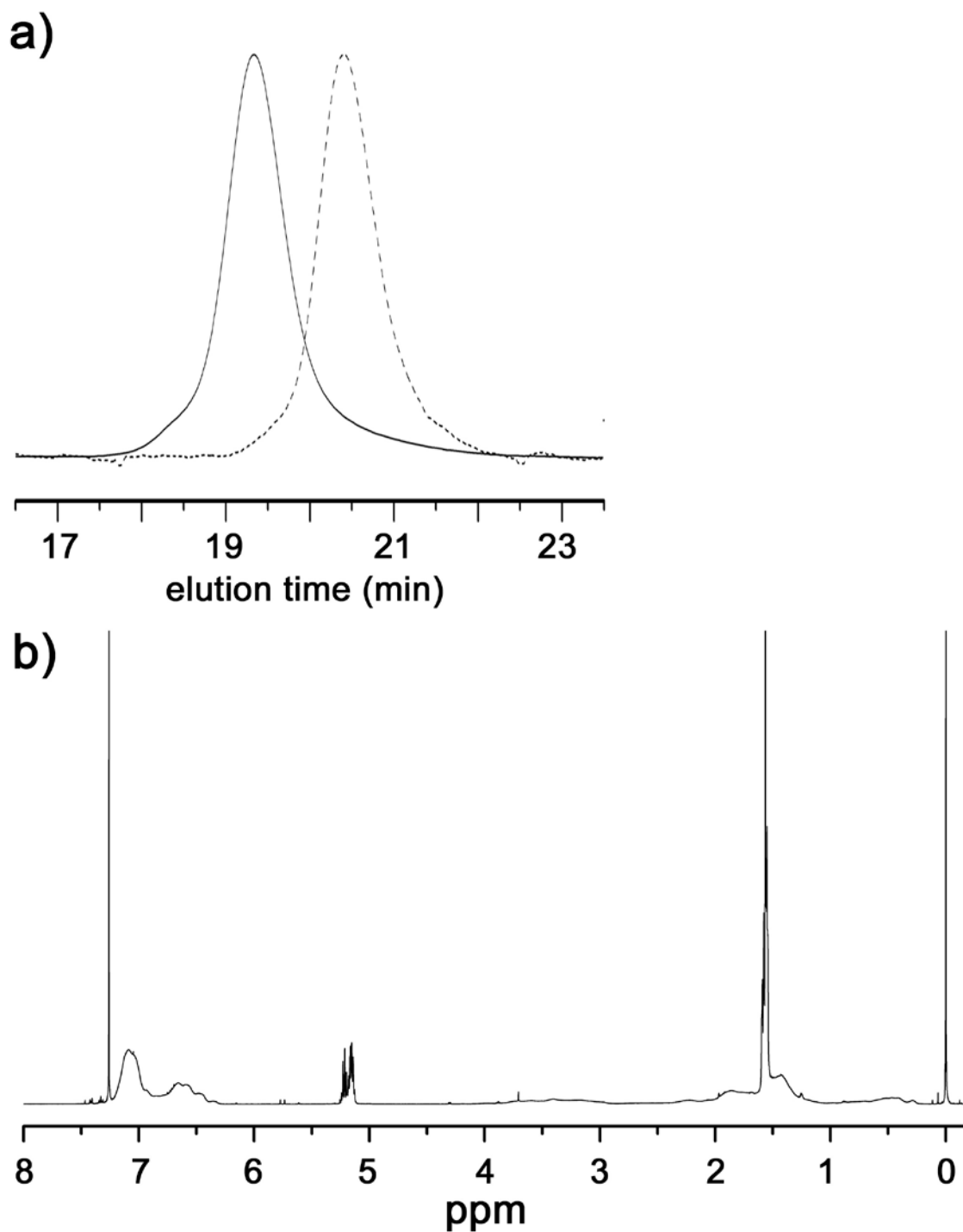


Figure S3. a) SEC profile of PLA-*b*-P(S-*co*-HEMA) (solid). PLA-CTA is shown for comparison (dashed). b) ¹H NMR spectrum of PLA-*b*-P(S-*co*-HEMA) (CDCl₃, 500 MHz, 20 °C). The number-average molecular weight ($M_{n, \text{NMR}}$) and the mole fraction of HEMA (x_{HEMA}) were calculated from integration of PS (5H, 6.5-7.2 ppm), PHEMA (4H, 2.9-4.0 ppm), and PLA (1H, 5.2 ppm).

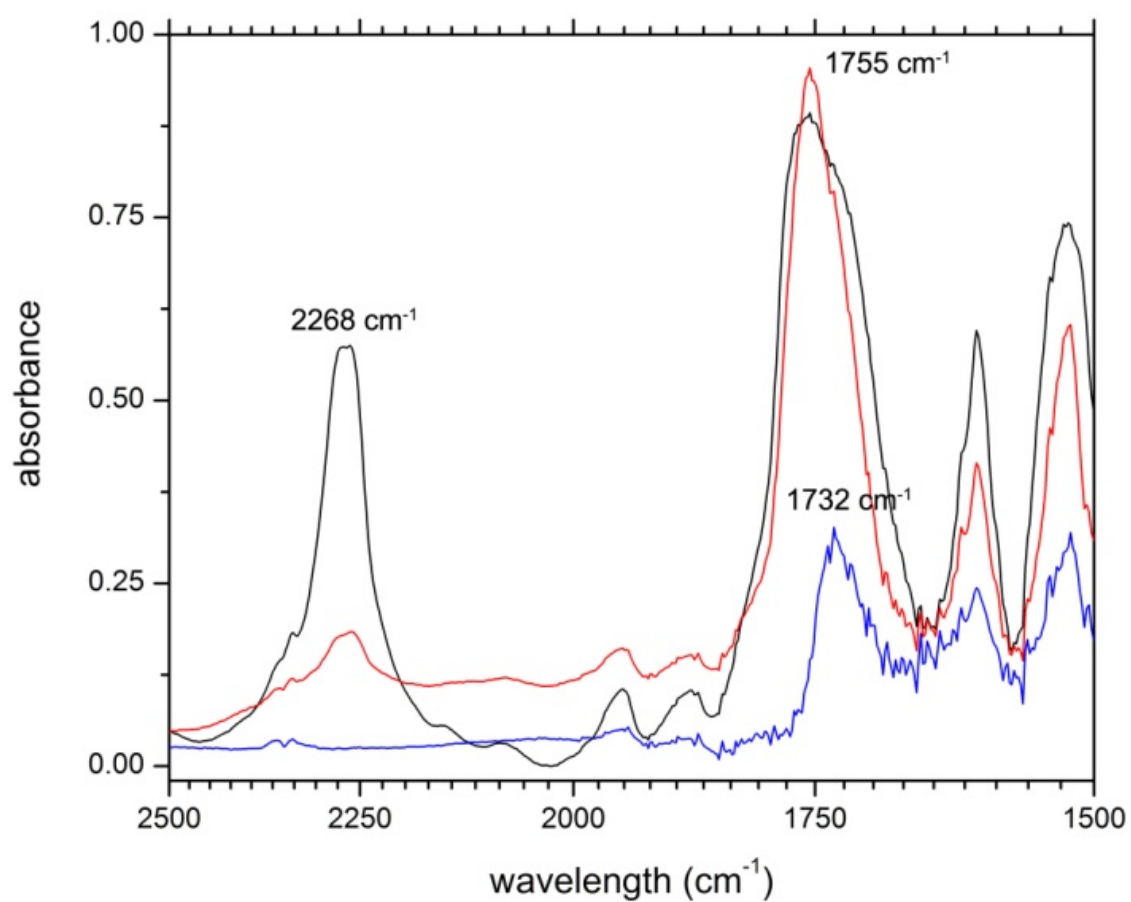


Figure S4. FTIR spectra of PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI after evaporation of solvent (black), after annealing at 150 °C for 5 h (red), and after etching PLA by basic hydrolysis.

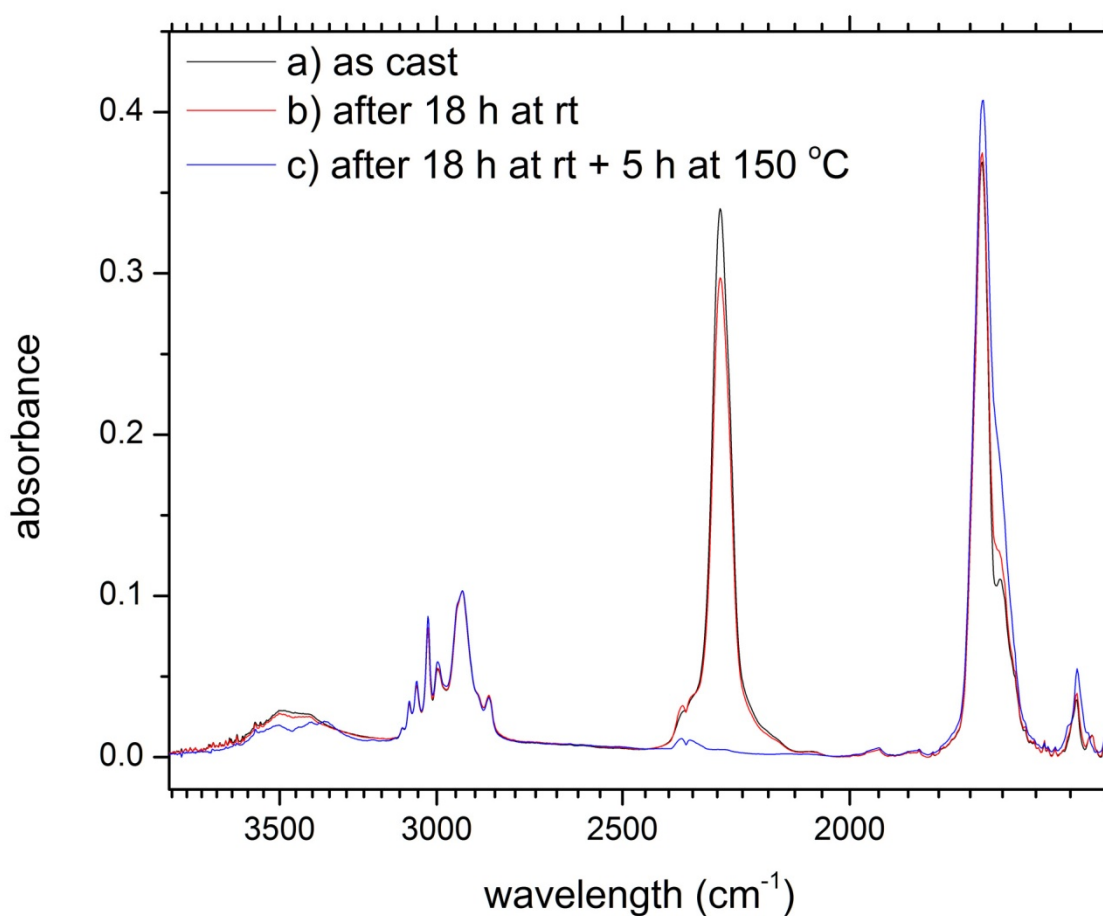


Figure S5. FT-IR spectra of PLA-*b*-P(S-*co*-HEMA) ($M_{n, \text{NMR}} = 62 \text{ kDa}$, $w_{\text{PLA}} = 30\%$, PDI = 1.26) + MDI cast on a NaCl plate from diluted dichloromethane solution. The spectra were normalized by the peak at 2925 cm^{-1} . a) As cast. b) After 18 h at room temperature. c) After 18 h at room temperature and 5 h at $150 \text{ }^{\circ}\text{C}$.

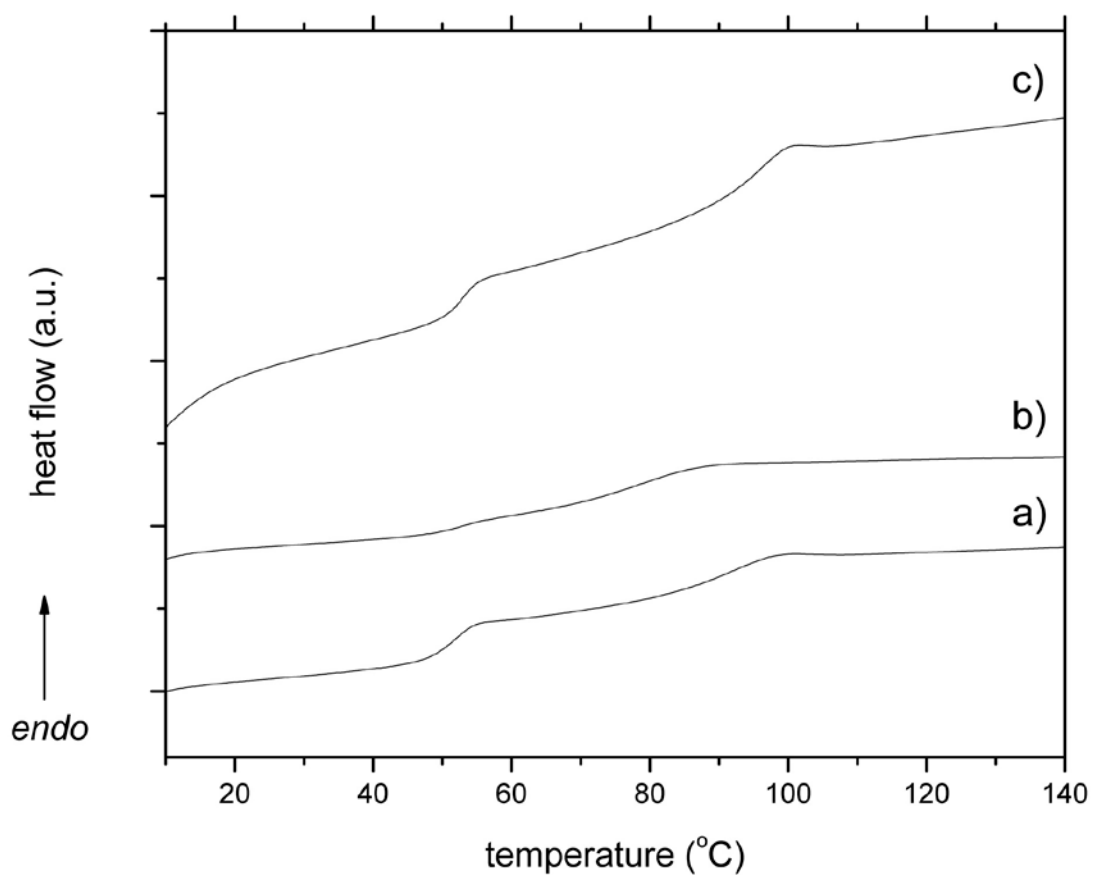


Figure S6. DSC thermograms of polymers based on PLA-*b*-P(S-*co*-HEMA). a) PLA-*b*-P(S-*co*-HEMA) after evaporation of solvent. b) PLA-*b*-P(S-*co*-HEMA) after annealing at 150 °C for 5 h. c) hydroxyl group-capped PLA-*b*-P(S-*co*-HEMA) after annealing at 150 °C for 5 h. All the thermograms were obtained with a heating rate of 10 °C/min under inert atmosphere.

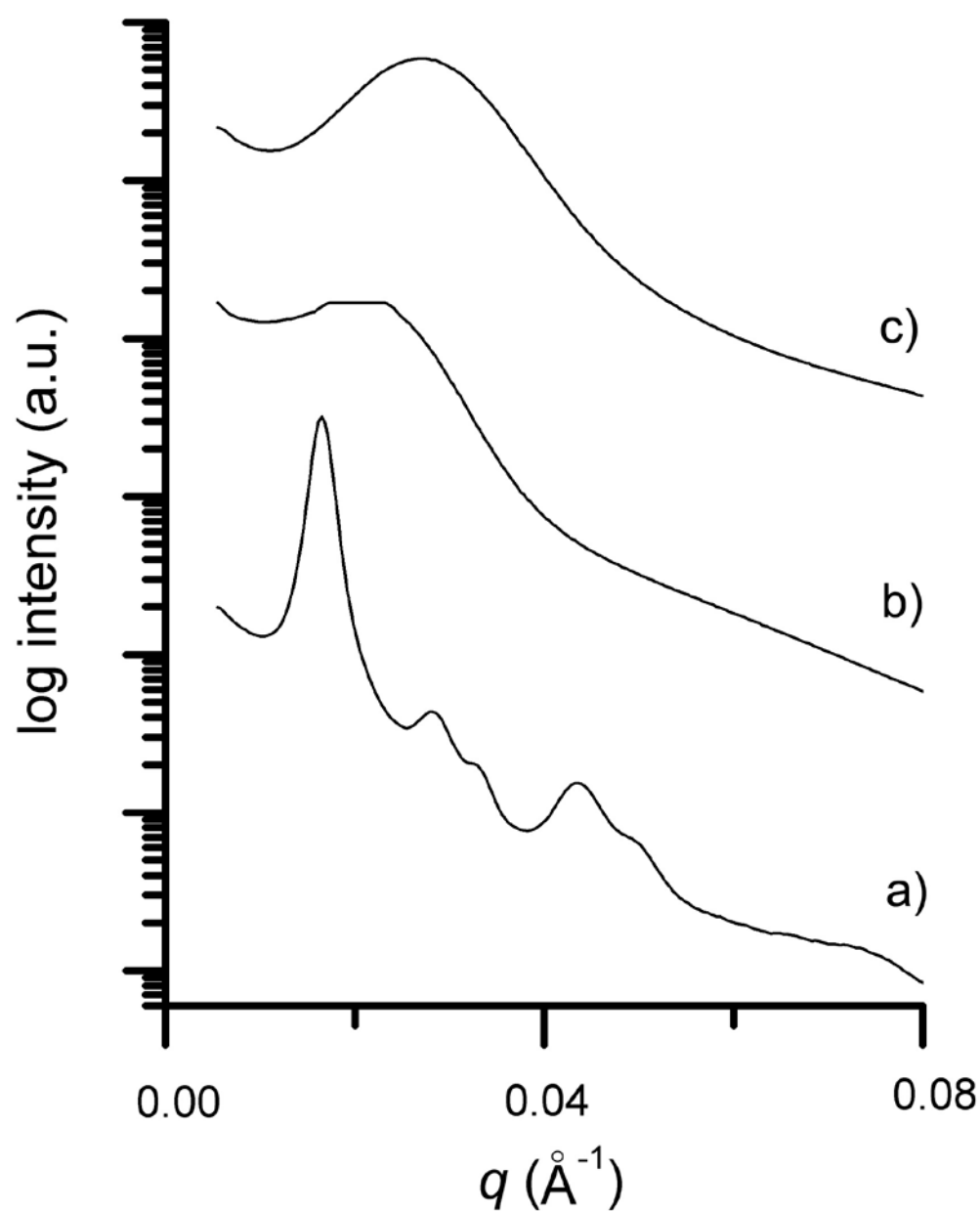


Figure S7. SAXS patterns of a) PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI after etching, b) PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI in the presence of 0.001 eq of DBTDL after etching, and c) PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI in the presence of 0.01 eq of DBTDL after etching. Notice the oversaturated principal scattering in b) due to long exposure time.

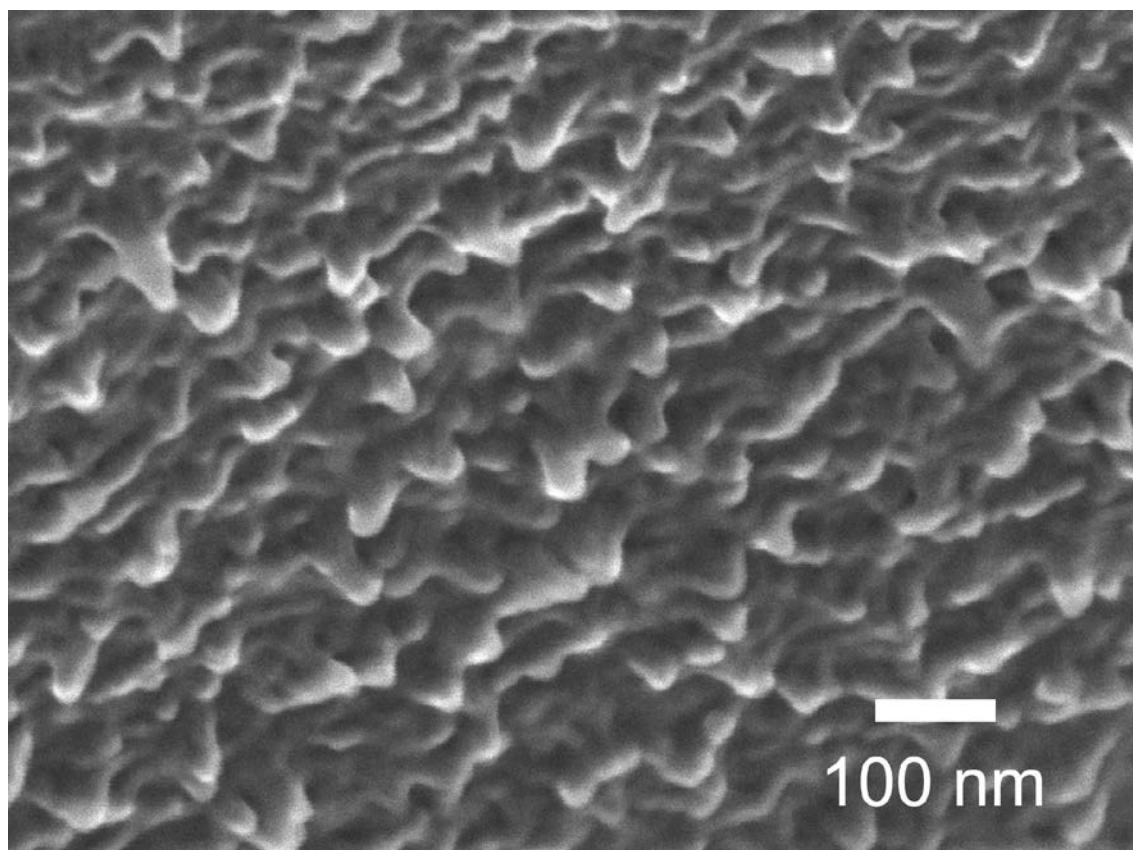
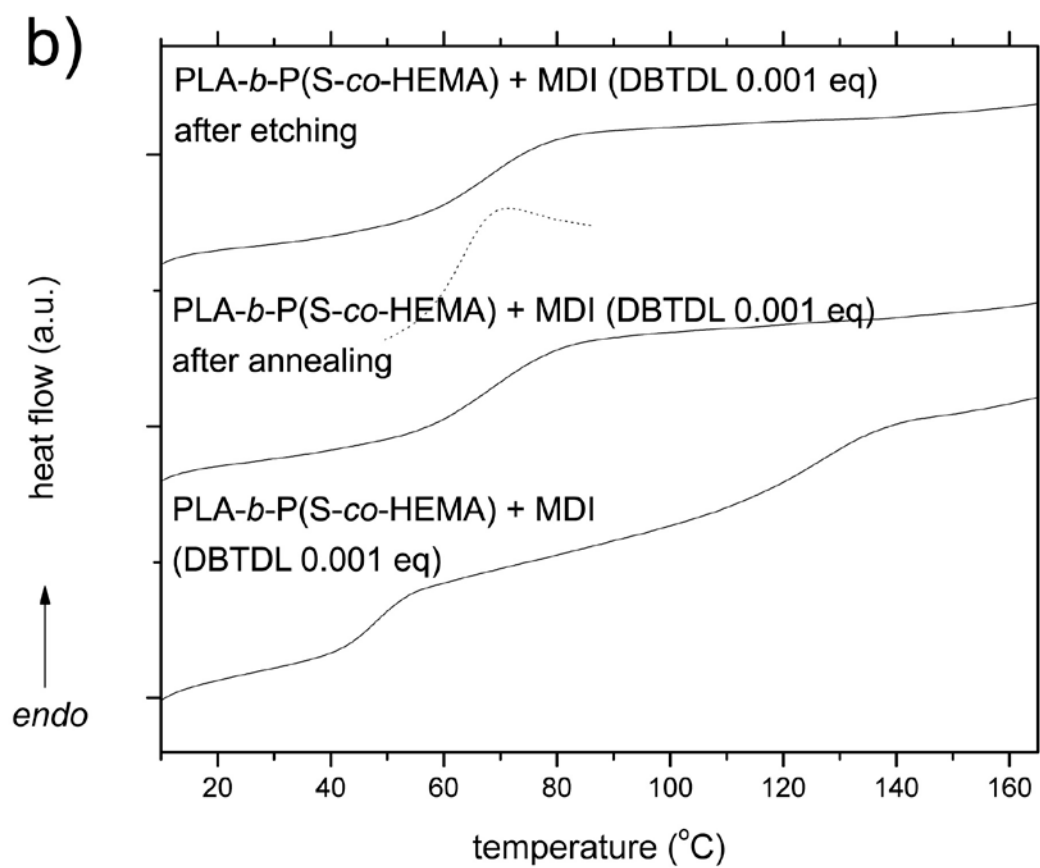
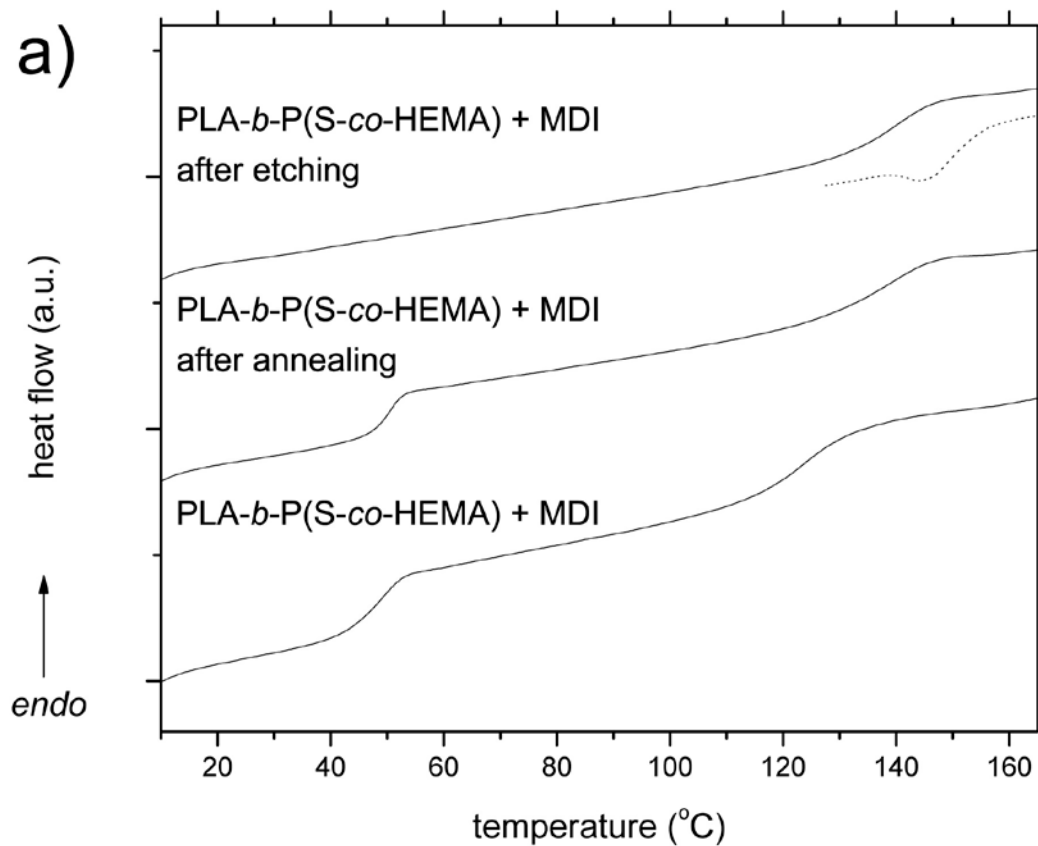


Figure S8. FE-SEM images of fractured sample from PLA-*b*-P(S-*co*-HEMA) and MDI in the presence of 0.001 eq of DBTDL after etching.



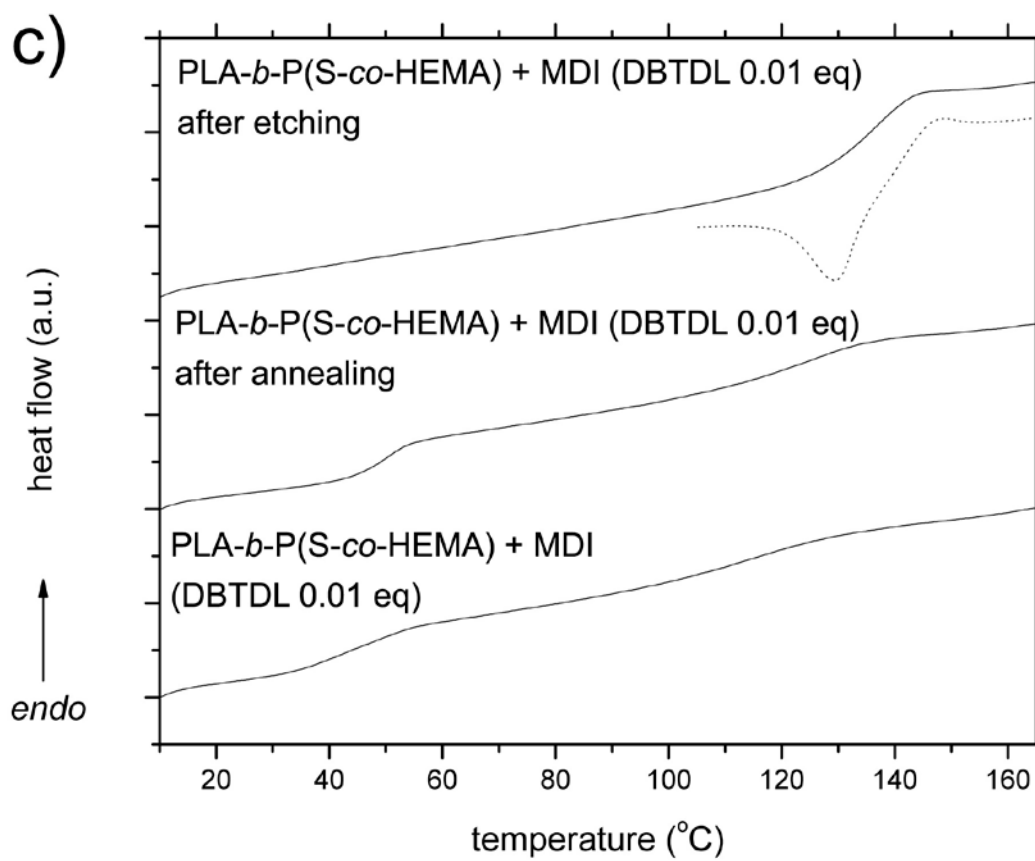


Figure S9. DSC thermograms of a) PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI, b) PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI in the presence of 0.001 eq of DBTDL, and c) PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI in the presence of 0.01 eq of DBTDL. All the thermograms were obtained with a heating rate of 10 °C/min under inert atmosphere. Solid lines: second heating cycle. Dotted lines: first heating cycle.

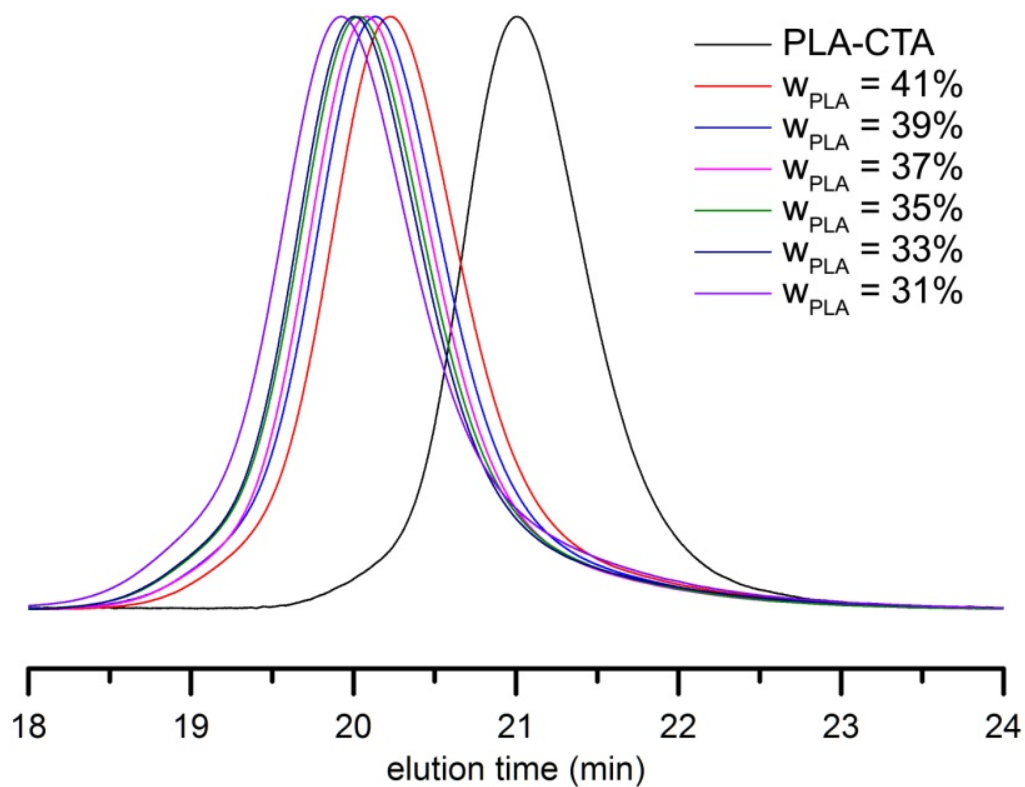


Figure S10. SEC profiles of PLA-*b*-P(S-*co*-HEMA)s with different weight fraction of PLA. 20k PLA-CTA (black) used for the synthesis was also shown as a comparison ($M_{n, \text{SEC}} = 31$ kDa, PDI = 1.11).

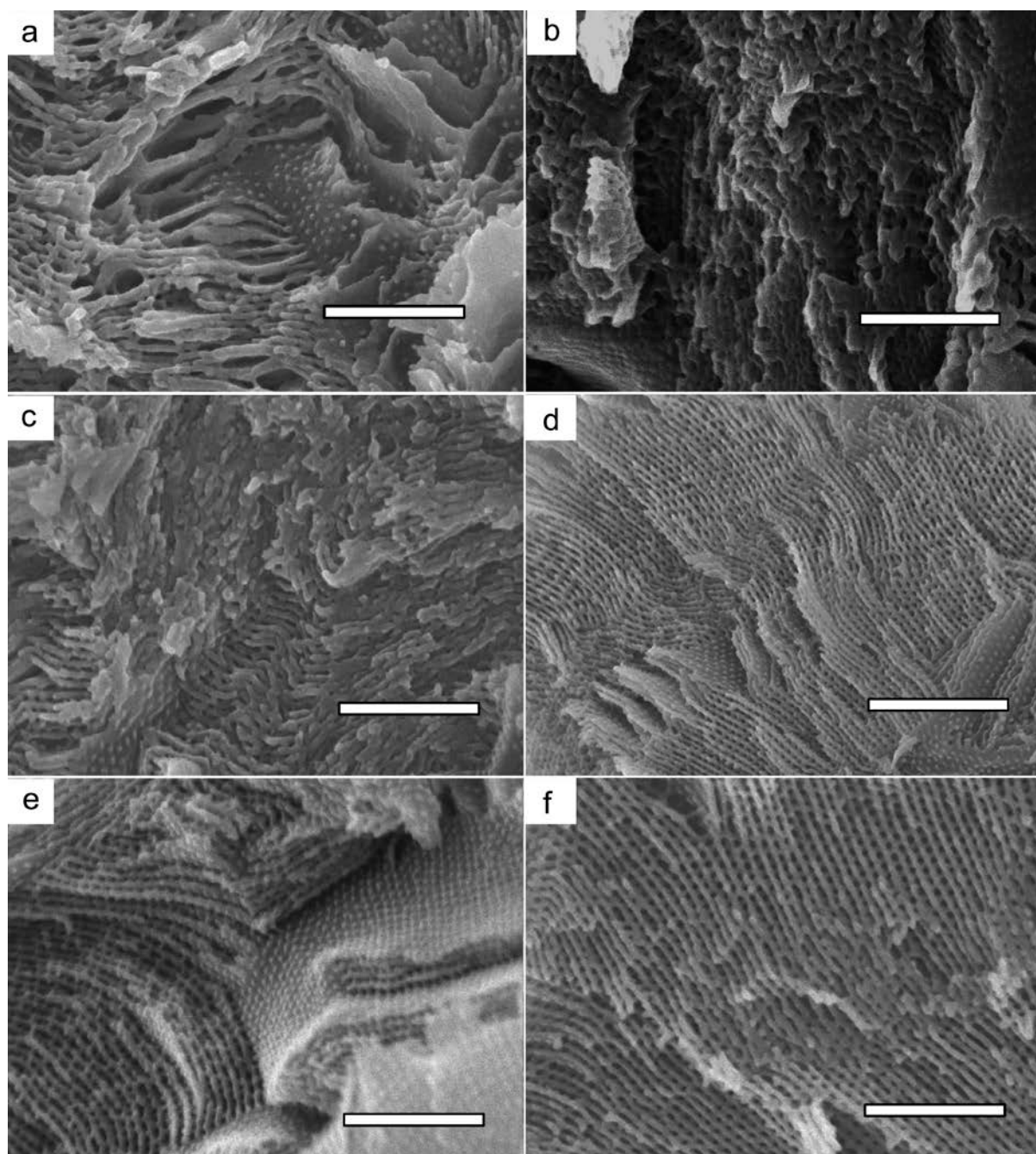


Figure S11. FE-SEM images of crosslinked nanoporous polymers based on PLA-*b*-P(S-*co*-HEMA) and MDI after annealing for a) 0 h, b) 1 h, c) 2 h, d) 4 h, e) 6 h, and f) 24 h. Scale bars represent 200 nm.

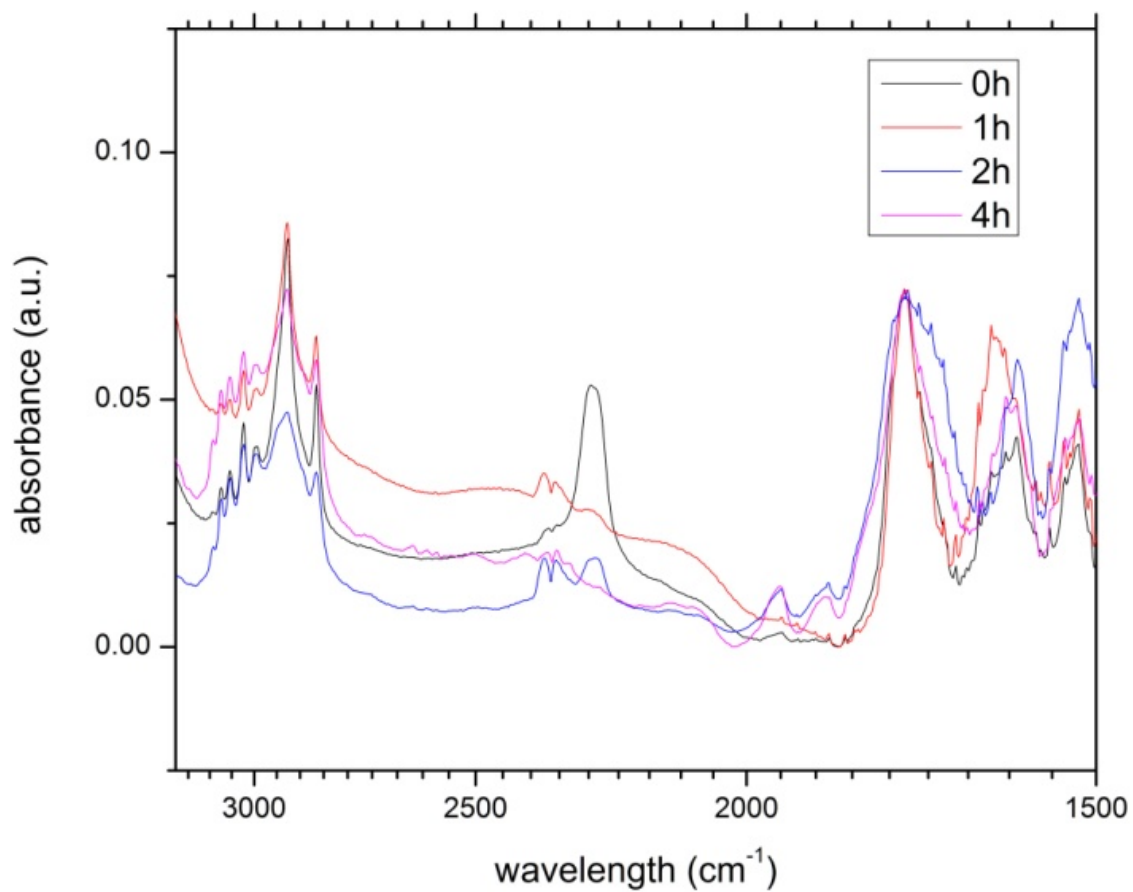


Figure S12. FT-IR spectra of PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI after evaporation of solvent (black), after annealing at 150 °C for 1 h (red), 2 h (blue) and 4 h (violet). Spectra were normalized by the peak at 1755 cm⁻¹. Notice the peak at 2268 cm⁻¹ decreased over annealing time.

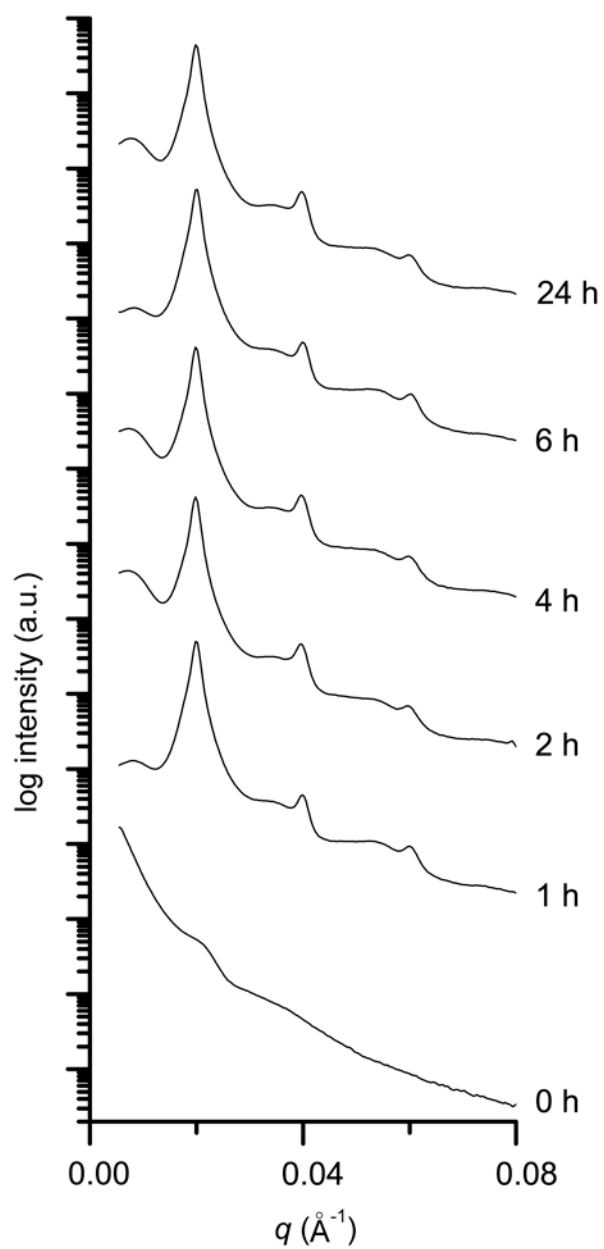


Figure S13. SAXS patterns of PLA-*b*-P(S-*co*-HEMA) crosslinked with MDI after annealing at 150 °C and etching PLA. Annealing time was specified for each pattern.

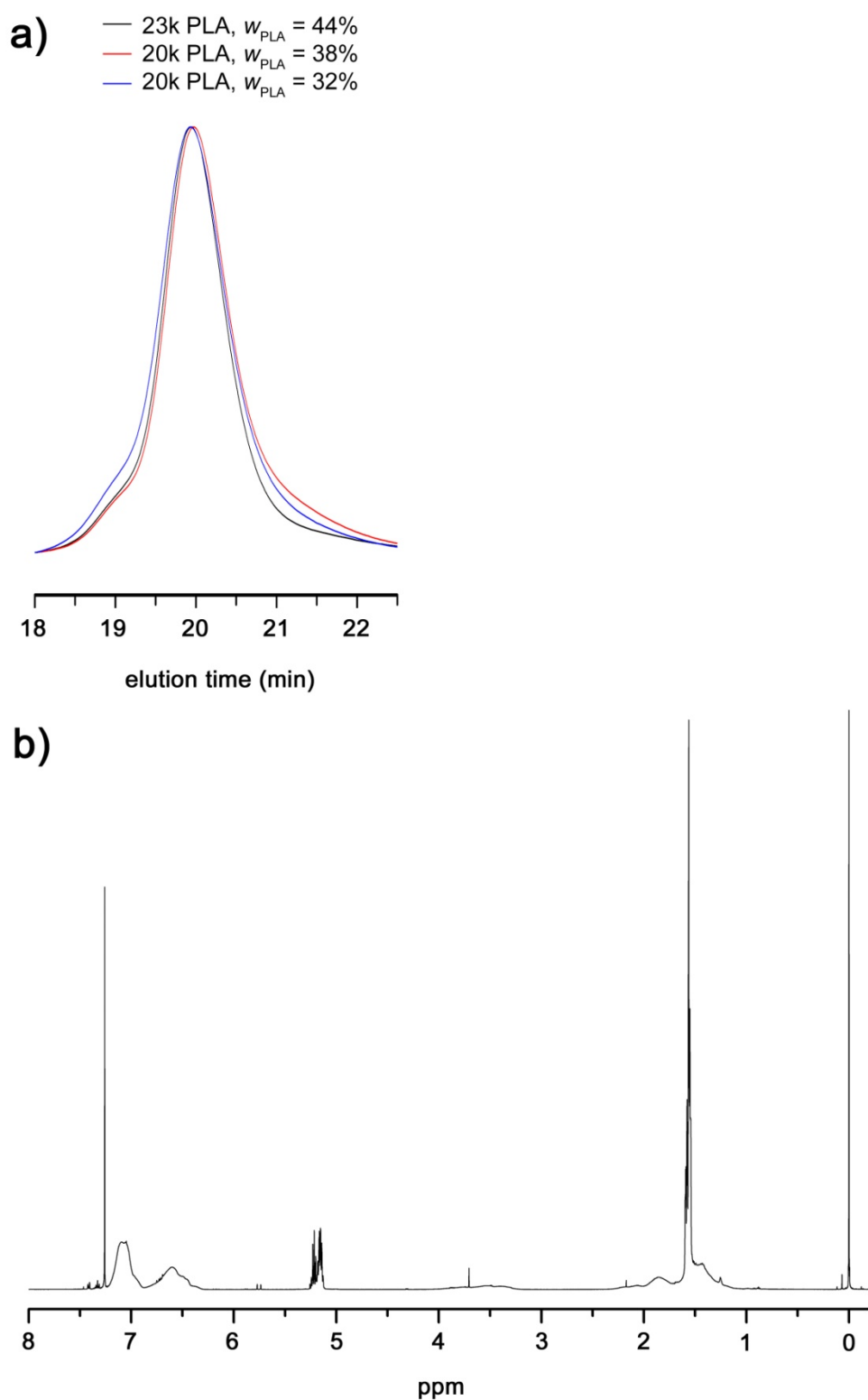
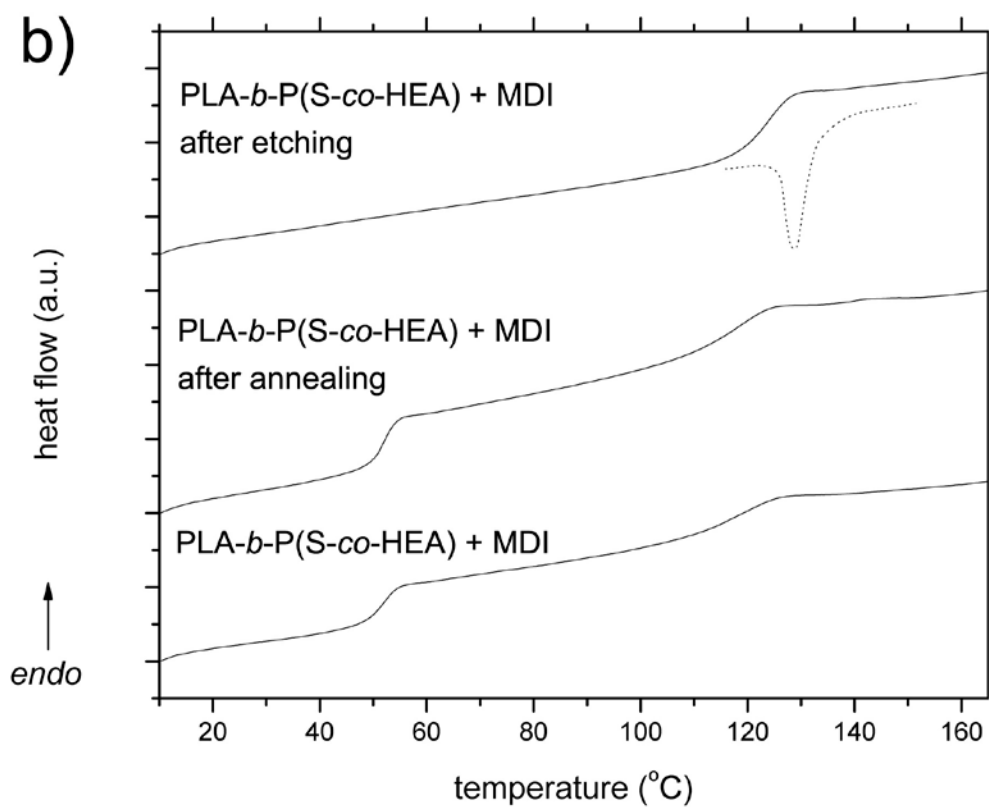
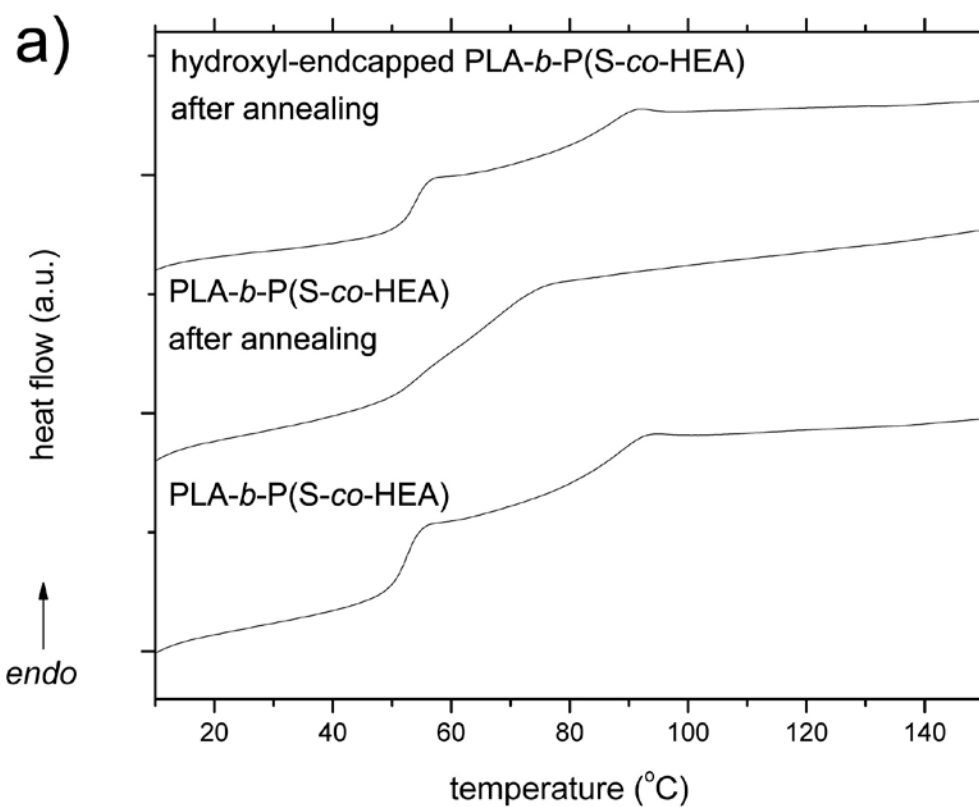


Figure S14. a) SEC profile of PLA-*b*-P(S-*co*-HEA)s. b) ^1H NMR spectrum of PLA-*b*-P(S-*co*-HEA) with $w_{\text{PLA}} = 38\%$ (CDCl_3 , 500 MHz, 20 °C). $M_{n,\text{NMR}}$ and x_{HEA} were calculated based on the integration of PS (5H, 6.5-7.2 ppm), PHEA (4H, 3.0-4.0 ppm), and PLA (1H, 5.2 ppm).



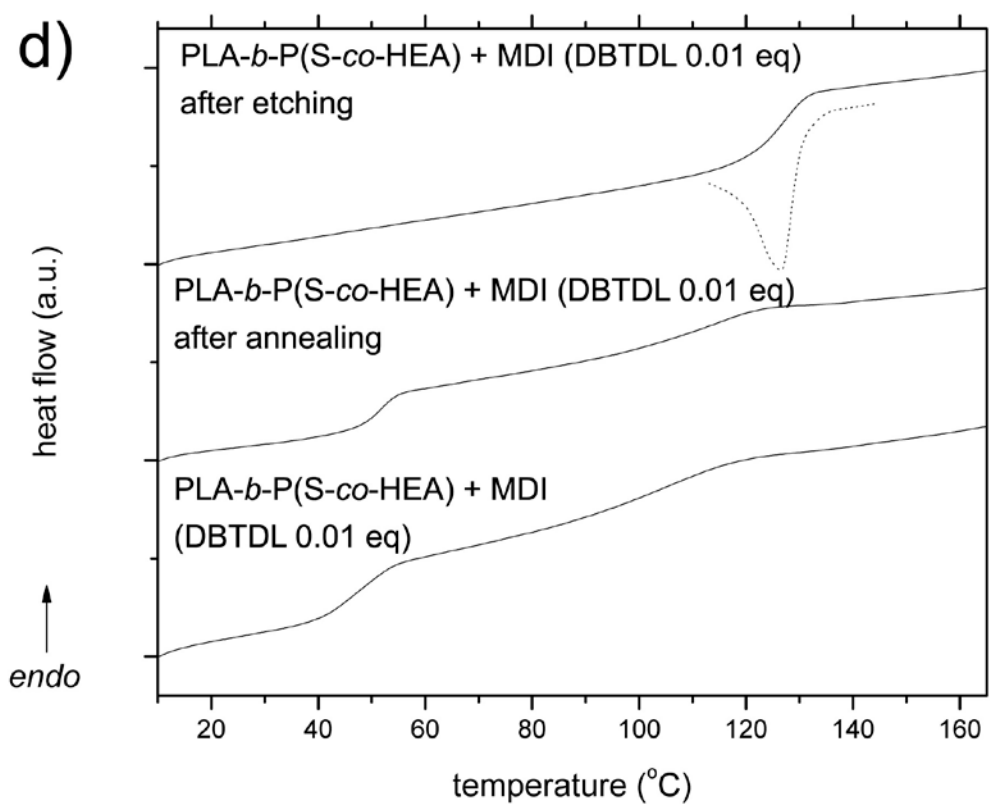
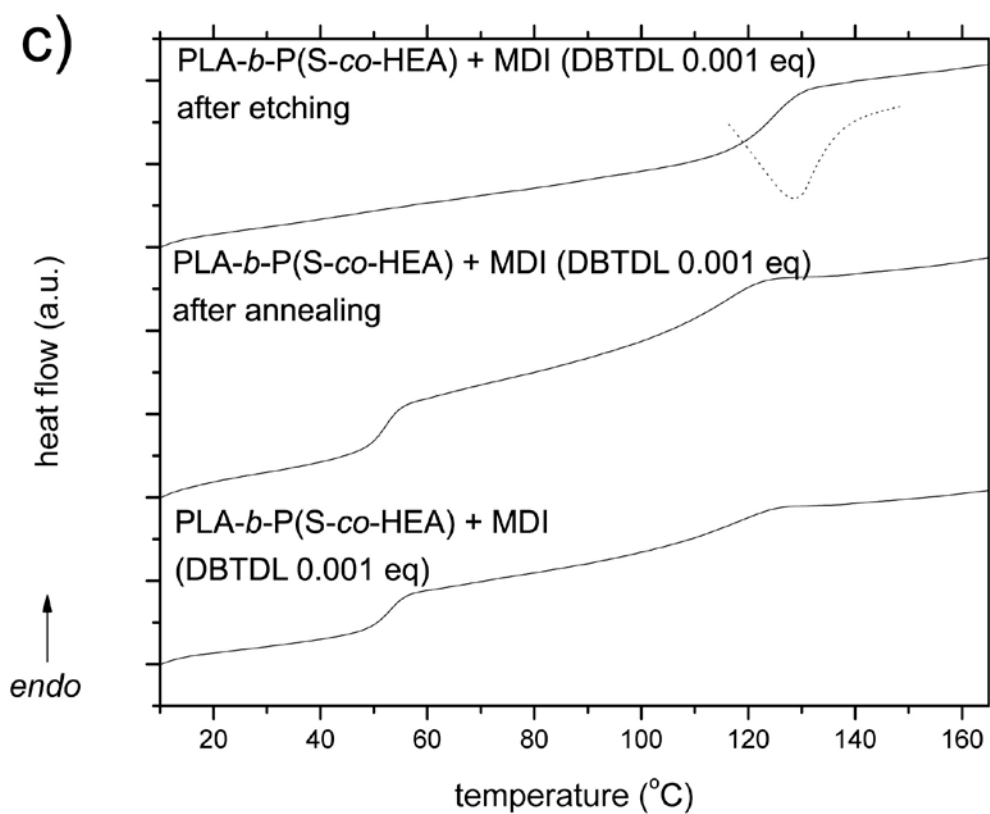


Figure S15. DSC thermograms of polymers based on PLA-*b*-P(S-*co*-HEA) with 38 wt% PLA.

a) PLA-*b*-P(S-*co*-HEA) and hydroxyl-endcapped PLA-*b*-P(S-*co*-HEA). b) PLA-*b*-P(S-*co*-

HEA) crosslinked with MDI. c) PLA-*b*-P(S-*co*-HEA) crosslinked with MDI in the presence of 0.001 eq of DBTDL. d) PLA-*b*-P(S-*co*-HEA) crosslinked with MDI in the presence of 0.01 eq of DBTDL. All the thermograms were obtained with a heating rate of 10 °C/min under inert atmosphere. Solid lines: second heating cycle. Dotted lines: first heating cycle.