

Electronic Supplementary Information

Heteroarm Core Cross-linked Star Polymers via RAFT Copolymerization of Styrene and Bismaleimide

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This Information Includes:

Table S1

Figures S1 – S7

Table S1. Variation of [S]:[BMI]:[PLA-CTA]

Entry	[S]:[BMI]:[PLA-CTA]	Conversion (%) ^a	$M_{n,NMR}$ (kg mol ⁻¹) ^b	f_{PS}^c	$M_{n,SEC}$ (kg mol ⁻¹) ^d	\bar{D}^d
1	500:1:1	18	11	0.30	65	1.31
2	500:2:1	19	11	0.30	76	1.45
3	500:4:1	22	13	0.34	221	1.28
4	500:6:1	19	12	0.32	296	1.33
5	500:8:1	25	13	0.34	487	1.37
6	200:2:1	34	7	0.22	175	1.22

^aEstimated by ¹H NMR analysis of the aliquots.

^bEstimated by ¹H NMR analysis of the polymers based on the integration of PLA and PS protons assuming $M_{n,PLA} = 30$ kg mol⁻¹.

^cAssuming the polymer is only composed of PLA and PS, and their densities are 1.25 and 1.05 g mL⁻¹, respectively.

^dDetermined by CHCl₃-SEC based on linear PS standards.

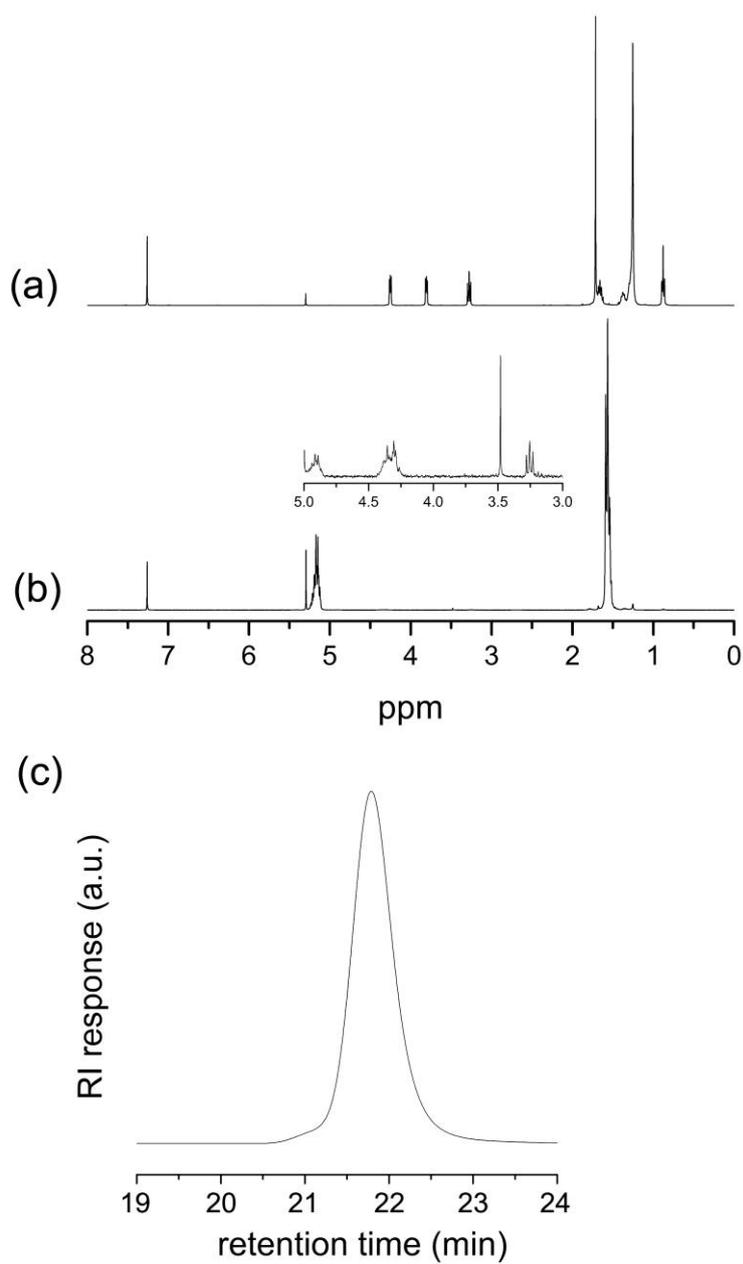


Figure S1. (a) ^1H NMR spectrum of PLA-CTA (400 MHz, CDCl_3 , 20 $^\circ\text{C}$). The inset shows a magnified spectrum of PLA-CTA in the range of 3 – 5 ppm used for M_n determination by end group analysis. (b) SEC trace of PLA-CTA (chloroform, 35 $^\circ\text{C}$, 1 mL min^{-1} , RI detector).

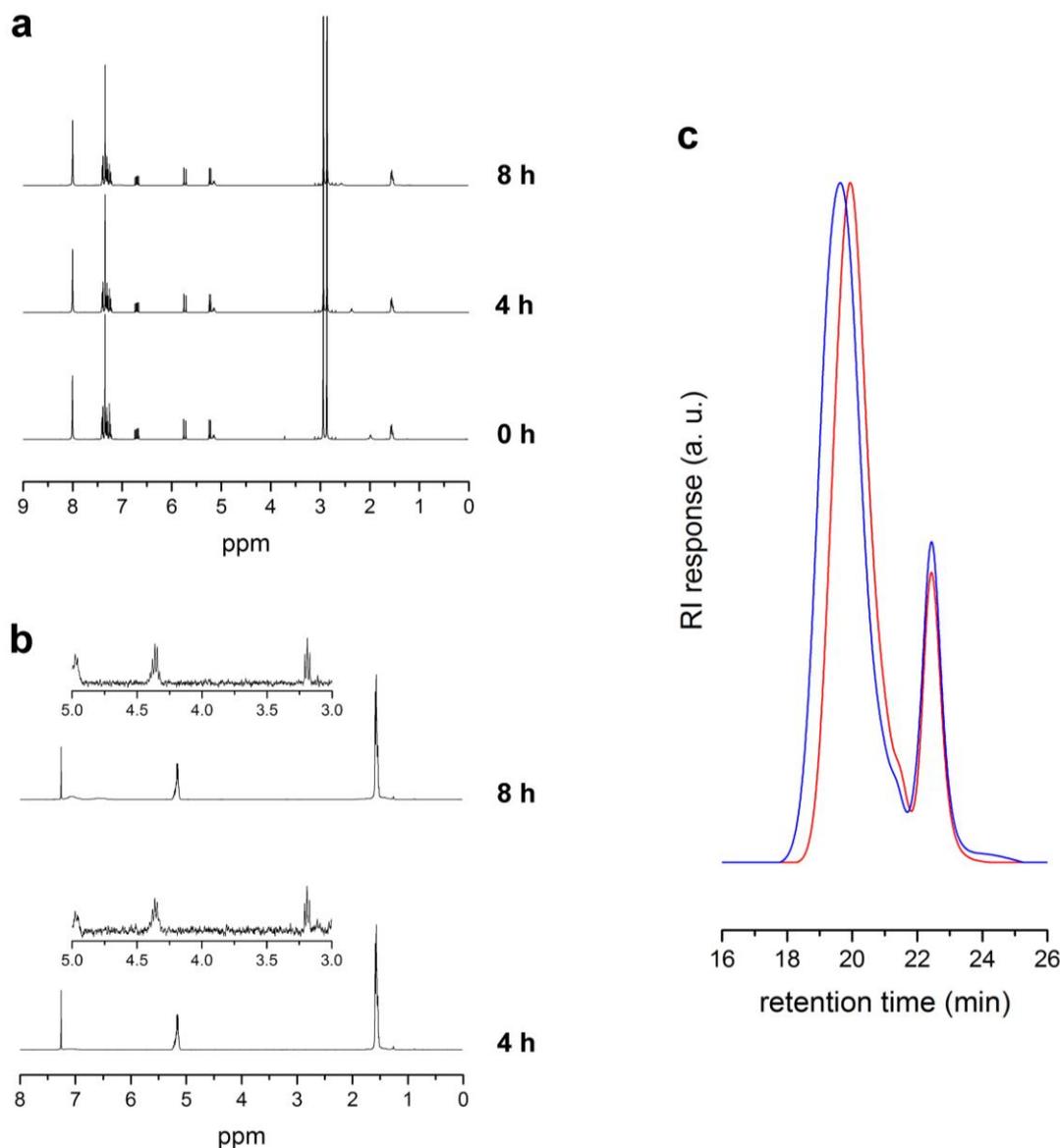


Figure S2. (a) ¹H NMR spectra of the polymerization mixture containing S, BMI, PLA-CTA ($M_{n, \text{PLA-CTA}} = 22 \text{ kg mol}^{-1}$, $[\text{S}]:[\text{BMI}]:[\text{PLA-CTA}] = 500:8:1$), and DMF after 0 (bottom), 4 (middle), and 8 h (top) of polymerization at 60 °C (400 MHz, CDCl_3 , 20 °C). A peak at 3.7 ppm disappearing after 4 h corresponds to ethylene protons of BMI. (b) ¹H NMR spectra of the polymers synthesized by 4 (bottom) and 8 h (top) of polymerization and obtained by precipitation in methanol. Insets provide a magnified view in the range of 5 – 3 ppm showing absence of peak corresponding to BMI repeating units. (c) SEC traces of the polymers obtained by 4 (red) and 8 h (blue) of polymerization (chloroform, 35 °C, 1 mL min⁻¹, RI detector).

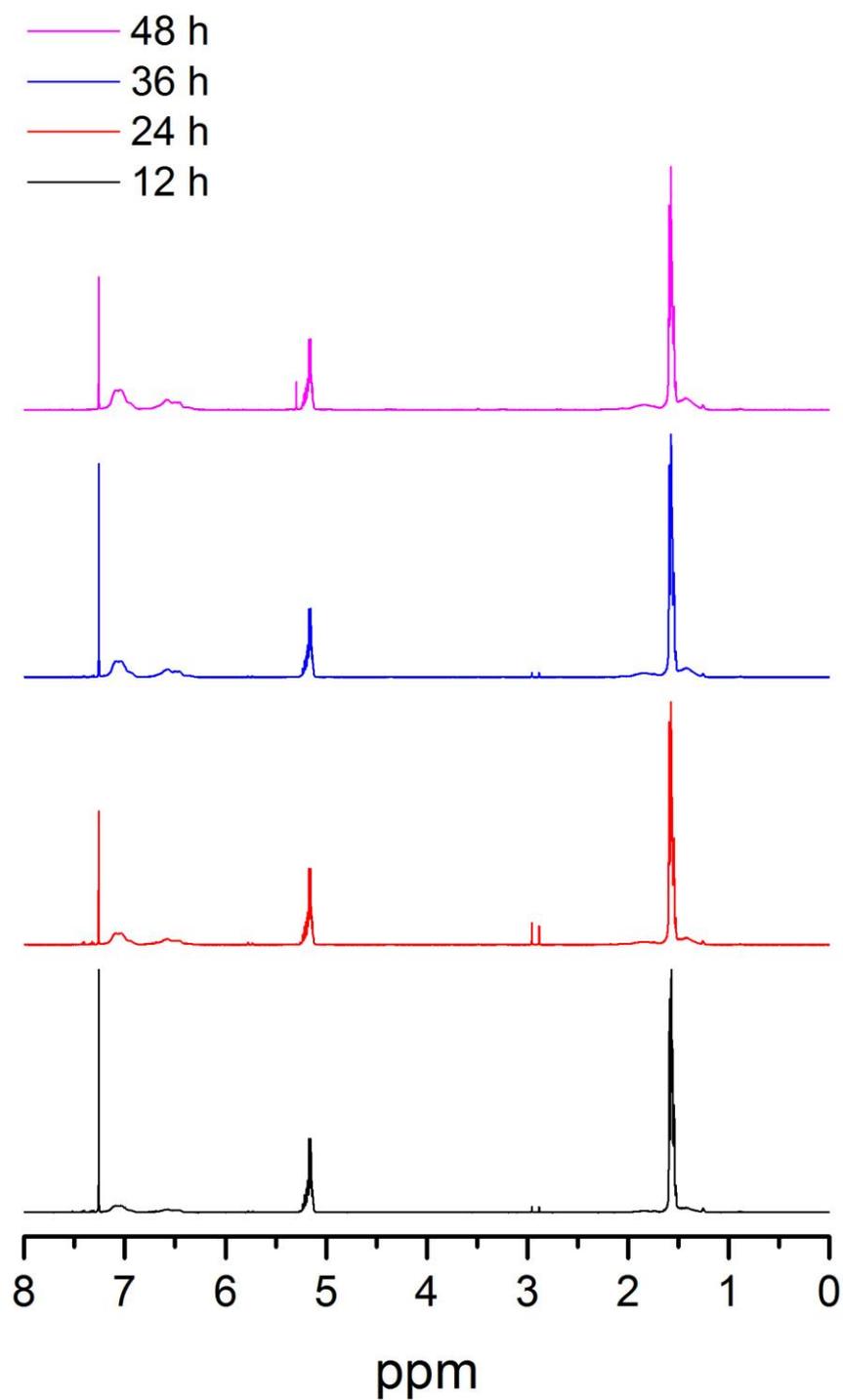


Figure S3. ¹H NMR spectra of PLAnPS_n obtained with different polymerization time (400 MHz, CDCl₃, 20 °C). Two small singlets at 3.0 – 2.8 ppm originate from residual DMF which was the reaction solvent.

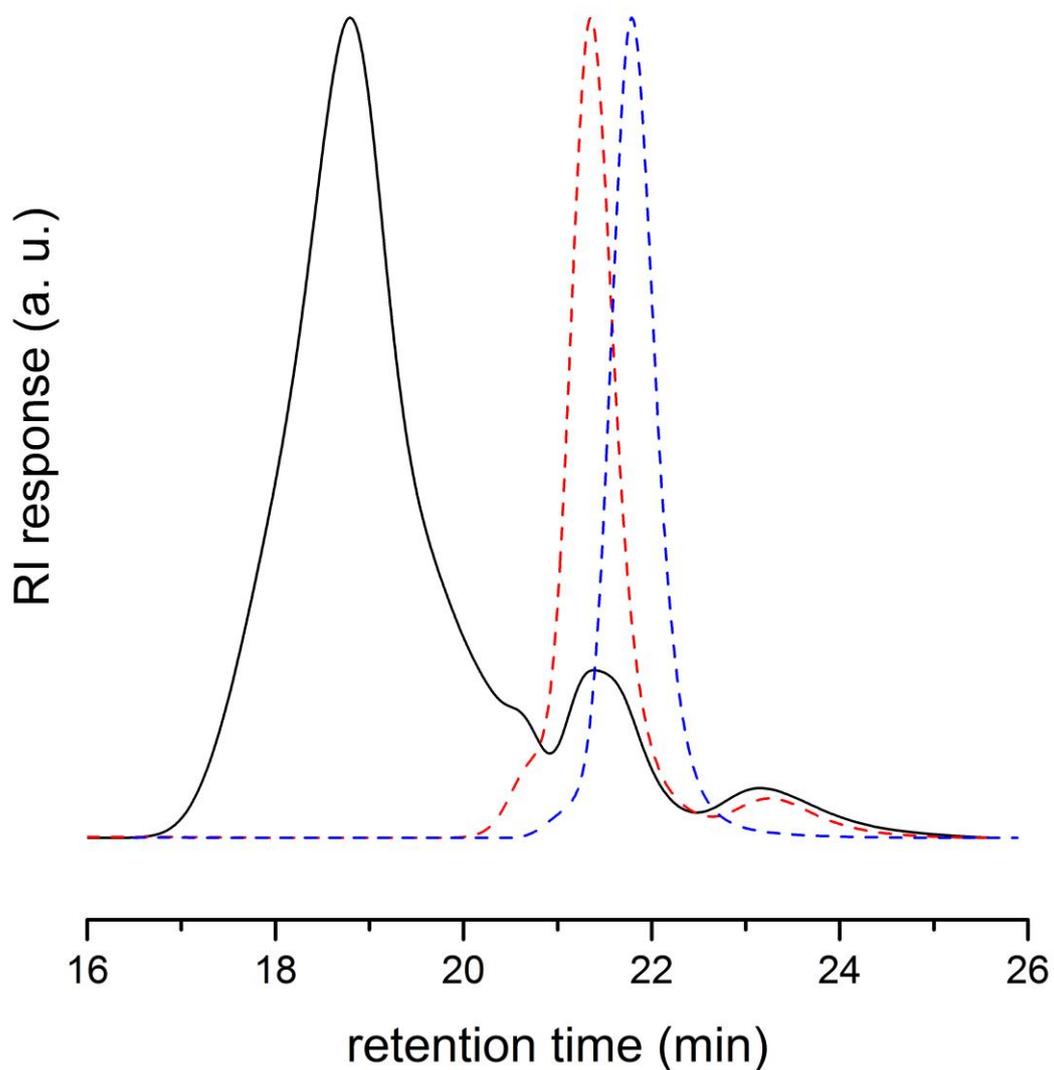


Figure S4. SEC traces of PLA-CTA (30 kg mol^{-1} , blue dashed line), linear PLA-b-PS which was obtained by polymerization of S in the presence of PLA-CTA ($[\text{S}]:[\text{PLA-CTA}] = 500:1$) at $60 \text{ }^\circ\text{C}$ for 24 h (red dashed line), and PLA_nPS_n (Entry 3 in Table 1, black solid line). The traces were recorded with a RI detector using chloroform as eluent at $35 \text{ }^\circ\text{C}$ with flow rate of 1 mL min^{-1} .

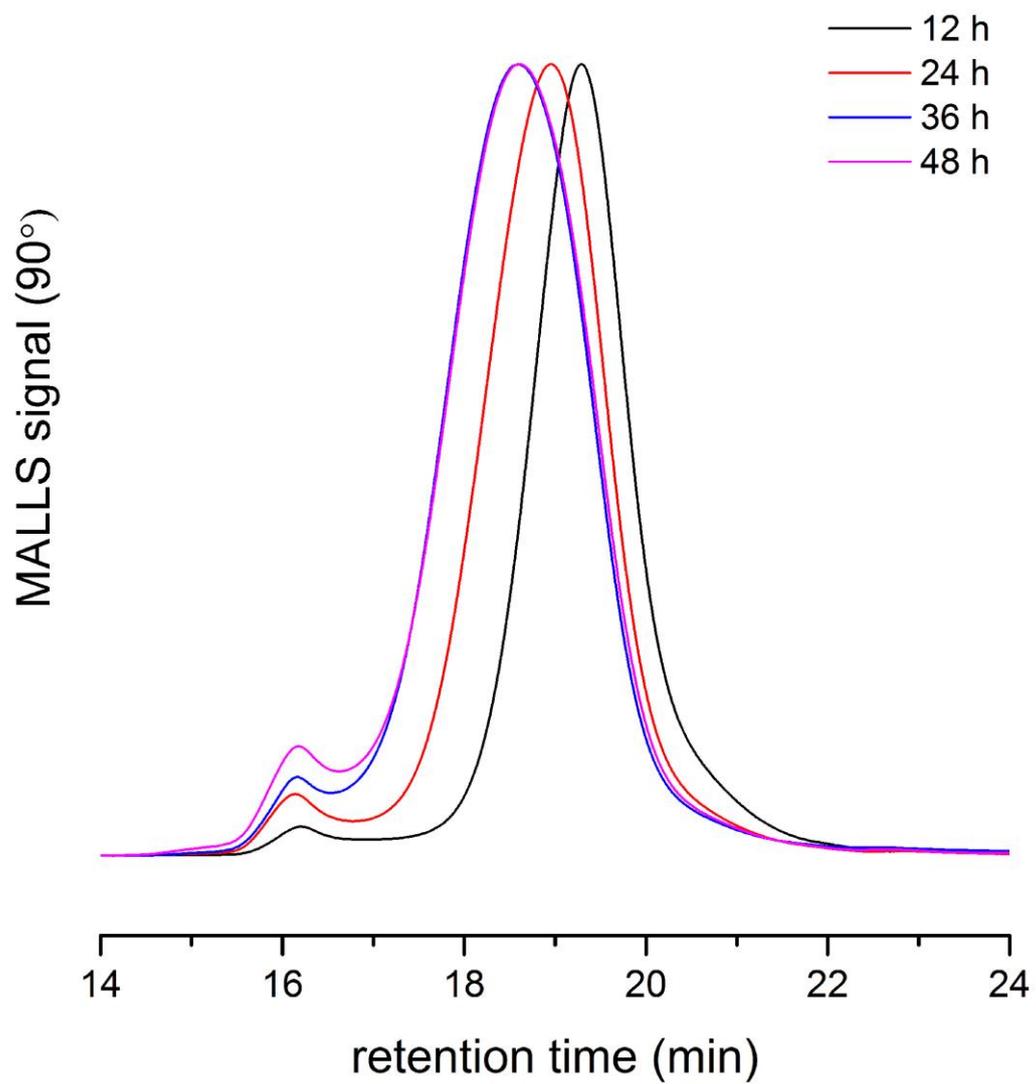


Figure S5. SEC traces of PLA_nPS_n shown in Table 1 recorded with a MALLS detector (THF, 40 °C, 1 mL min⁻¹).

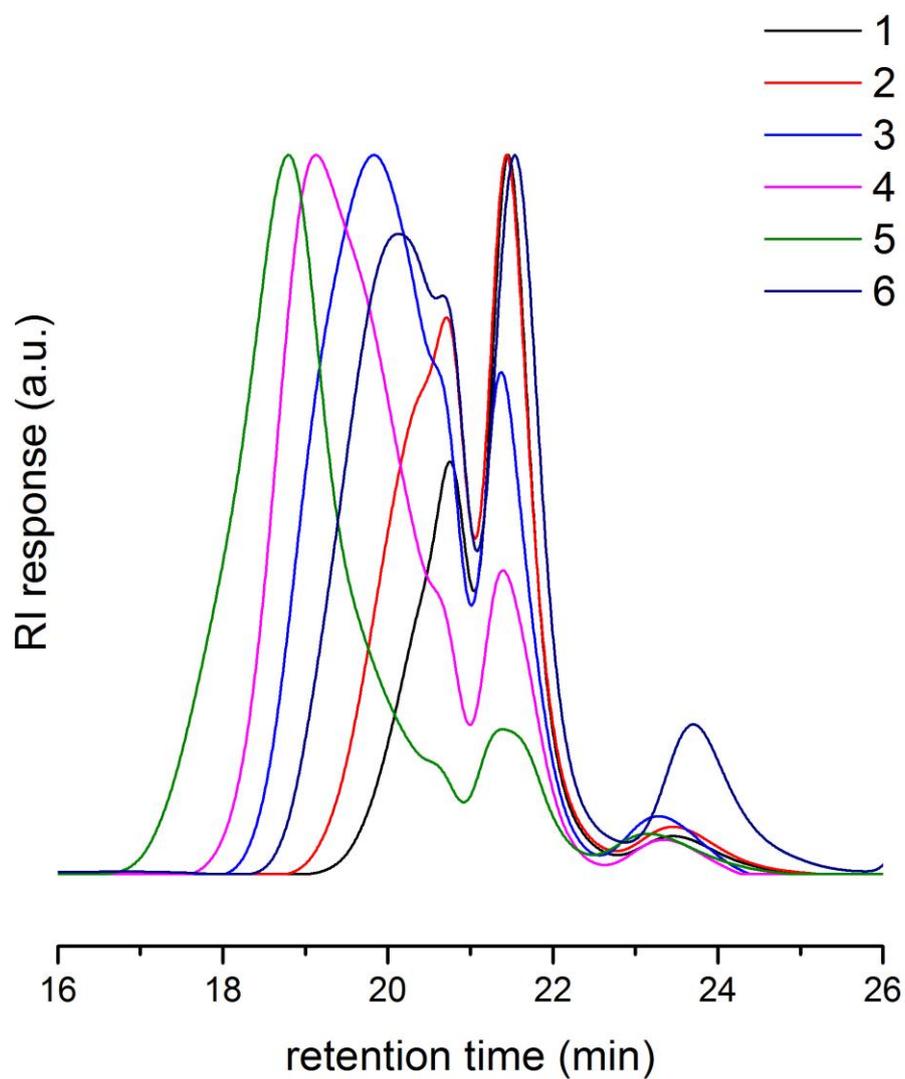


Figure S6. SEC traces of PLA-b-PSs obtained with different [S]:[BMI]:[PLA-CTA] ratios shown in Table S1. The number in the legend indicates the Entry number in Table S1.

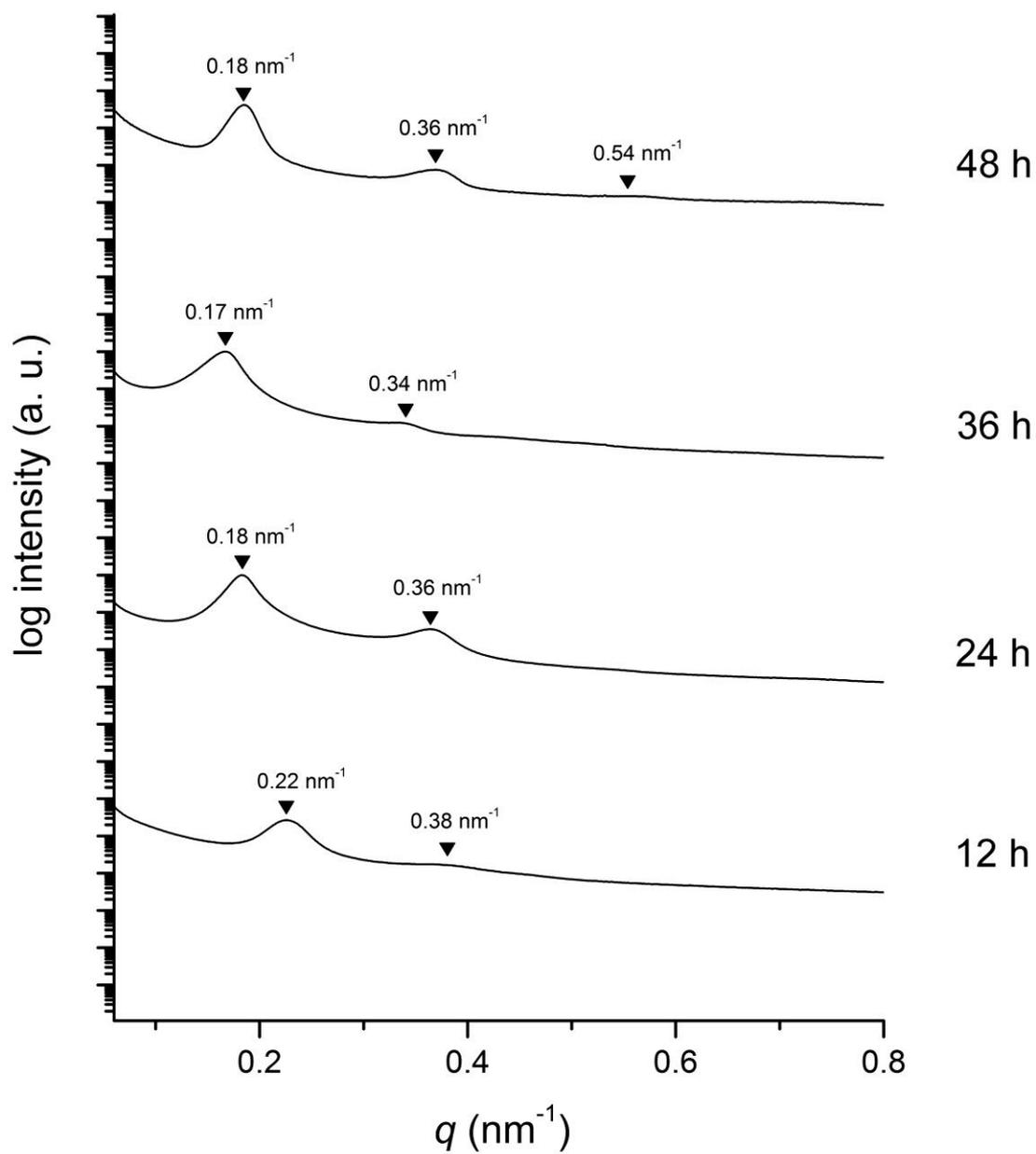


Figure S7. SAXS data of PLA_nPS_n shown in Table 1. The data was obtained from as-cast films from toluene solutions at rt.