Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Synthetic Route-Dependent Intramolecular Segregation in Heteroarm Core Cross-Linked Star Polymers as Janus-Like Nanoobjects

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This Information Includes:

Figure S1-S13

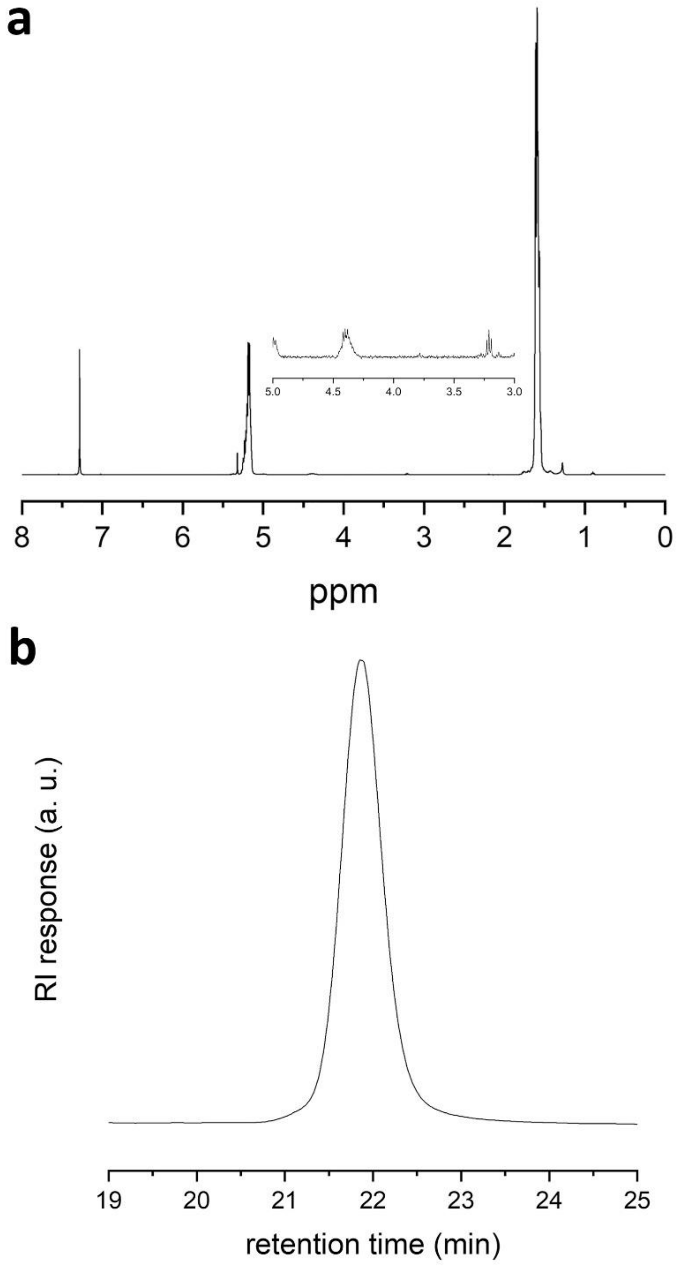

Figure S1. (a) ^{1}H NMR spectrum of PLA-CTA (400 MHz, CDCl$_3$, 20 °C). The inset shows a magnified spectrum of PLA-CTA in the range of 3-5 ppm used for M_n determination by end group analysis. (b) SEC trace of PLA-CTA (chloroform, 35 °C, 1 mL min^{-1}, RI detector).

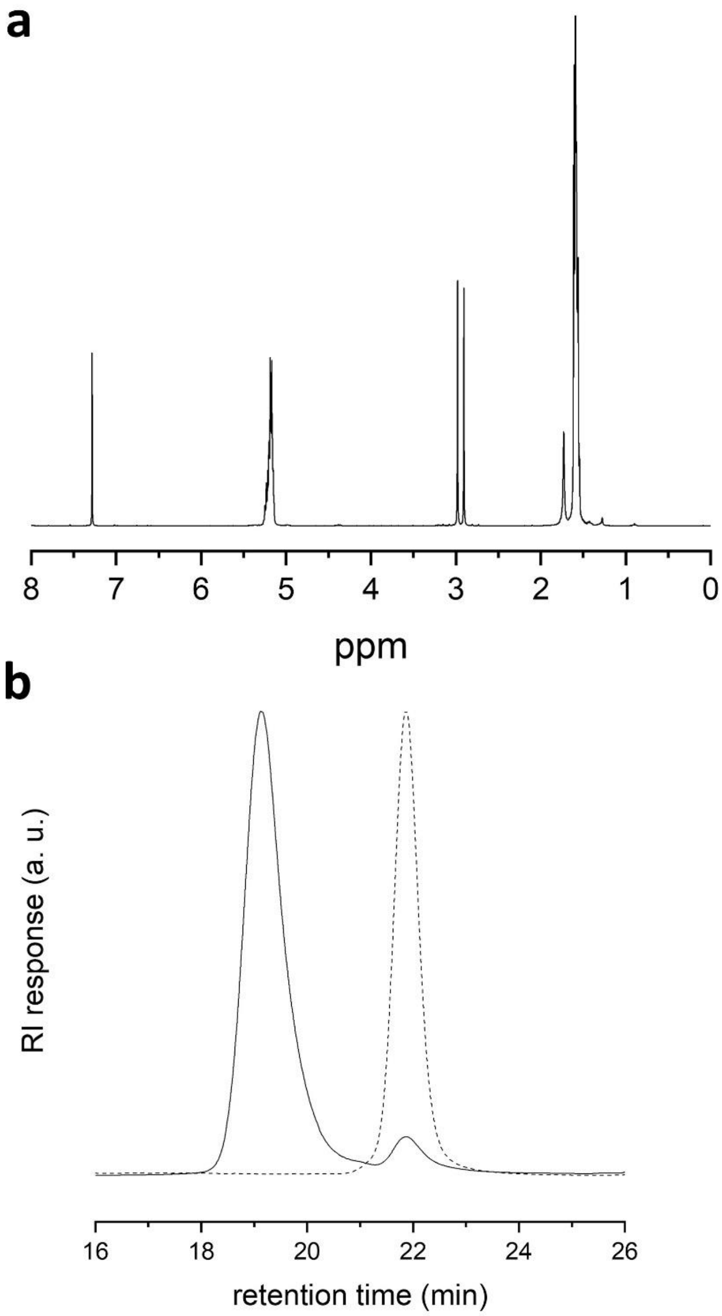

Figure S2. (a) ^{1}H NMR spectrum of PLA$_n$ (400 MHz, CDCl$_3$, 20 °C). (b) SEC traces of PLA$_n$ (solid line) and PLA-CTA (dashed line). The traces were recorded with a RI detector using chloroform as eluent at 35 °C with flow rate of 1 mL min^{-1}.

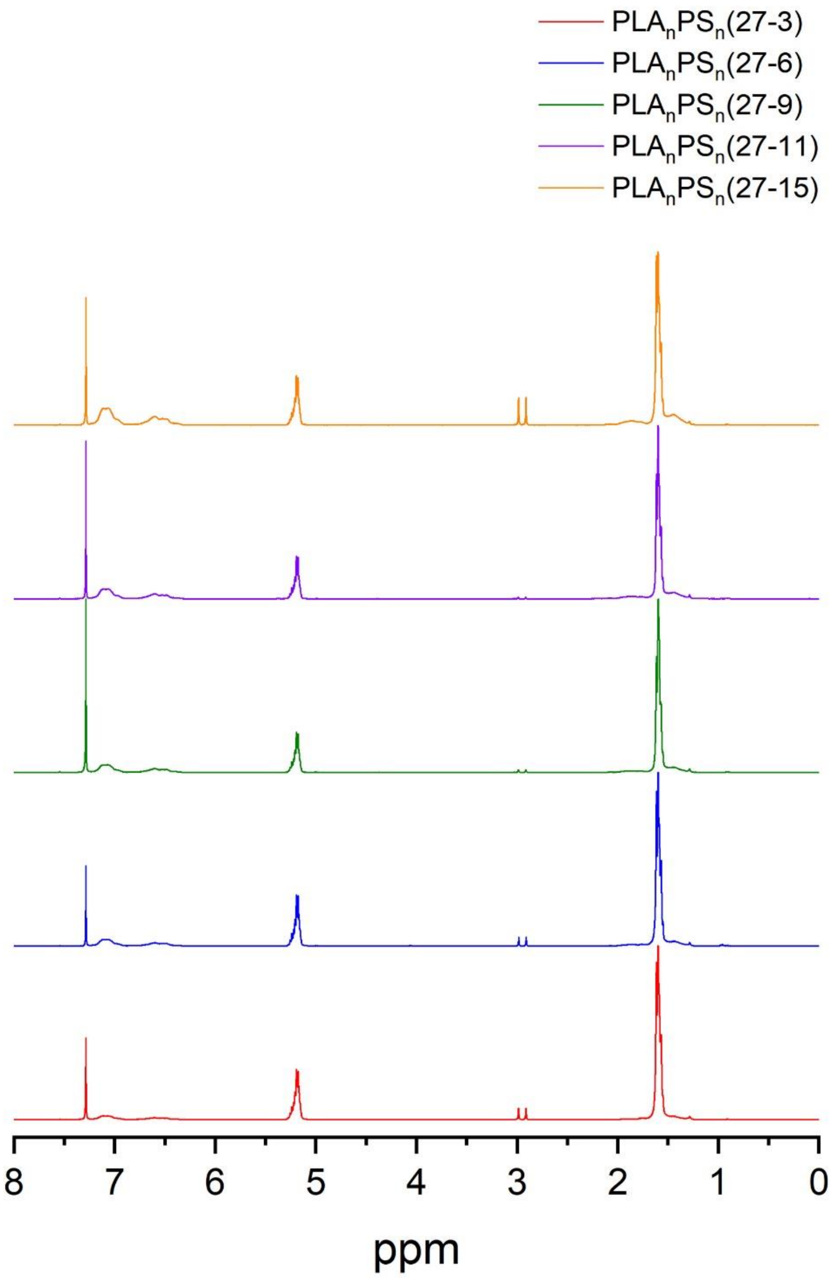

Figure S3. ^{1}H NMR spectra of PLA$_n$PS$_n$ obtained with different polymerization time via in-out approach (400 MHz, $CDCl_3$, 20 °C). Two small singlets appearing at 3.0 – 2.8 ppm originate from residual DMF which was the reaction solvent.

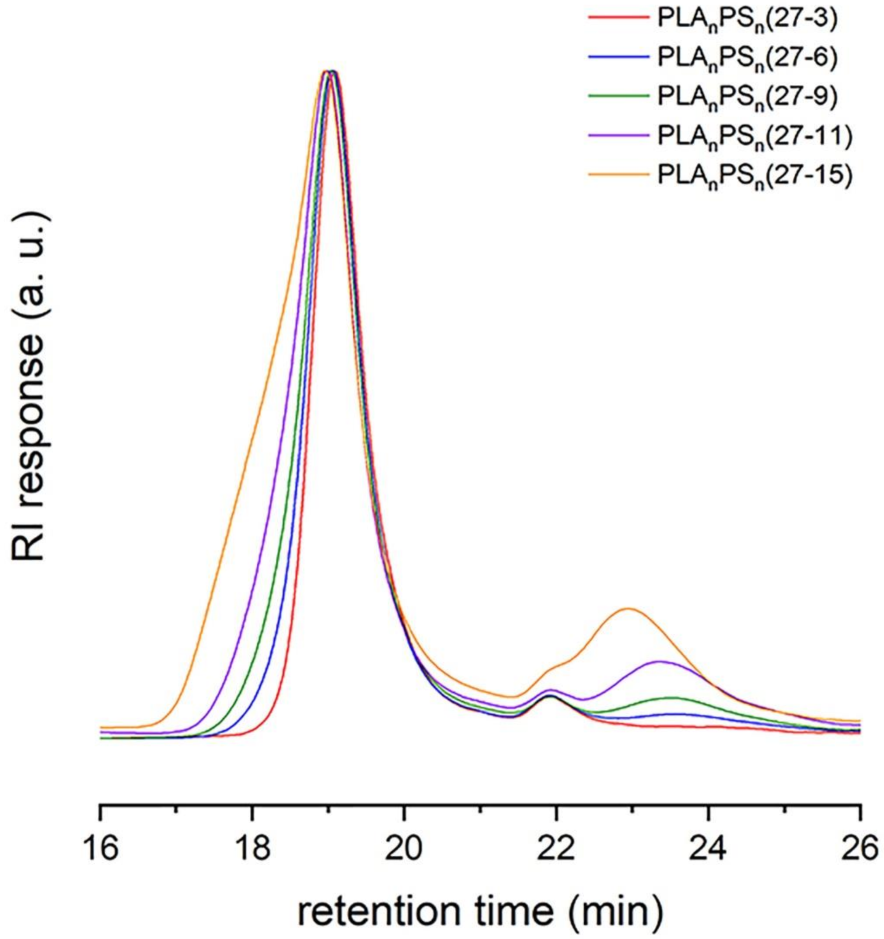

Figure S4. SEC overlay of PLA$_n$PS$_n$ obtained with different polymerization time via in-out approach prior to purification.

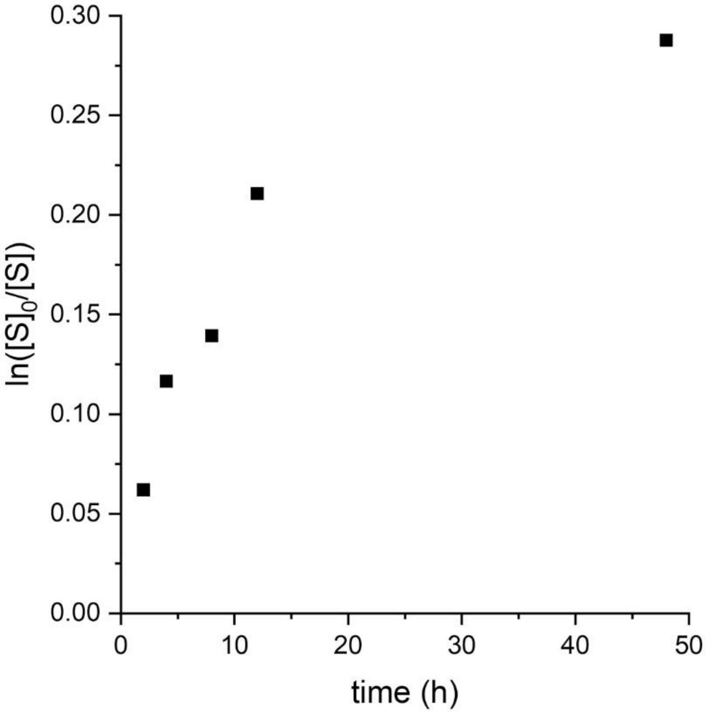

Figure S5. First-order kinetic plot with respect to styrene concentration.

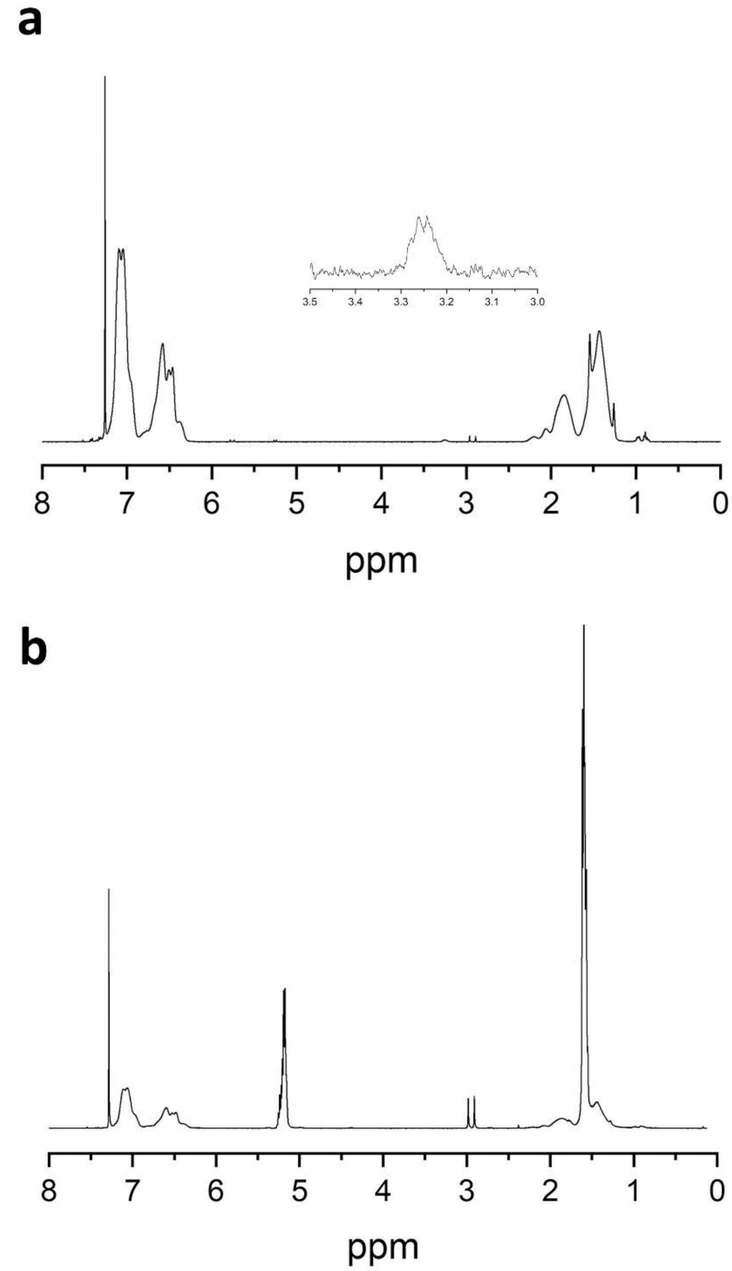

Figure S6. ^{1}H NMR spectra of (a) PS-CTA and (b) PLA$_n$PS$_n$(27-13)_Multi MI (400 MHz, CDCl$_3$, 20 °C). The inset in a shows a magnified spectrum of PS-CTA in the range of 3.2-3.3 ppm used for M_n determination by end group analysis.

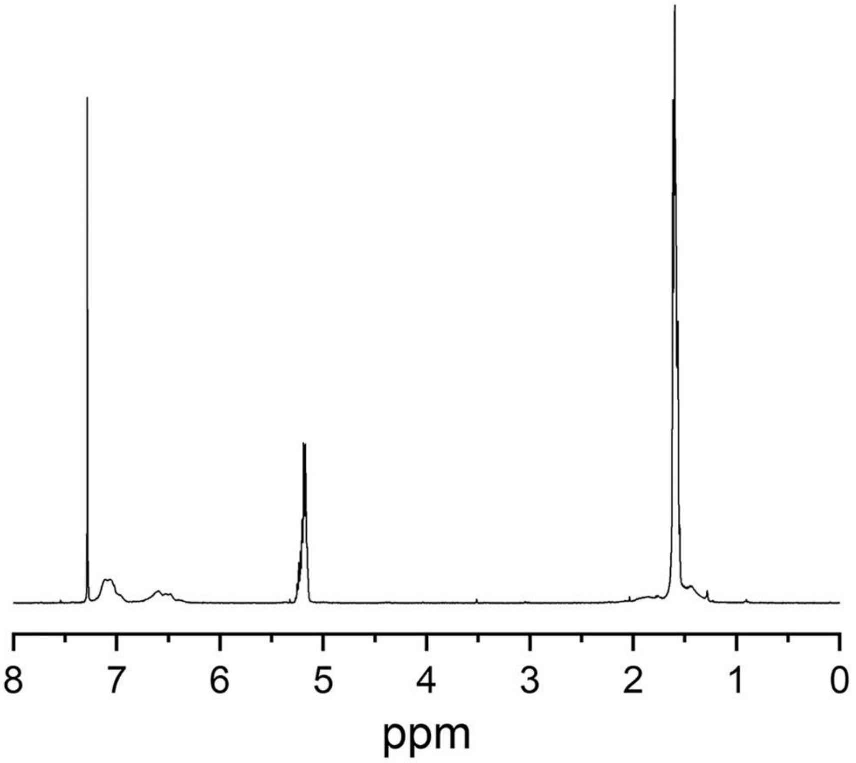

Figure S7. (a) ^{1}H NMR spectrum of PLA$_n$PS$_n$(27-7)_MeCN (400 MHz, CDCl$_3$, 20 °C).

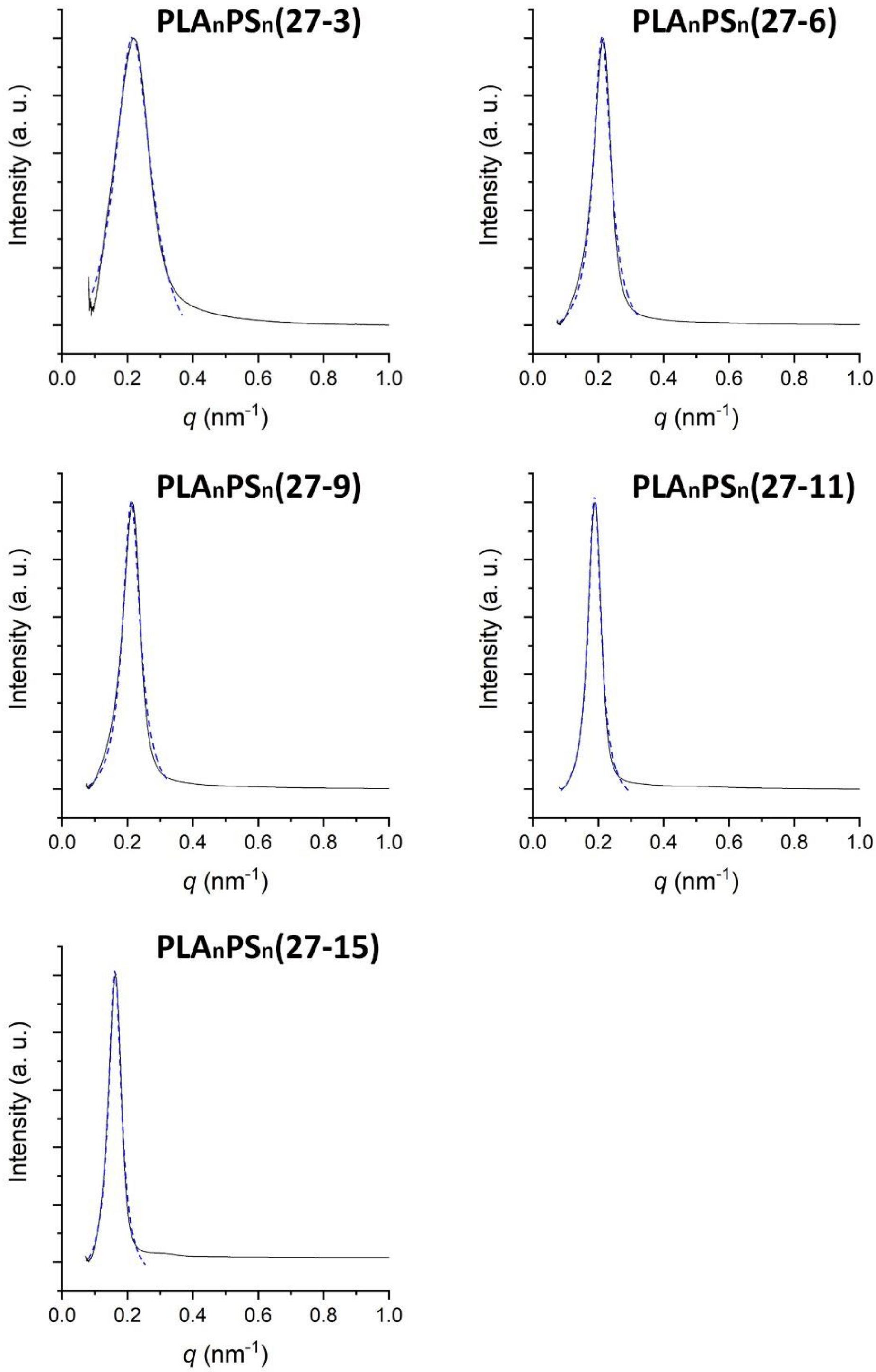

Figure S8. Lorentzian fitting of the SAXS principal peak of PLA$_n$PS$_n$ in toluene. The samples were obtained via the in-out route in DMF. The Lorentzian-fitted peak is shown as a blue dashed line.

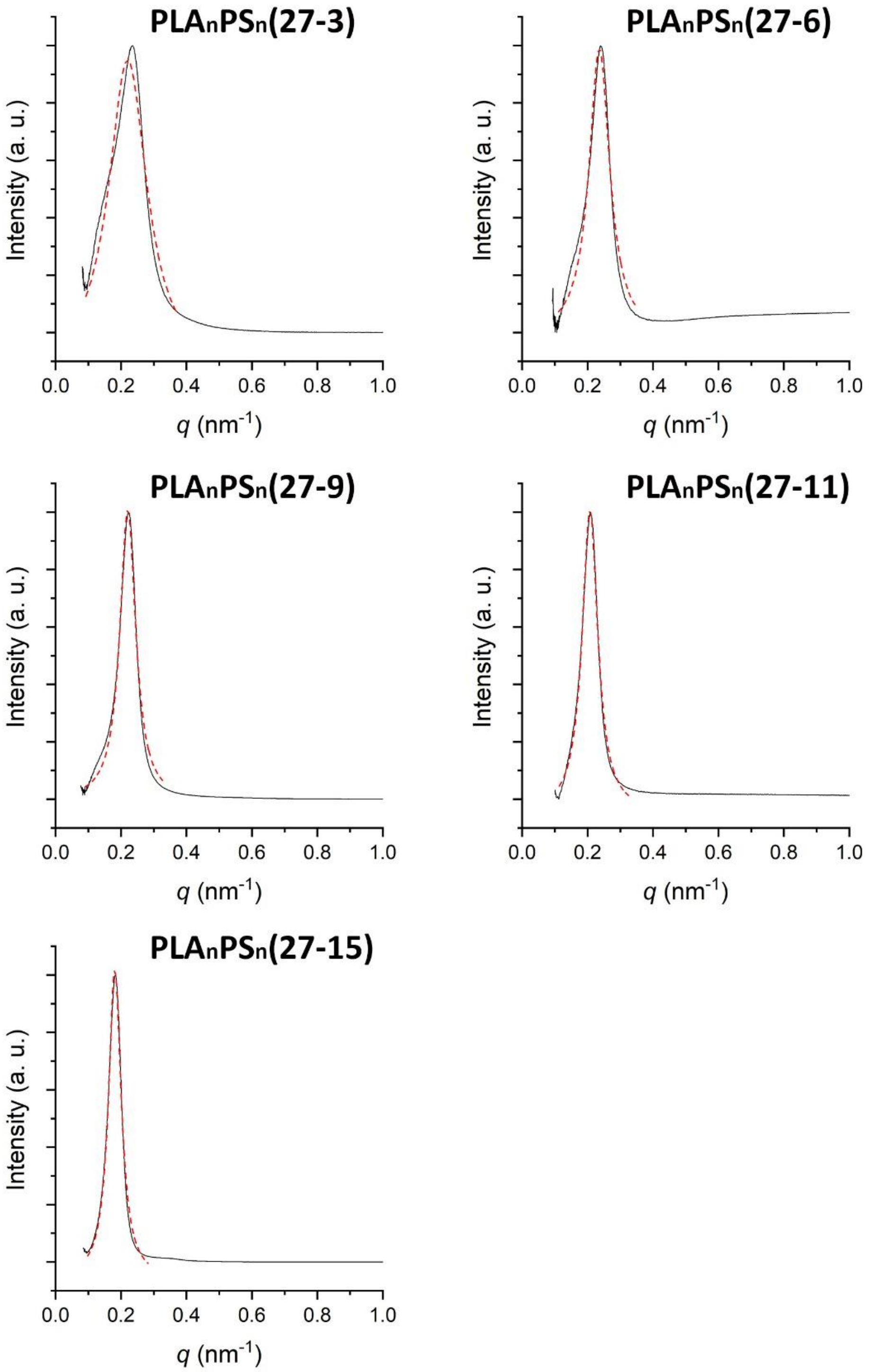

Figure S9. Lorentzian fitting of the SAXS principal peak of PLA_nPS_n in acetonitrile. The samples were obtained via the in-out route in DMF. The Lorentzian-fitted peak is shown as a red dashed line.

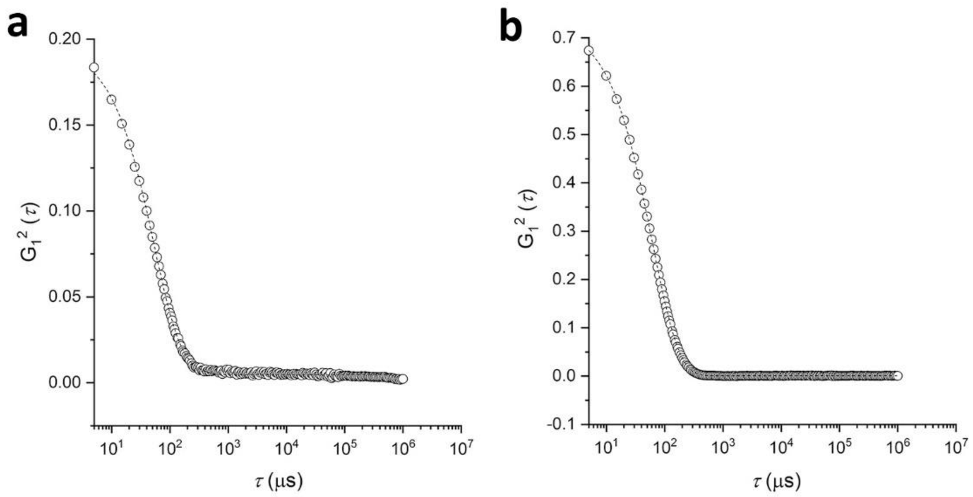

Figure S10. Autocorrelation functions of PLA_nPS_n(27-13)_Multi MI in toluene (a) and acetonitrile (b).

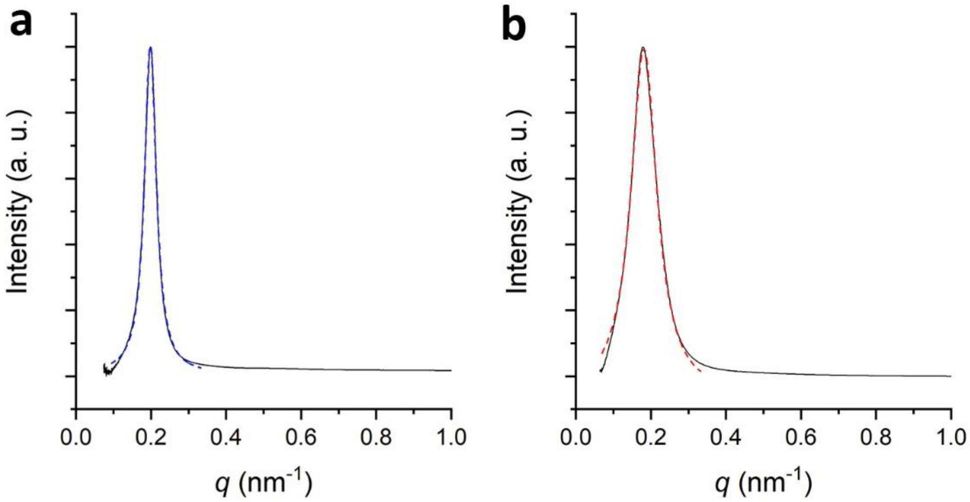

Figure S11. Lorentzian fitting of the SAXS principal peak of PLA_nPS_n(27-13)_Multi MI from toluene (a) and acetonitrile (b) solutions. The samples were obtained via the multi MI route in DMF. The Lorentzian-fitted peak is shown as a dashed line.

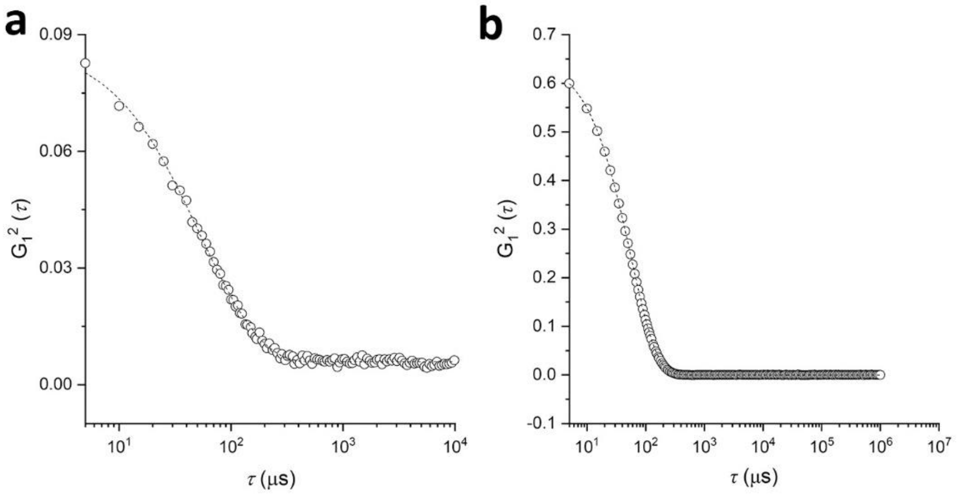

Figure S12. Autocorrelation functions of PLA$_n$PS$_n$(27-7)_MeCN in (a) toluene and (b) MeCN . Concentration of the solutions was 3 mg mL^{-1}.

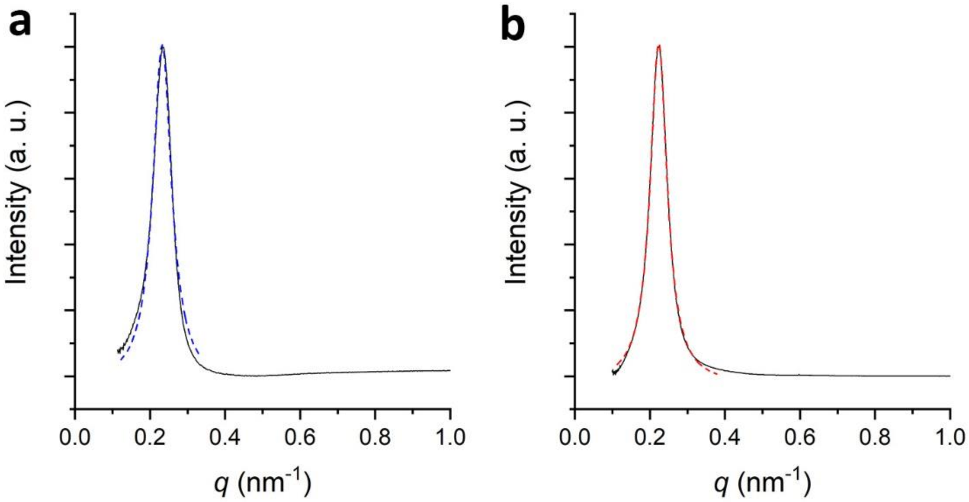

Figure S13. Lorentzian fitting of the SAXS principal peak of PLA$_n$PS$_n$(27-7)_MeCN from toluene (a) and acetonitrile (b) solutions. The samples were obtained via the in-out route in acetonitrile. The Lorentzian-fitted peak is shown as a dashed line.