Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Effect of poly[oligo(ethylene glycol) methyl ether methacrylate] side chain length on the swelling behavior in A/B/A-B ternary blends with polystyrene

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Materials Poly[oligo(ethylene glycol) methyl ether methacrylate]–*b*–polystyrene diblock copolymers ($POEGMA_x$-PS) are synthesized using reversible addition-fragmentation chain transfer polymerization (RAFT) as in our previous work.[1] Polystyrene was purchased from Scientific Polymer Products and used as received.

Synthesis of $POEGMA_x$ homopolymers

Synthesis of POEGMA homopolymers involved RAFT polymerization, followed by end-group removal. For POEGMA with different side chains, the synthesis only differs in the monomers employed. Here, we describe the synthesis of $POEGMA_1$ as an example. First, monomer 2-methoxyethyl methacrylate (8.00 g, 5.5 mmol) was mixed with the chain transfer agent (CTA) 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (0.81 g, 2.0 mmol) and azobisisobutyronitrile (AIBN) (0.033 g, 0.2 mmol) in a 100 mL round-bottom flask. After the addition of dioxane (24 mL), the flask was sealed by with a septum and purged under argon for 40 min. The mixture was then heated to 70 °C and left to react for 16 h. After quenching in liquid N_2, the product was purified 3 times by precipitating in hexane. The purified homopolymers (2.5 g) were then mixed with AIBN (0.32 g, 1.9 mmol) and dissolved in 100 mL dioxane in a sealed 250 mL round-bottom flask. Following a 1 h purge under argon, tributyltin hydride (6.5 g, 2.2 mmol) was added to the mixture by a syringe. The reaction was then conducted at 70 °C for 2.5 h and the yellow color of the solution faded in 30 min. The resulting $POEGMA_1$ was purified by precipitation in hexane 3 times then freeze-dried in benzene overnight.

Supplementary Table and Figures

Nuclear magnetic resonance (NMR) spectroscopy

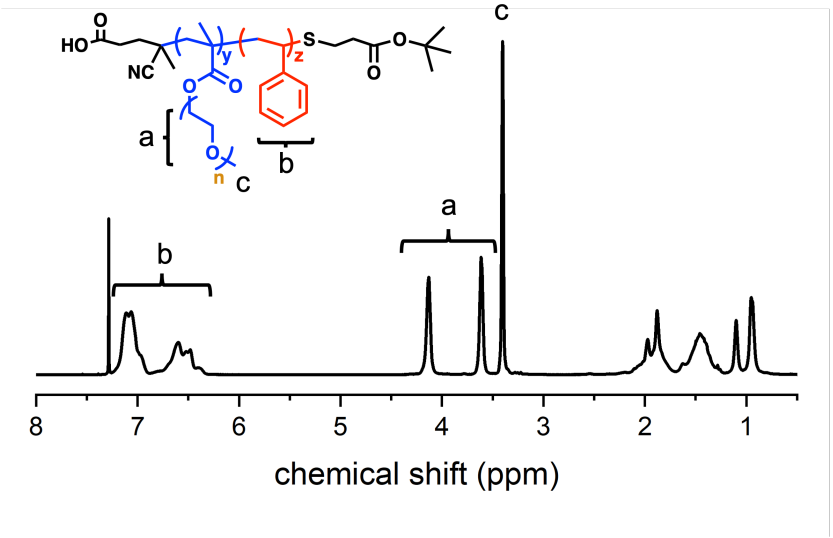

Figure S1. ^{1}H-NMR spectrum for POEGMA$_1$-PS in $CDCl_3$.

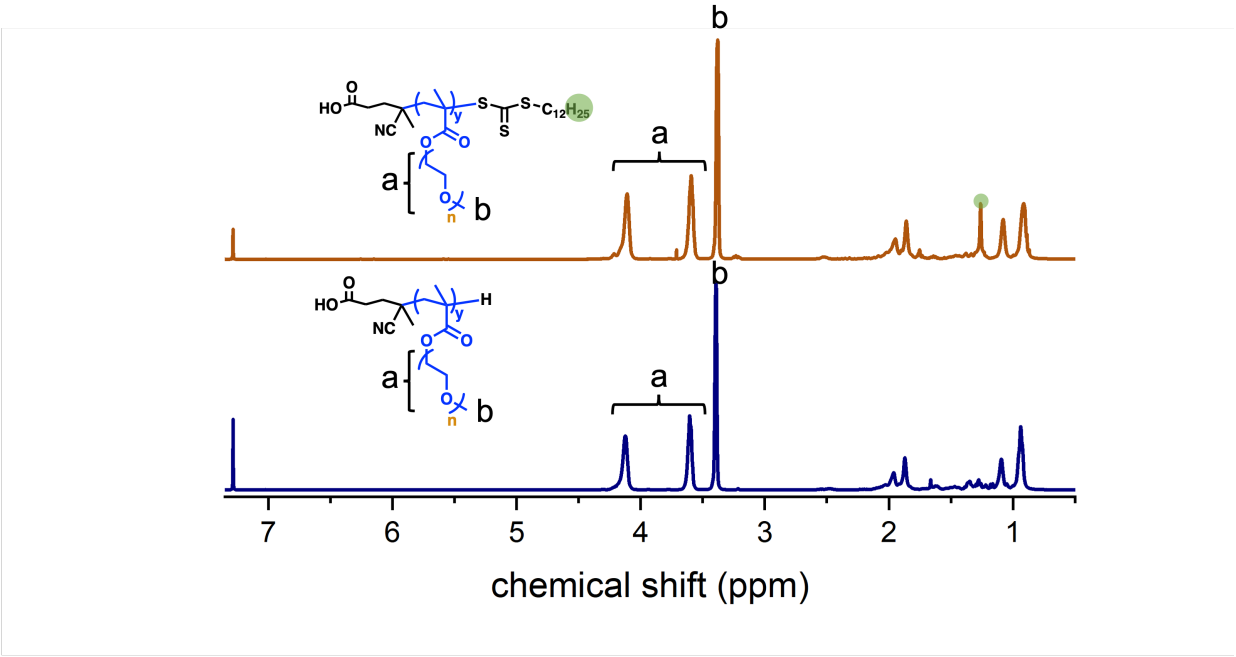

Figure S2. ^{1}H-NMR spectrum for POEGMA$_1$ in $CDCl_3$ before and after end group removal.

Size exclusion chromatography (SEC)

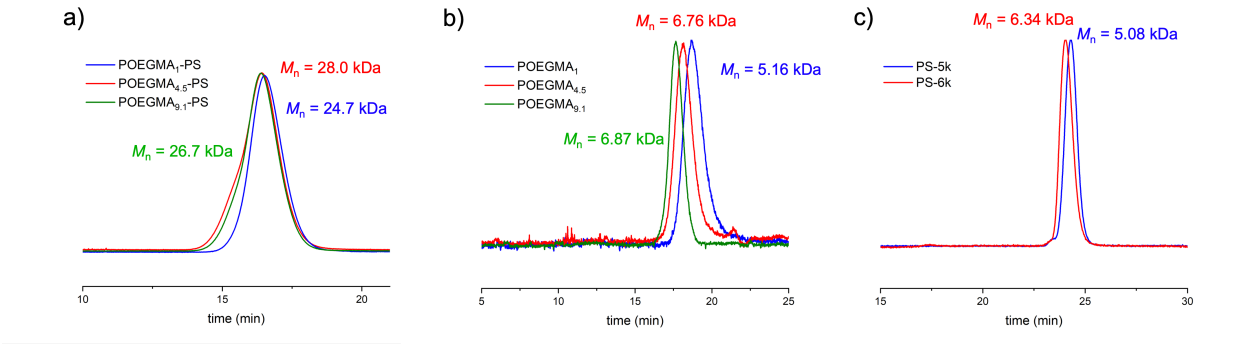

Figure S3. SEC LS traces for a) POEGMA$_x$-PS block polymers, b) POEGMA$_x$ homopolymers, c) polystyrene homopolymers.

Small-angle X-ray scattering (SAXS) patterns

POEGMA$_1$-PS/POEGMA$_1$/PS (T1)

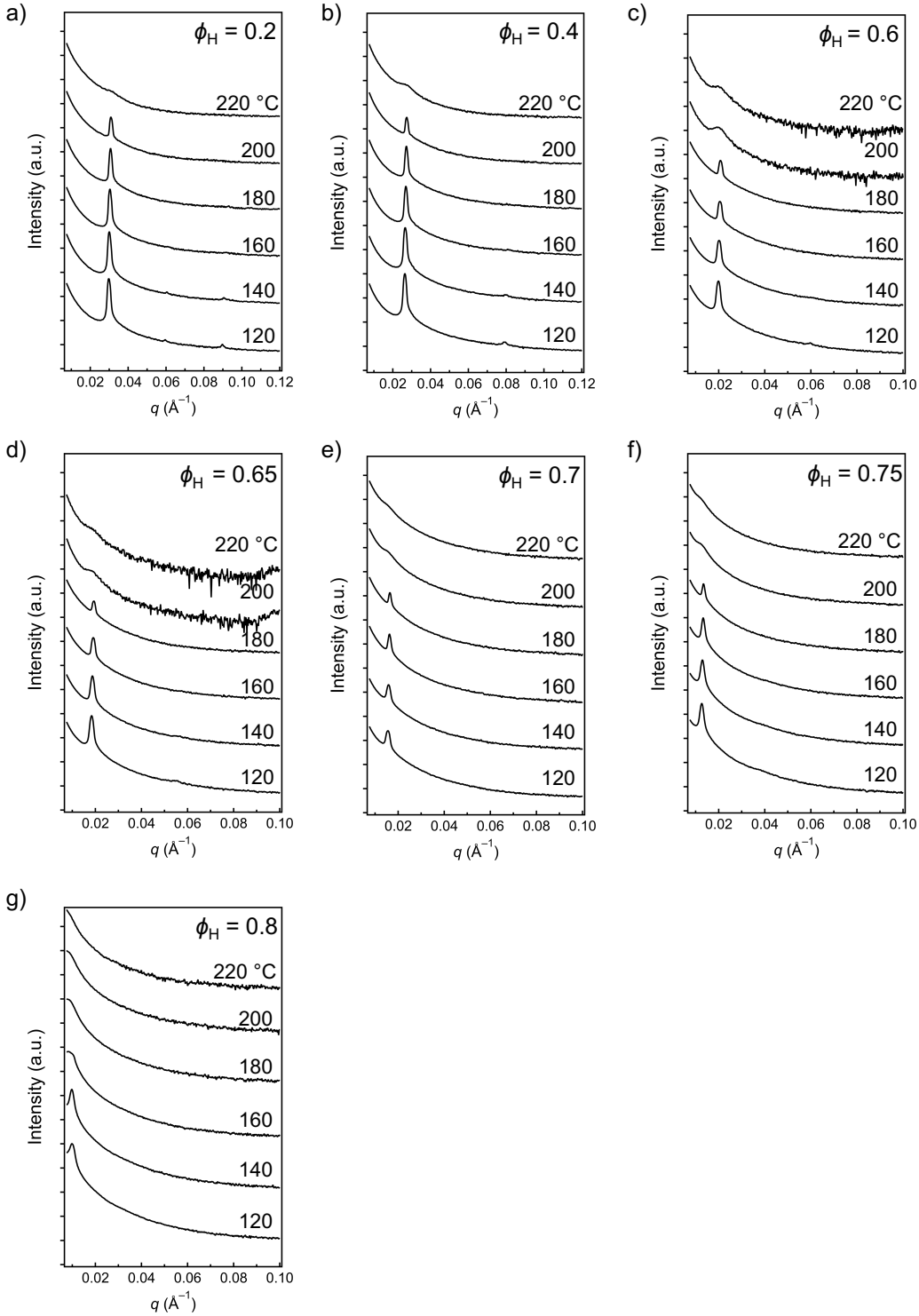

Figure S4. Scattering patterns for T1 at 120, 140, 160, 180, 200 and 220 °C along the volumetrically symmetric isopleth ($\phi_{POEGMA1}$ /ϕ_{PS} = 1) at different compositions.

POEGMA$_{4.5}$-PS/POEGMA$_{4.5}$/PS (T2)

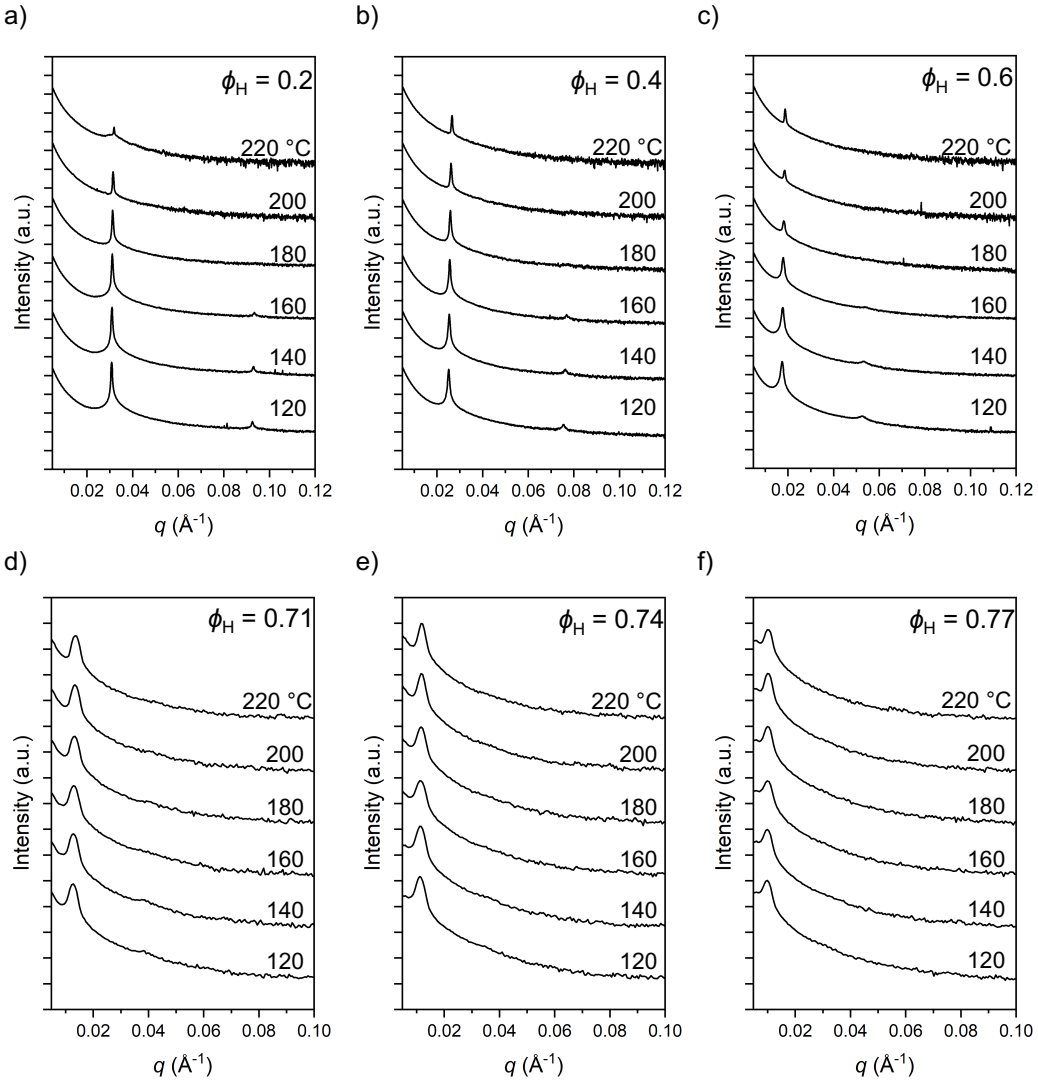

Figure S5. Scattering patterns for T2 at 120, 140, 160, 180, 200 and 220 °C along the volumetrically symmetric isopleth ($\phi_{POEGMA4.5}$ / ϕ_{PS} = 1) at different compositions.

POEGMA$_{9.1}$-PS/POEGMA$_{9.1}$/PS (T3)

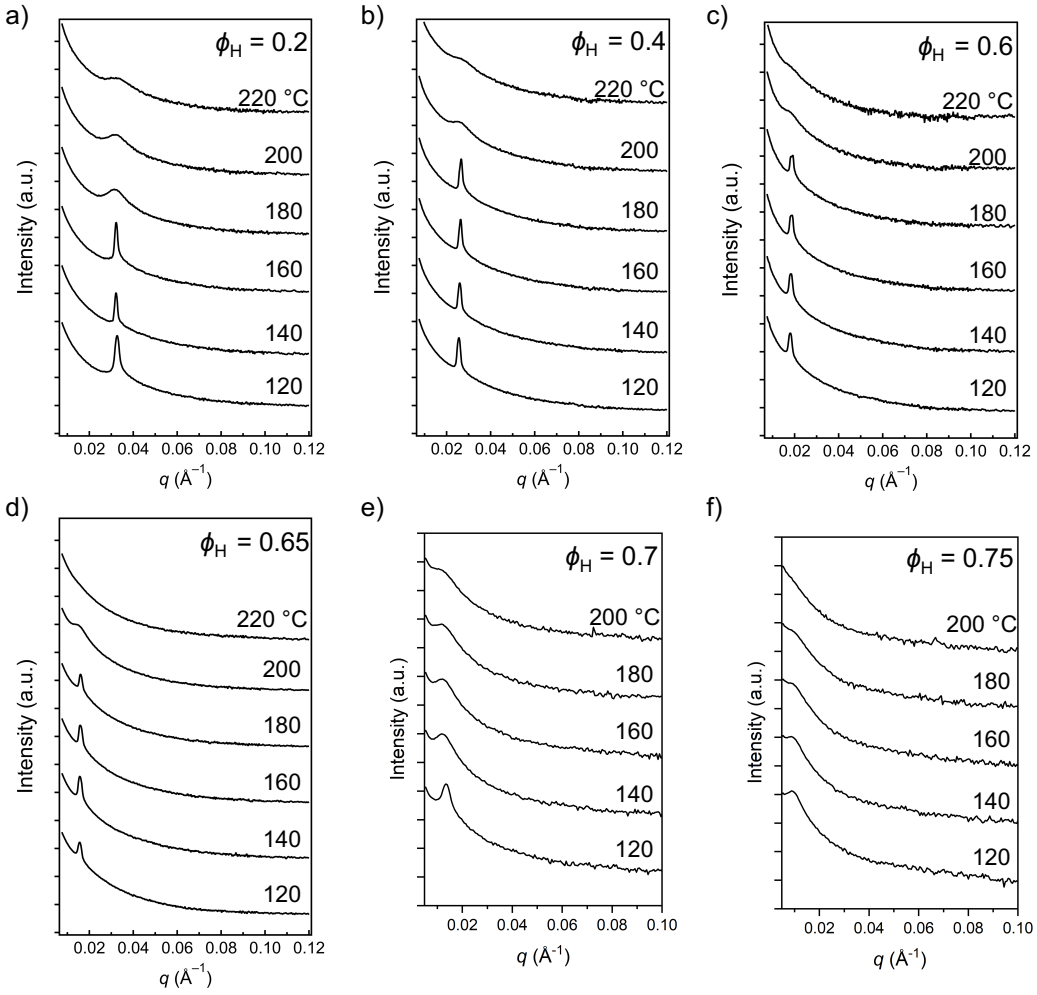

Figure S6. Scattering patterns for T3 at 120, 140, 160, 180, 200 and 220 °C along the volumetrically symmetric isopleth ($\phi_{POEGMA9.1}$ /ϕ_{PS} = 1) at different compositions.

References

(1) Zheng, C.; Zhang, B.; S. Bates, F.; P. Lodge, T. Self-Assembly of Partially Charged Diblock Copolymer-Homopolymer Ternary Blends. *Macromolecules* **2022**, *55*, 4766–4775