

Supporting Information

Figure S1. Characterization data for the modification steps performed to obtain star-shaped $[\text{PEO}_{28}\text{-N}_3]_8$ via: (A) reaction scheme for the tosylation and azidation of $[\text{PEO}_{28}\text{-OH}]_8$ and the characterization via: (B) ATR-FT-IR; (C) $^1\text{H-NMR}$ $[\text{PEO}_{28}\text{-OH}]_8$ (black curve), $[\text{PEO}_{28}\text{-Ts}]_8$ (red curve), and $[\text{PEO}_{28}\text{-N}_3]_8$ (blue curve); (D) SEC (DMAC) of $[\text{PEO}_{28}\text{-OH}]_8$ (dashed line) and $[\text{PEO}_{28}\text{-N}_3]_8$ (solid line).

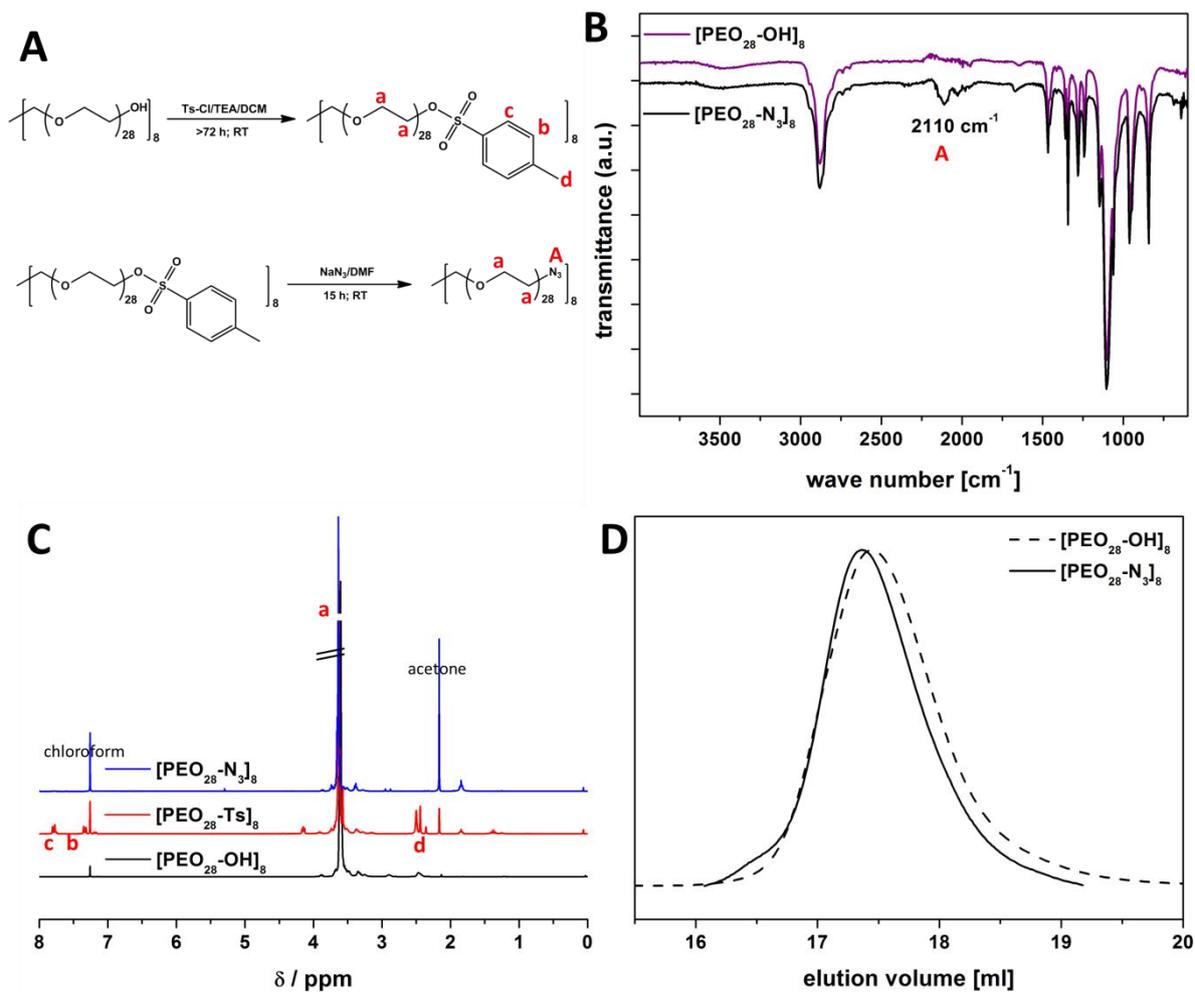


Figure S2. LCCC chromatograms at the critical conditions of PEO standards from PSS ($\text{H}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ (mobile phase composition acetonitrile and water (55/45, v/v))).

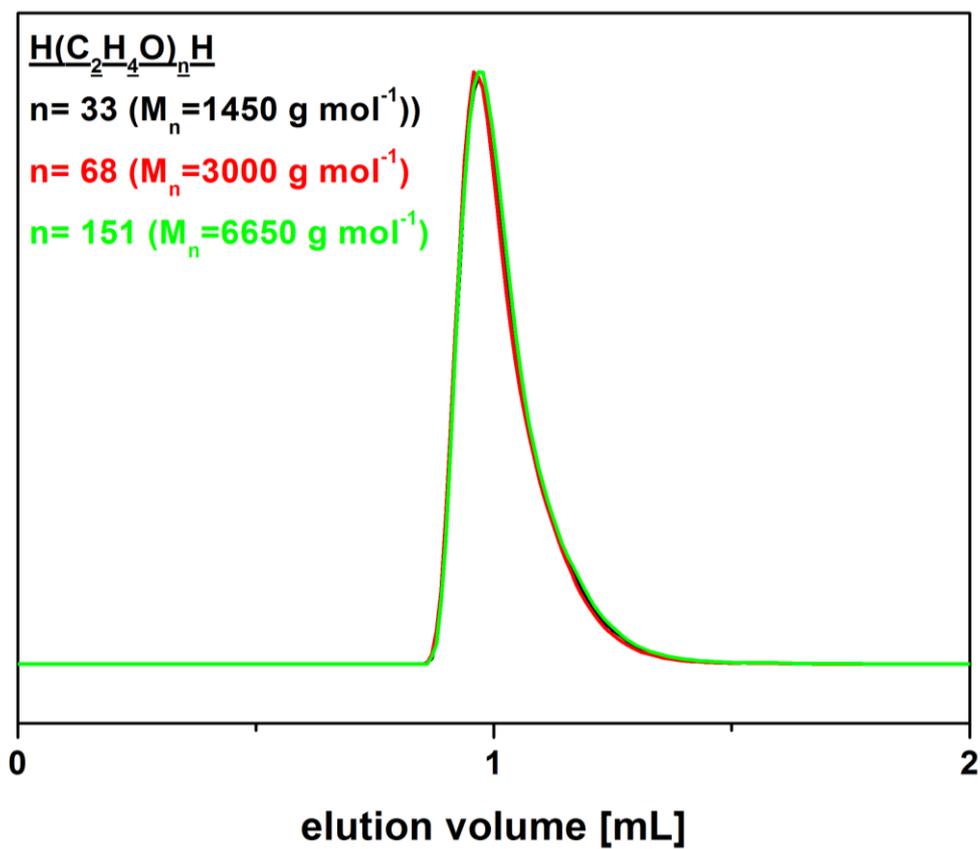


Figure S3. Comparison of 2D-LC results obtained for [PEO₂₈-N₃]₈ after different times in solution; (A) freshly prepared; (B) 30 min after preparation; (C) stored overnight in ACN/H₂O mixture of the eluent; *y*-axis elution at critical conditions (LCCC), *x*-axis SEC mode.

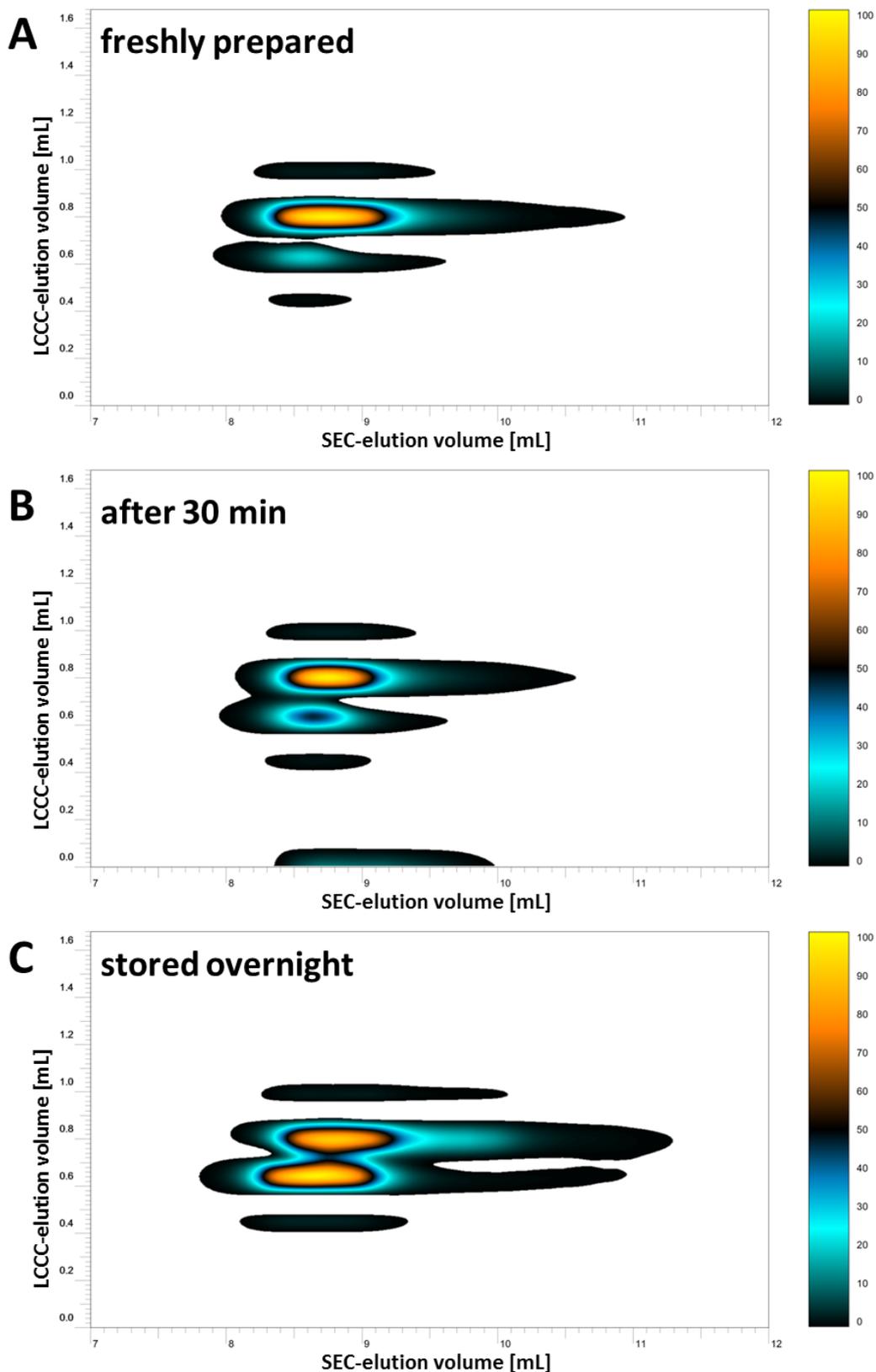


Figure S4. Comparison of characteristic signals in the ^{13}C -NMR spectra for $[\text{PEO}_{28}\text{-OH}]_8$ (black), $[\text{PEO}_{28}\text{-Ts}]_8$ (red), and $[\text{PEO}_{28}\text{-N}_3]_8$ (blue); (A) backbone $-\text{CH}_2-$ groups; (B) $-\text{CH}_2\text{-OH}$; (C) $-\text{CH}_2\text{-N}_3$.

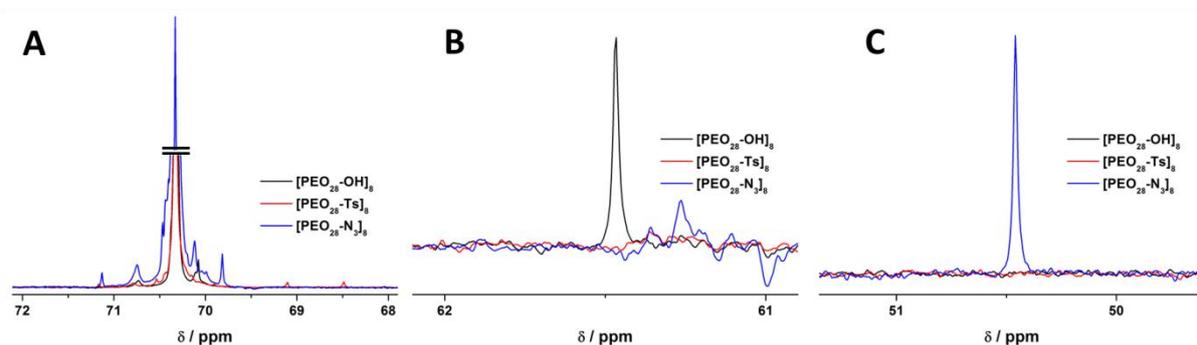


Figure S5. Schematic representation of the CROP of 2-ethyl-2-oxazoline initiated by $[\text{PEO}_{28}\text{-Ts}]_8$.

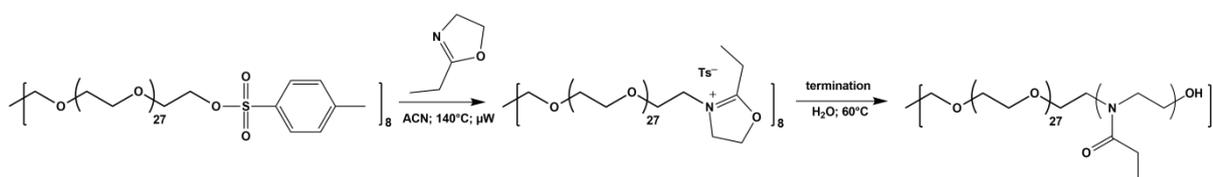


Figure S6. SEC traces for TB-PEtOx₂₀-OH (straight line), TB-PEtOx₆₀-OH (dashed line), and TB-PEtOx₈₀-OH (dotted line) on the chloroform (A) and dimethylacetamide (B) SEC.

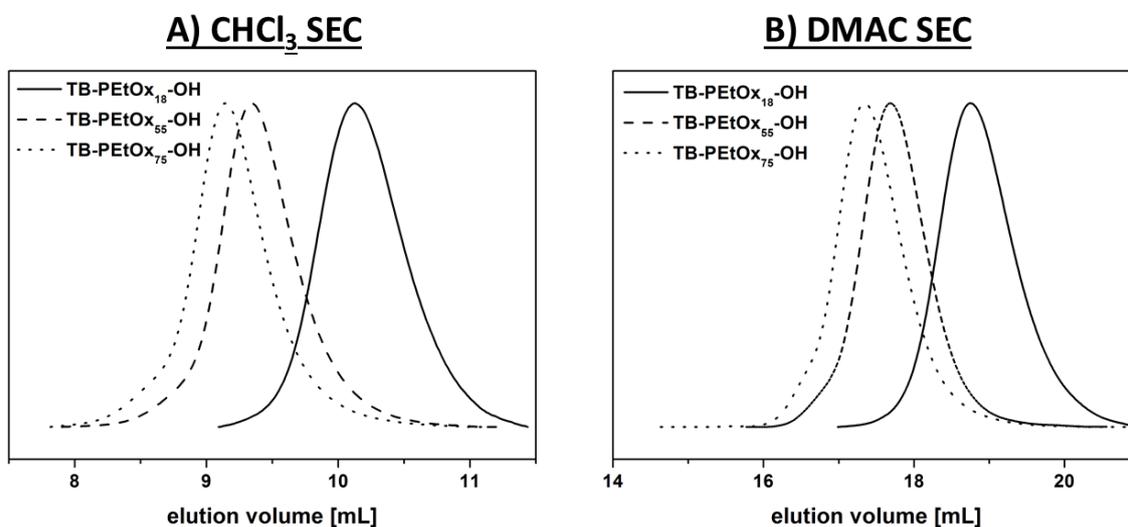


Figure S7. Characterization of the star-shaped block copolymer $[\text{PEO}_{28}\text{-}b\text{-PEtOx}_{55}]_8$ via: (A) NMR and (B) ATR-FT-IR.

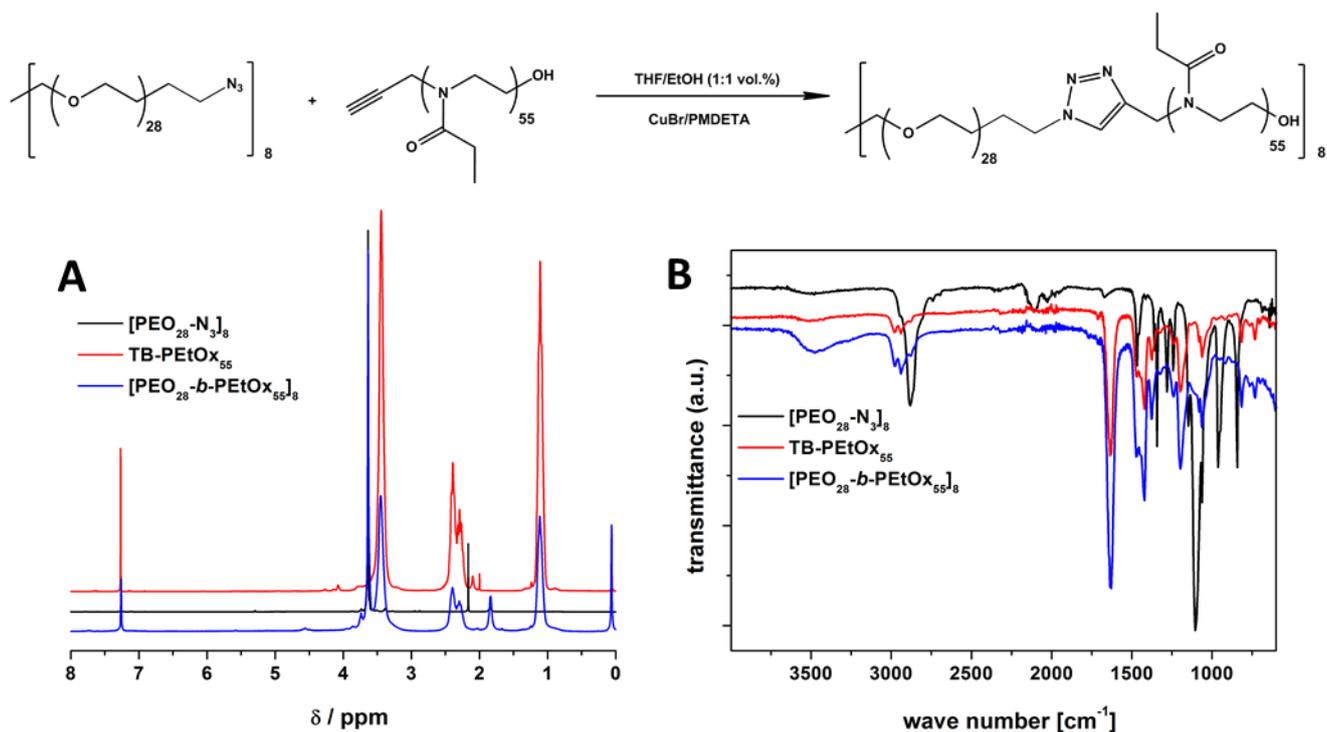
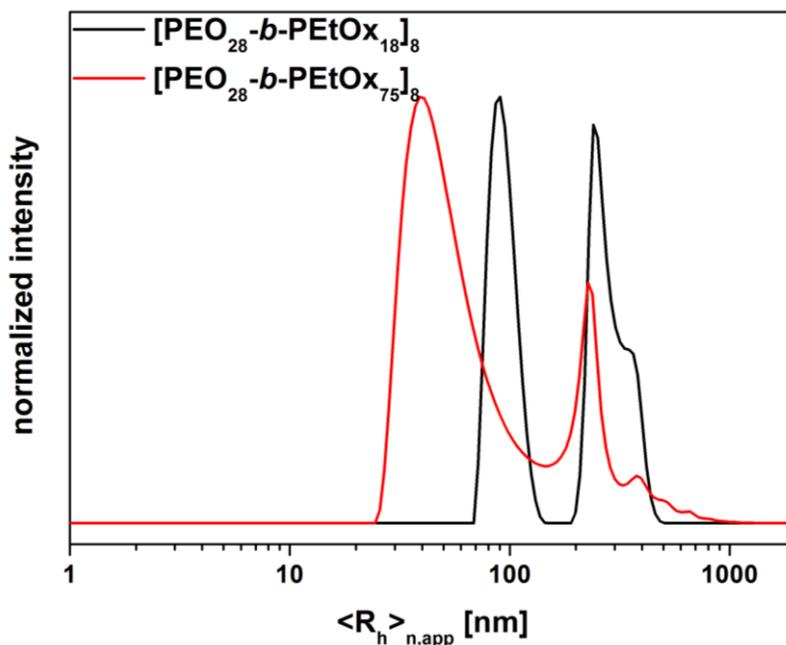


Figure S8. DLS CONTIN plots of the unfiltered samples of $[\text{PEO}_{28}\text{-}b\text{-PEtOx}_{18}]_8$ (black curve) and $[\text{PEO}_{28}\text{-}b\text{-PEtOx}_{75}]_8$ (red curve) in water.



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