Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

One-pot synthesis of PLA-*b*-PHEA *via* sequential ROP and RAFT polymerizations

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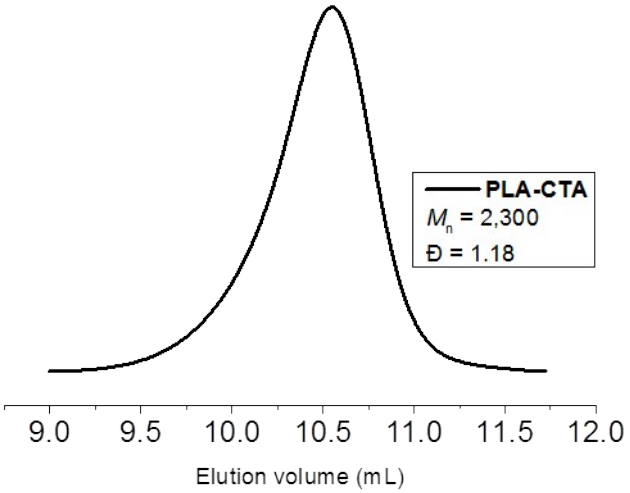

Figure S1. SEC trace of the isolated **PLA-CTA** (THF, RI detection, PLA calibration).

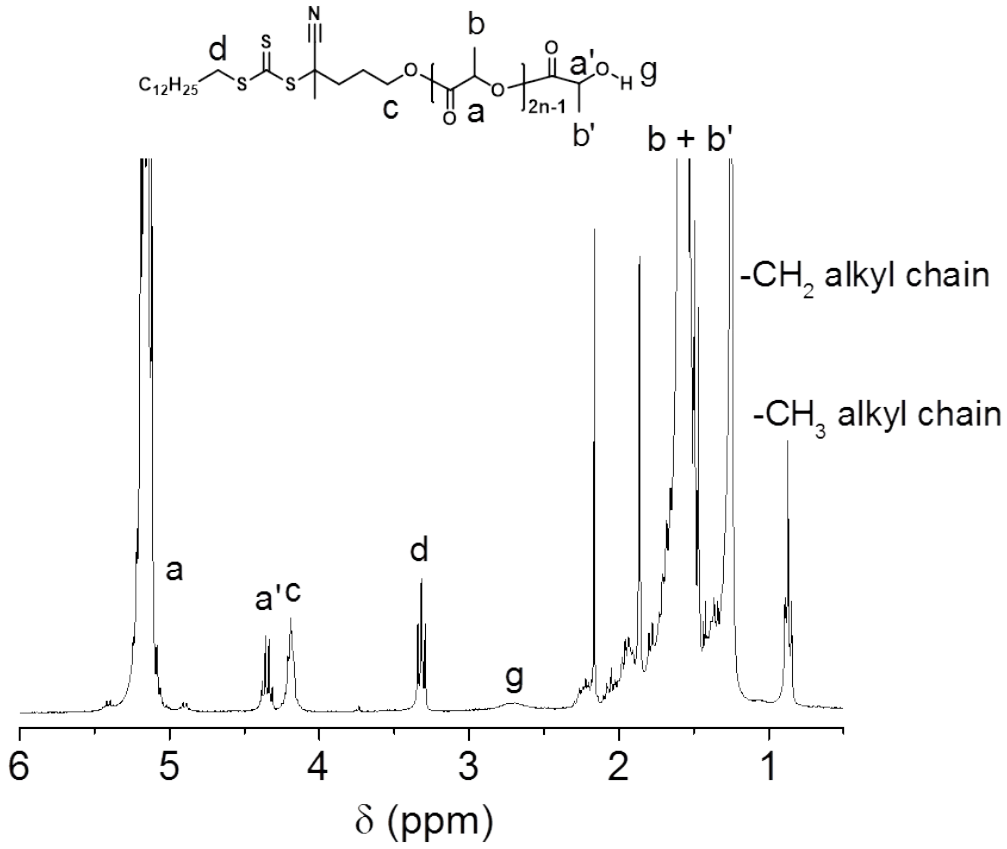

Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of the isolated **PLA-CTA** together with the assignment of the observed peaks.

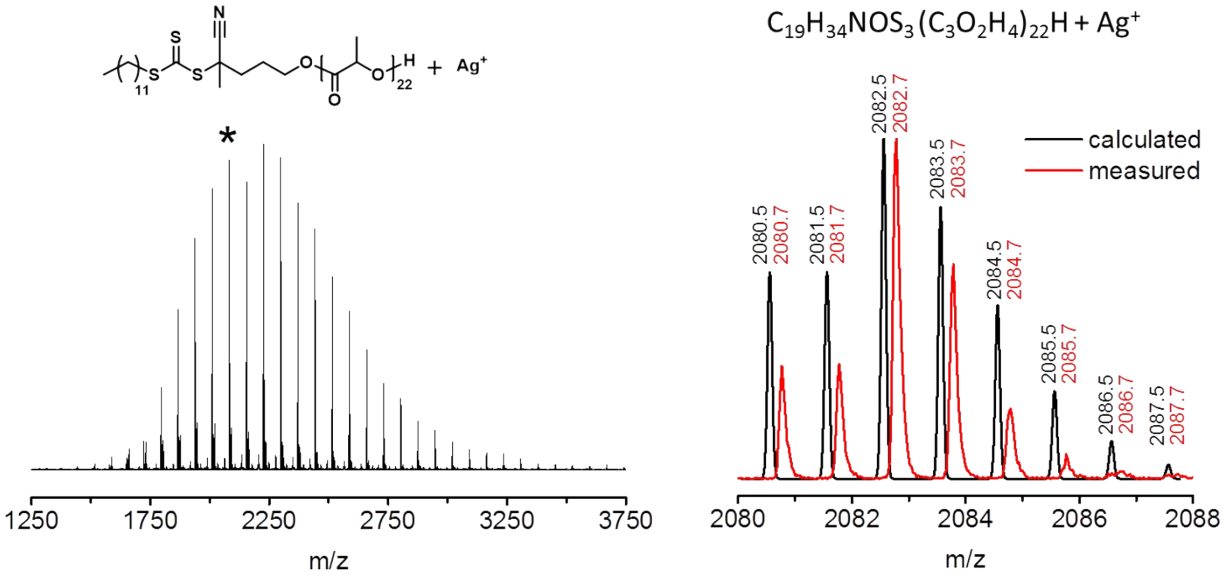

Figure S3. Left: MALDI-ToF mass spectrum of the **PLA-CTA**. **Right**: Overlay of the calculated and measured isotopic pattern for the structural assignment of the observed peaks.

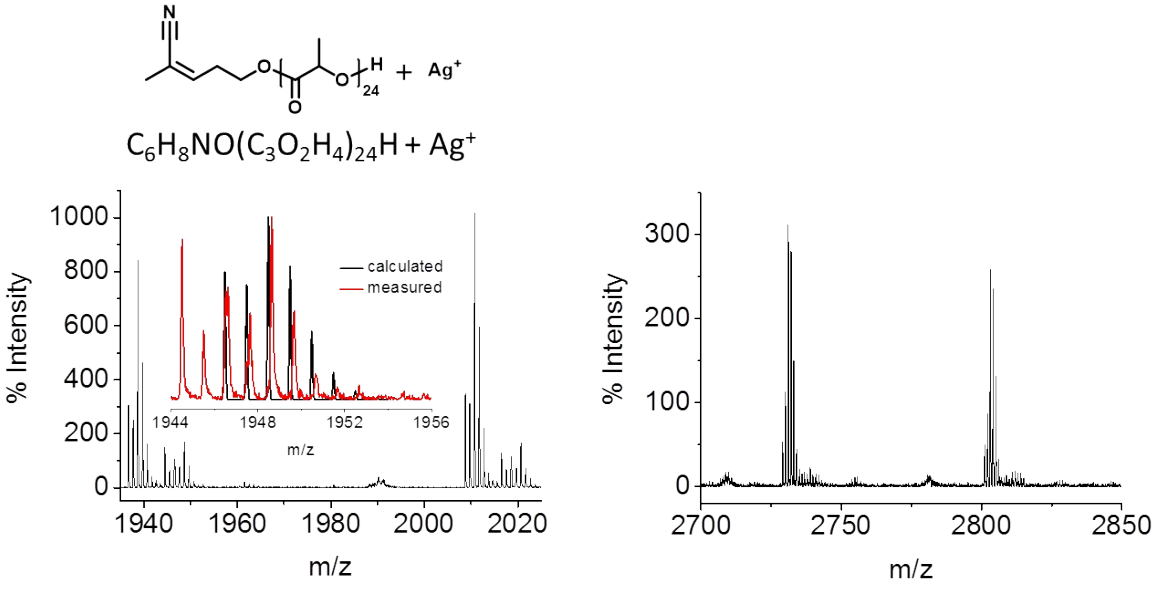

Figure S4. Left: Zoom into the lower *m/z* region of the MALDI-ToF mass spectrum of the PLA-CTA together with an overlay of the minor distribution assigned to fragmentation of the CTA. **Right:** Zoom into the higher *m/z* region of the MALDI-ToF mass spectrum of the PLA-CTA.

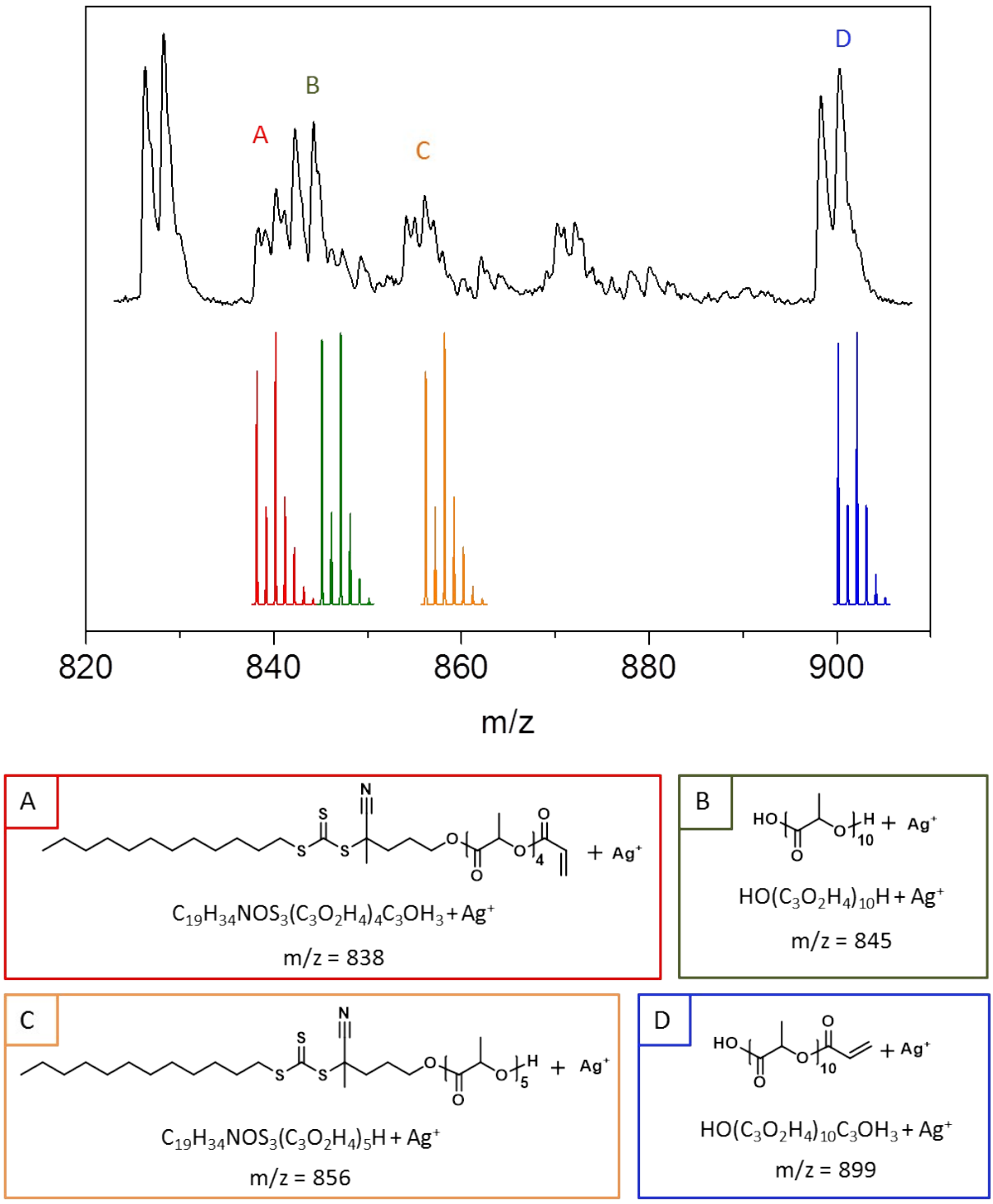

Figure S5. Zoom into the MALDI-ToF MS/MS spectrum of **PLA-CTA** (region from *m/z* 820 to *m/z* 910) together with the structural assignment of the observed peaks.

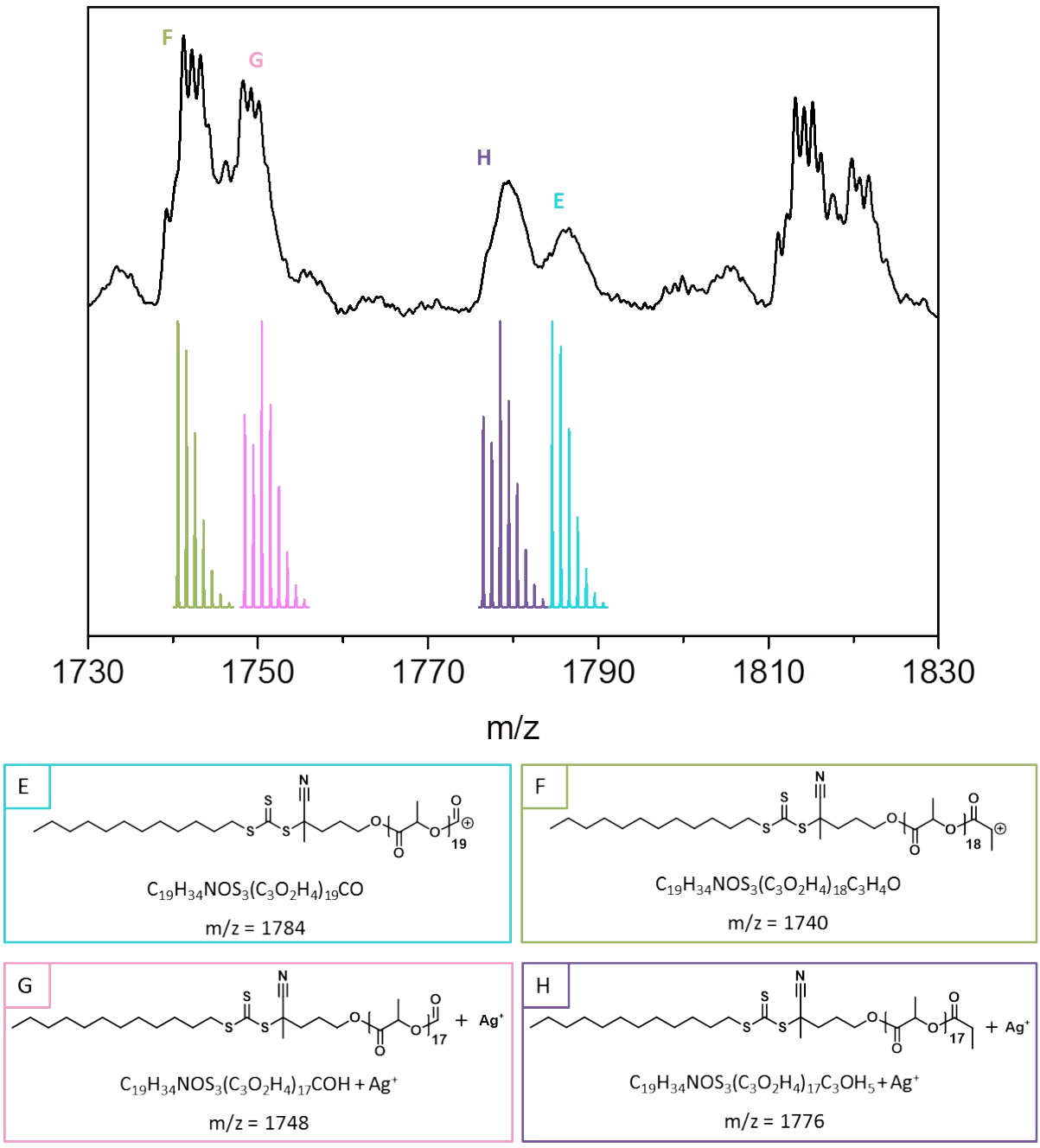

Figure S6. Zoom into the MALDI-ToF MS/MS spectrum of **PLA-CTA** (region from *m/z* 1910 to *m/z* 2040) together with the structural assignment of the observed peaks.

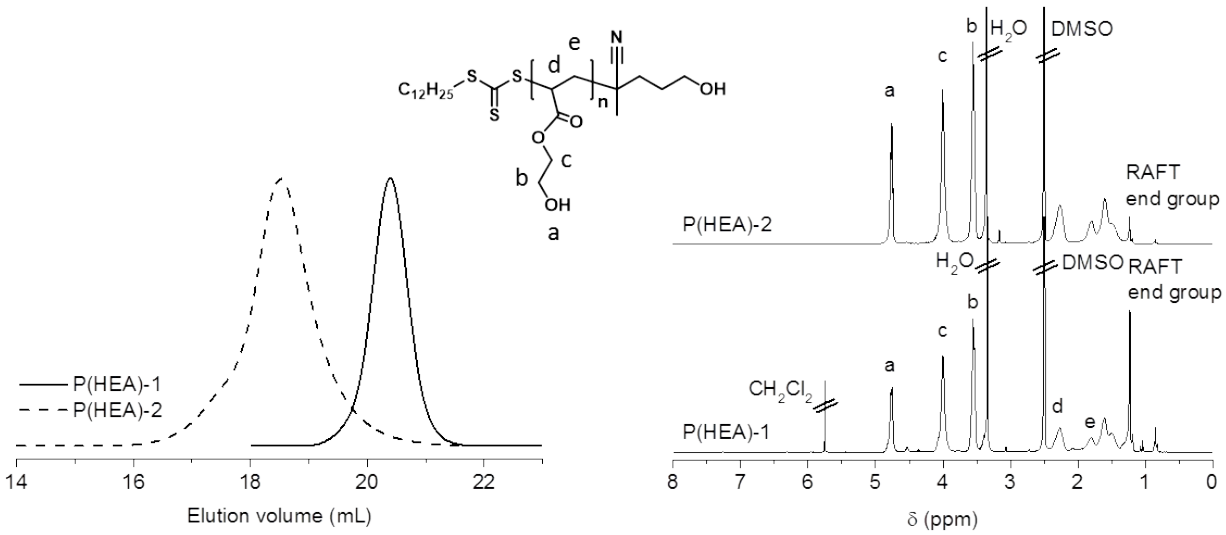

Figure S7. Analysis of the isolated **PHEA-1** and **PHEA-2**. **Left:** Overlay of the normalized SEC traces (DMAc, RI detection). **Right:** Overlay of the ^{1}H NMR spectra (DMSO-d_6, 300 MHz).

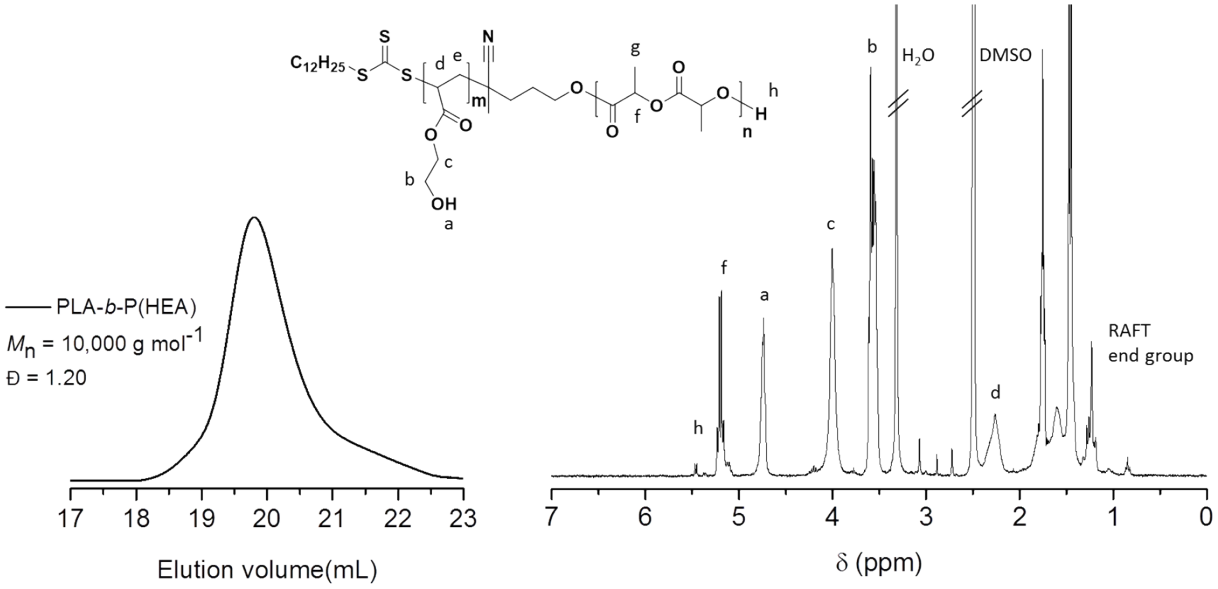

Figure S8. Analysis of the **PLA-*b*-PHEA** prepared in two steps *via* chain extension of the purified **PLA-CTA**. **Left:** SEC trace (DMAc, RI detection, PMMA calibration). **Right:** ^{1}H NMR spectrum (DMSO-d_6, 300 MHz).

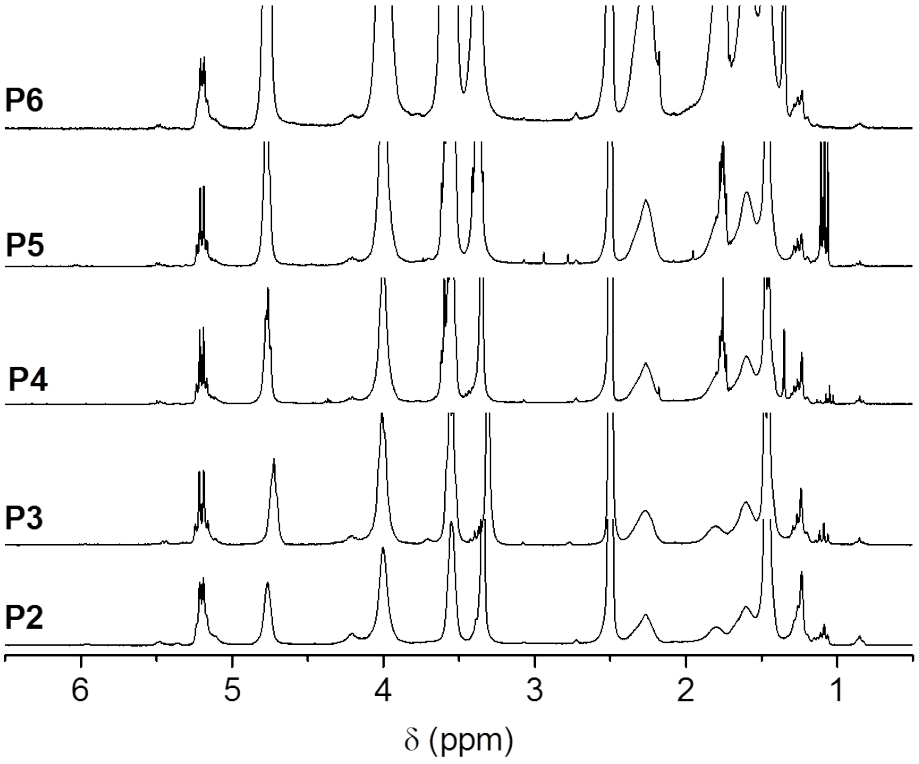

Figure S9. Overlay of the ^{1}H NMR spectra (DMSO-d_6, 300 MHz) of block copolymers **P2** to **P6** synthesized at one-pot. For clarity, the spectra were normalized according to the signal of the methine protons of PLA at $\delta = 5.16$ ppm.

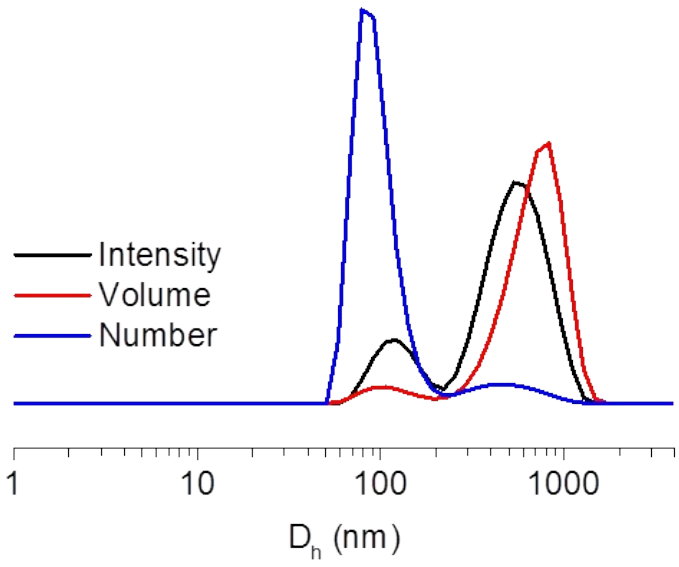

Figure S10. DLS size distribution of **P6** dissolved in DMSO.

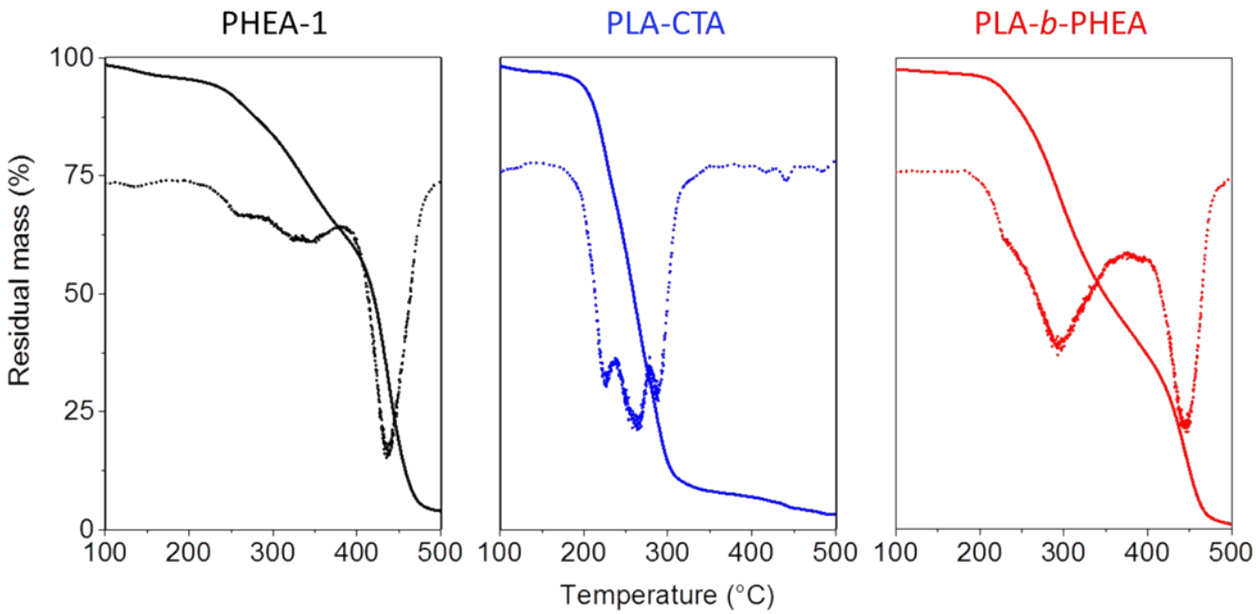

Figure S11. TGA thermograms of **PHEA-1**, the PLA macro-CTA, and **P1** (20 to 600 °C, 10.0 °C min^{-1}). The dotted lines represent the first derivative of the measured traces.

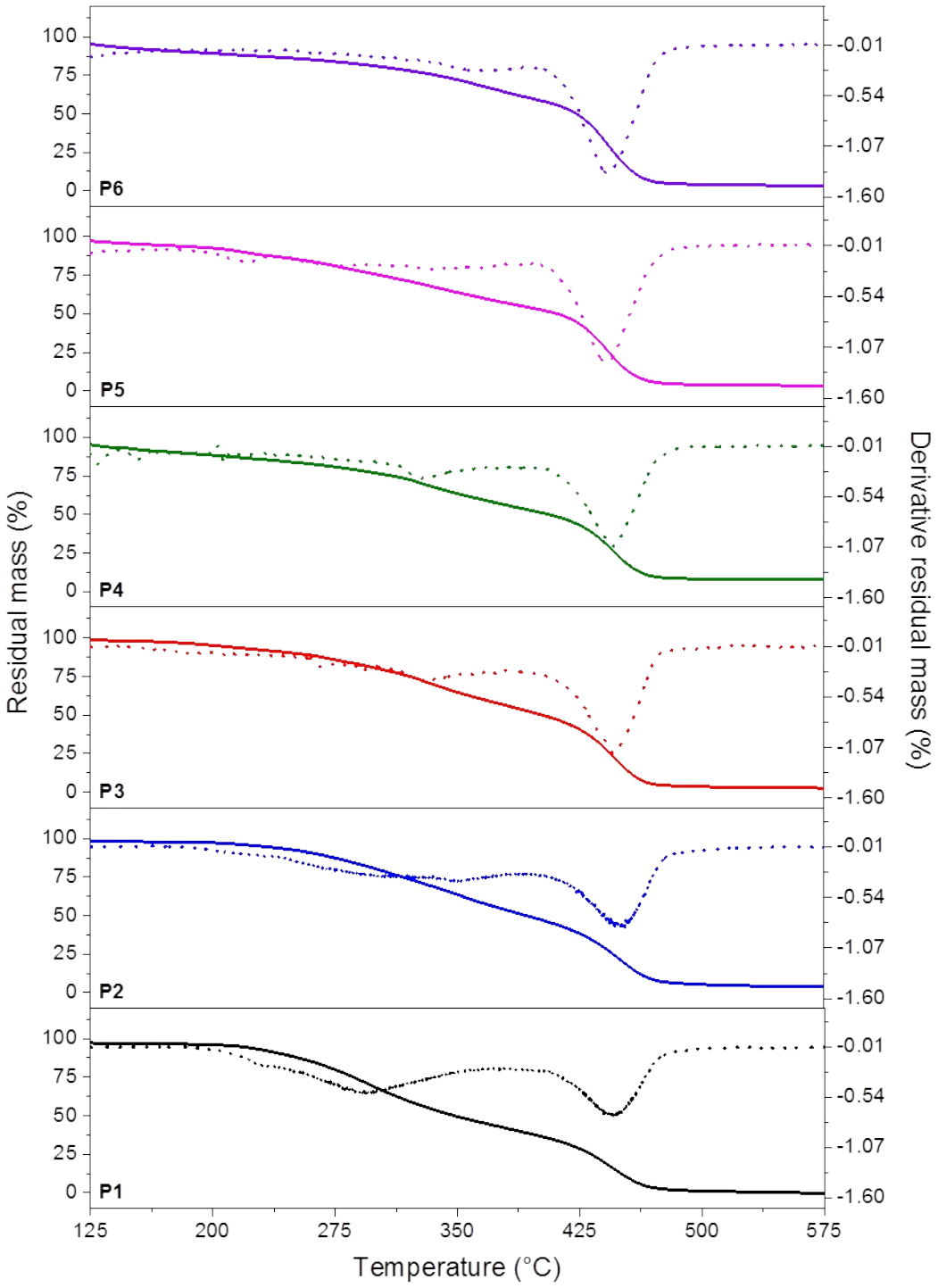

Figure S12. Overlay of the TGA thermograms of the block copolymers **P1** to **P6** synthesized in a one-pot approach (heating rate 10 K min^{-1}). The dotted lines depict the first derivative of each thermogram.

Table 1. Summary of the thermal characterization data obtained *via* DSC analysis.

	PLA-CTA	PHEA-1	PHEA-2	P1	P2	P3	P4	P5	P6
w_{HEA}*	0	100	100	0.46	0.56	0.60	0.68	0.73	0.82
$T_{g, Exp.}$ in °C[a] (inflection point)	38	–1	5	11 / 30	6	3	12	13	12
$T_{g, onset}$	32	–6	–3	4 / 28	–1	–9	5	7	4
$T_{g, mid}$	37	–1	4	10 / 33	5	2	11	12	10
$T_{g, end}$	42	4	11	17 / 39	10	13	17	17	17
Δ_{Cp} in J mol^{-1} K^{-1}	0.52	0.47	0.46	0.15 / 0.17	0.53	0.56	0.43	0.41	0.45
$T_{g, Fox}$ in °C[b]				20	17	15	13	11	8
$T_{g, Wood}$ in °C[c]				22	19	17	14	13	9

[a] Determined by DSC analysis (T_g values are reported as inflection point of the third heating trace). [b] Calculated according to $1/T_g = M_1/T_{g1} + M_2/T_{g2}$, where M_1 and M_2 are the weight fractions of ***HEA*** and ***LA***, respectively.[1, 2] [c] Calculated according to $T_g = (M_1\Delta C_{p1}T_{g1} + M_2\Delta C_{p2}T_{g2})/(M_1\Delta C_{p1} + M_2\Delta C_{p2})$.[2, 3] Averaged T_g and ΔC_p values of **PHEA** were used for the calculation of the T_g *via* Fox and Wood equations. * $\boldsymbol{M_1}$ and $\boldsymbol{M_2}$ values as estimated from feed and conversion.

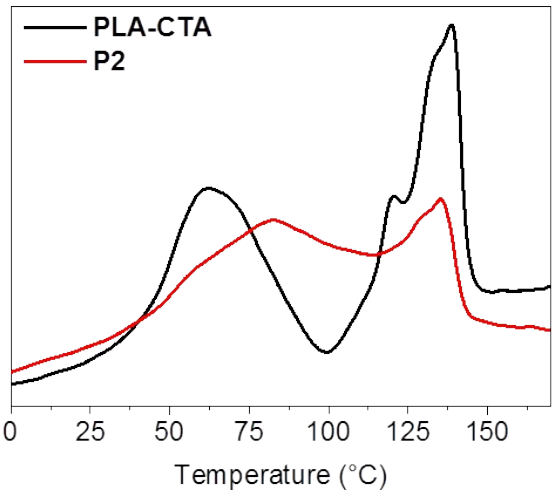

Figure S13. Overlay of the DSC thermograms of **PLA-CTA** and **P2** depicting the presence of crystallization and melting peaks (1st heating run, heating rate 20 K min^{-1}).

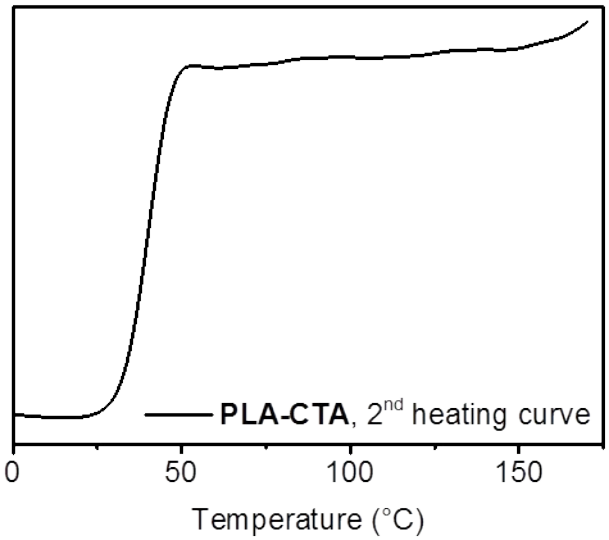

Figure S14. DSC thermogram of the **PLA-CTA** (heating rate 20 K min^{-1}) showing the absence of a melting peak in the second heating run.

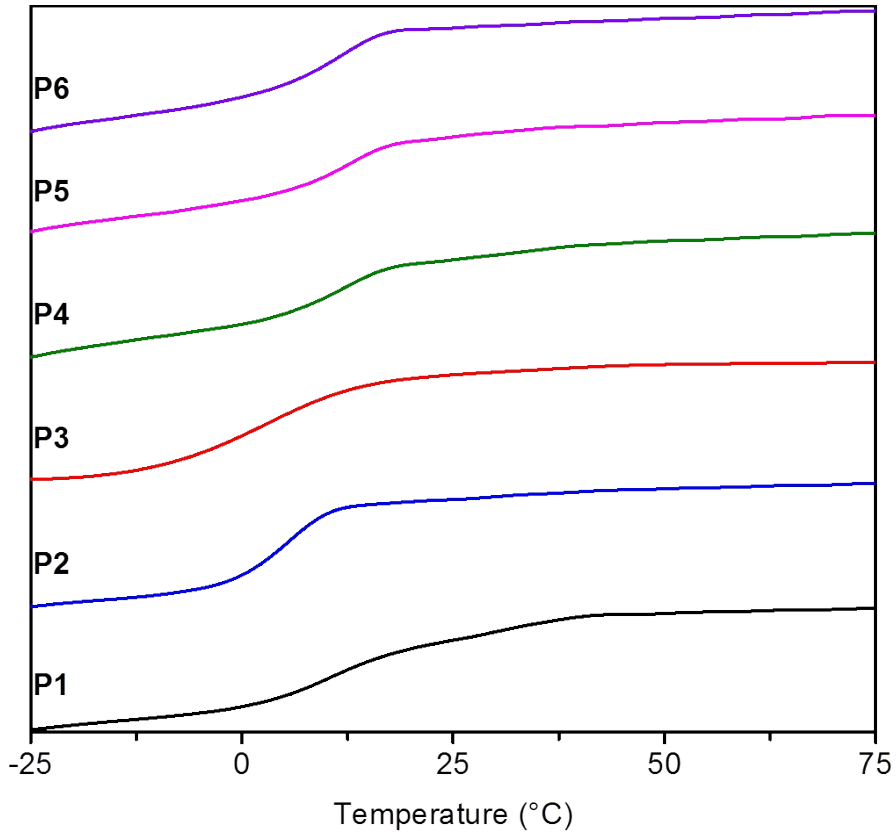

Figure S15. Overlay of the DSC thermograms of block copolymers **P1** to **P6** synthesized in a one pot approach (3rd heating run, heating rate 10 K min^{-1}). The individual thermograms are shifted vertically for clarity.

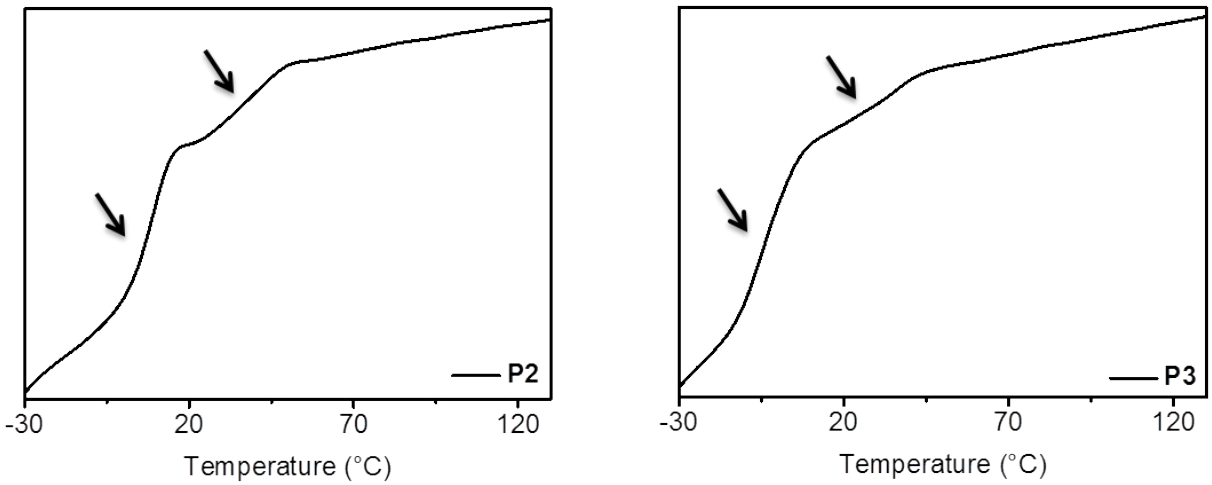

Figure S16. DSC thermograms of **P2** and **P3** obtained with a modified temperature program showing the presence of two glass transitions. The samples were heated to 170 °C and cooled to –50 °C at a rate of 5 K min^{-1}. The thermograms depict a subsequent heating run (rate 10 K min^{-1}). Increased heating rates did not improve the resolution of the two glass transitions.

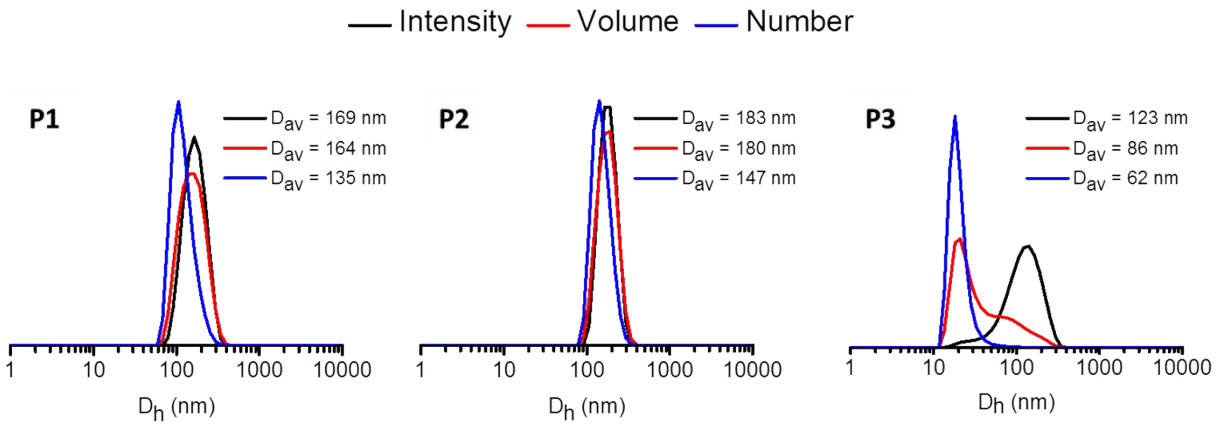

Figure S17. DLS size distributions of **P1**, **P2** and **P3** (c = 2 mg mL^{-1} in water).

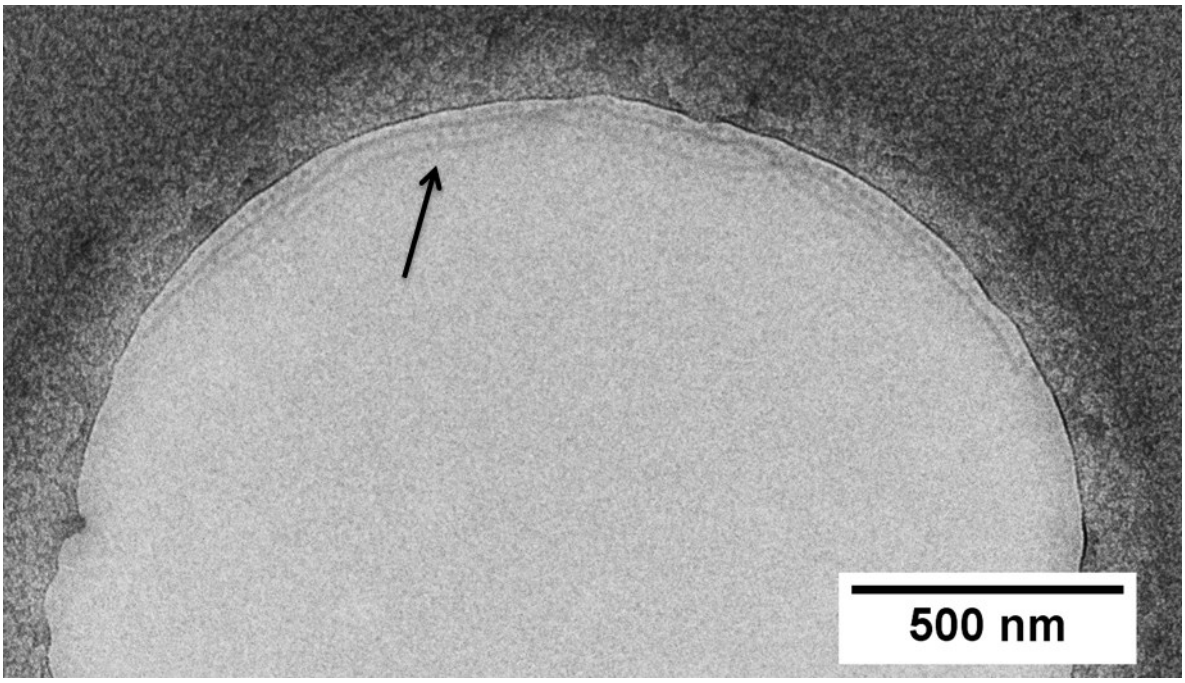

Figure S18. Additional cryo-TEM image of **P4** showing worm-like micelles occasionally found in the amorphous ice layers (c = 2 mg mL^{-1} in water).

1. T. G. Fox, *Bull. Am. Phys. Soc.,* 1956, **1**, 123.
2. P. R. Couchman, *Macromolecules,* 1978, **11**, 1156-1161.
3. L. A. Wood, *J. Polym. Sci.,* 1958, **28**, 319-330.