

Surface Modification of Gold Nanorods (GNRDs) using Double Thermo-responsive Block Copolymers: Evaluation of Self-assembly and Stability of Nanohybrids

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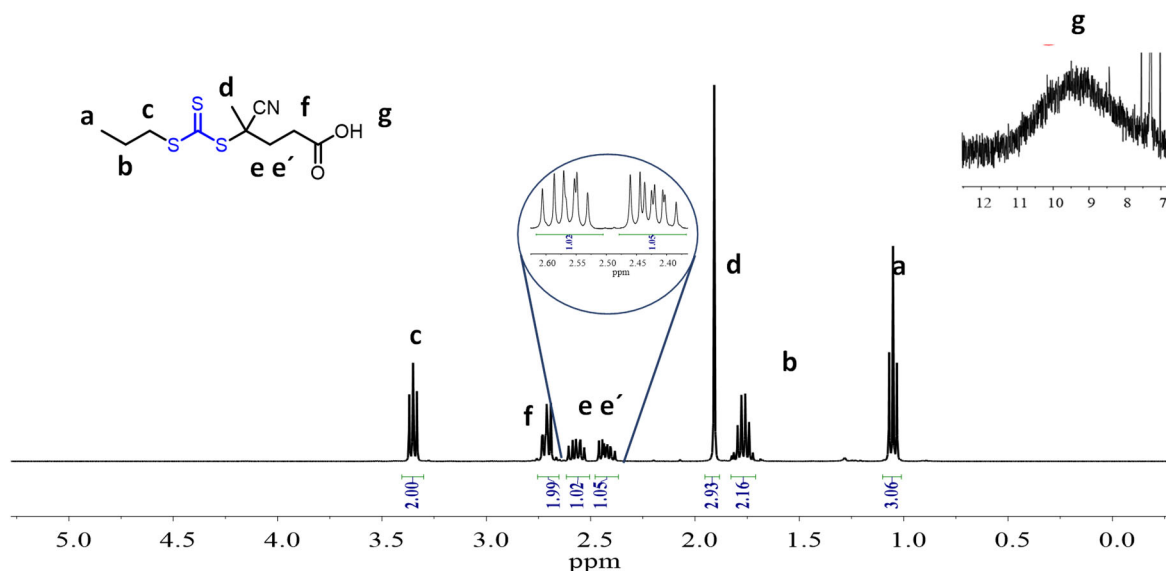


Figure S1. ¹H-NMR spectrum (400 MHz) in CDCl₃ of chain transfer agent (CTA).

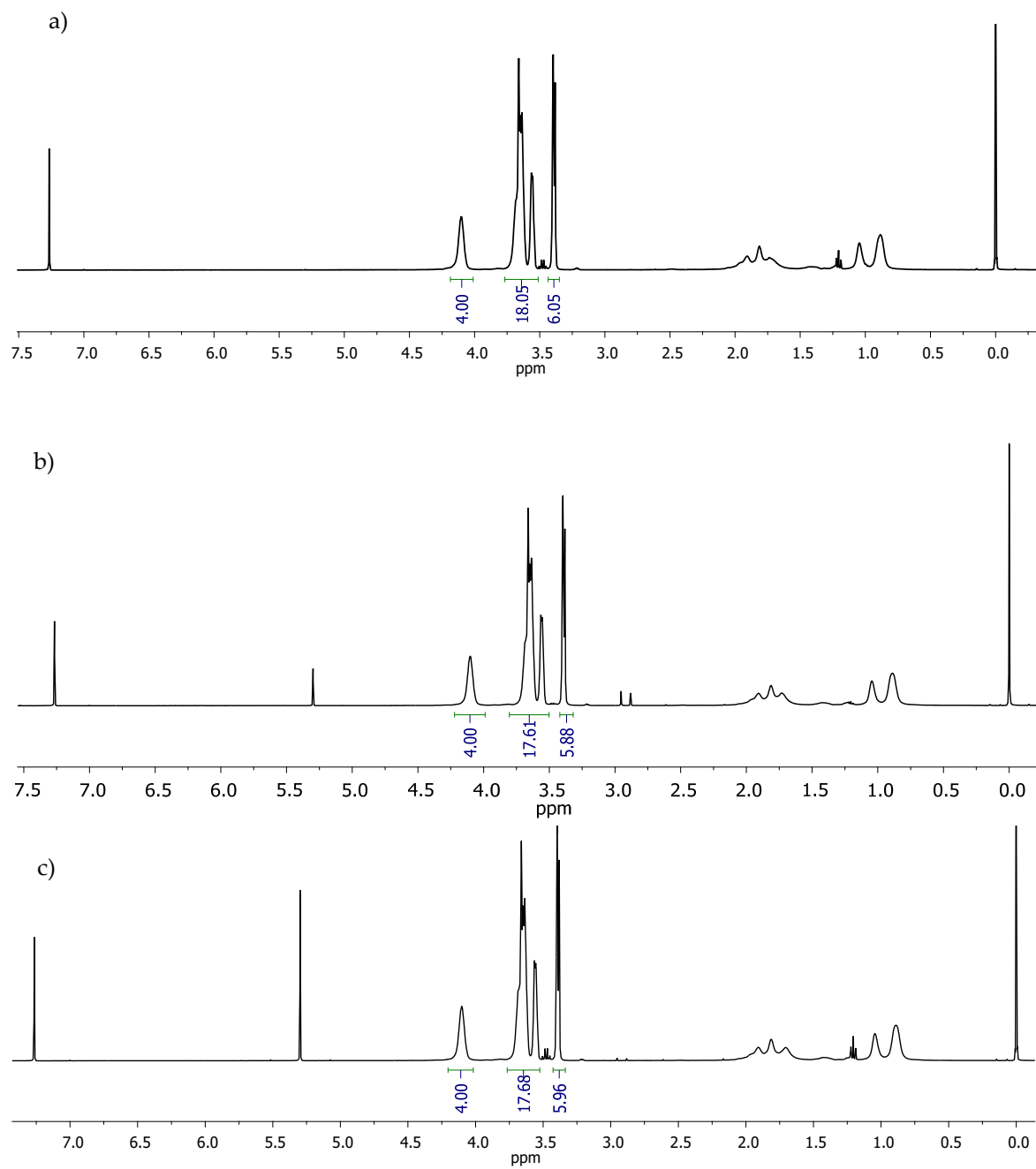


Figure S2. ^1H -NMR spectra (400 MHz) in CDCl_3 of P(DEGMA-co-OEGMA) copolymers: a) P1, b) P3, c) P4

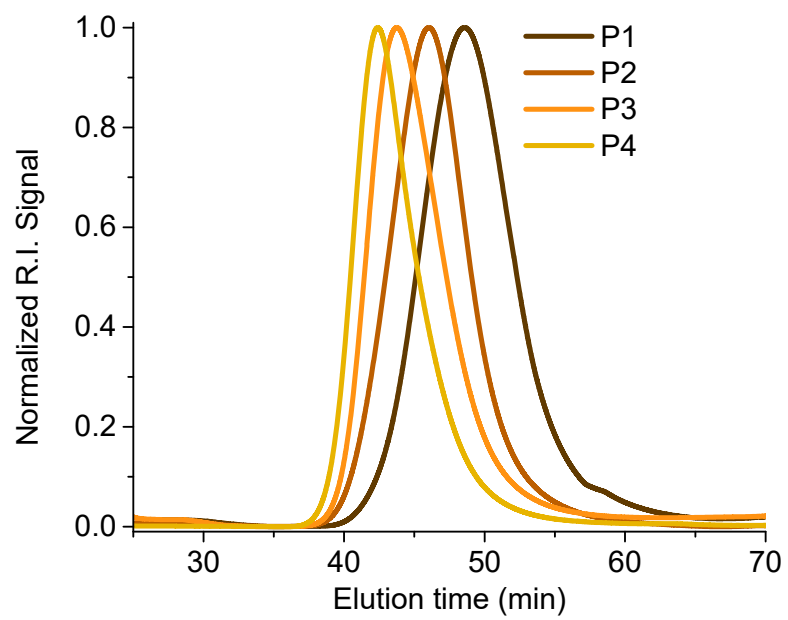


Figure S3. Normalized SEC traces (RI detector) of P(DEGMA-co-OEGMA) macro-CTA's.

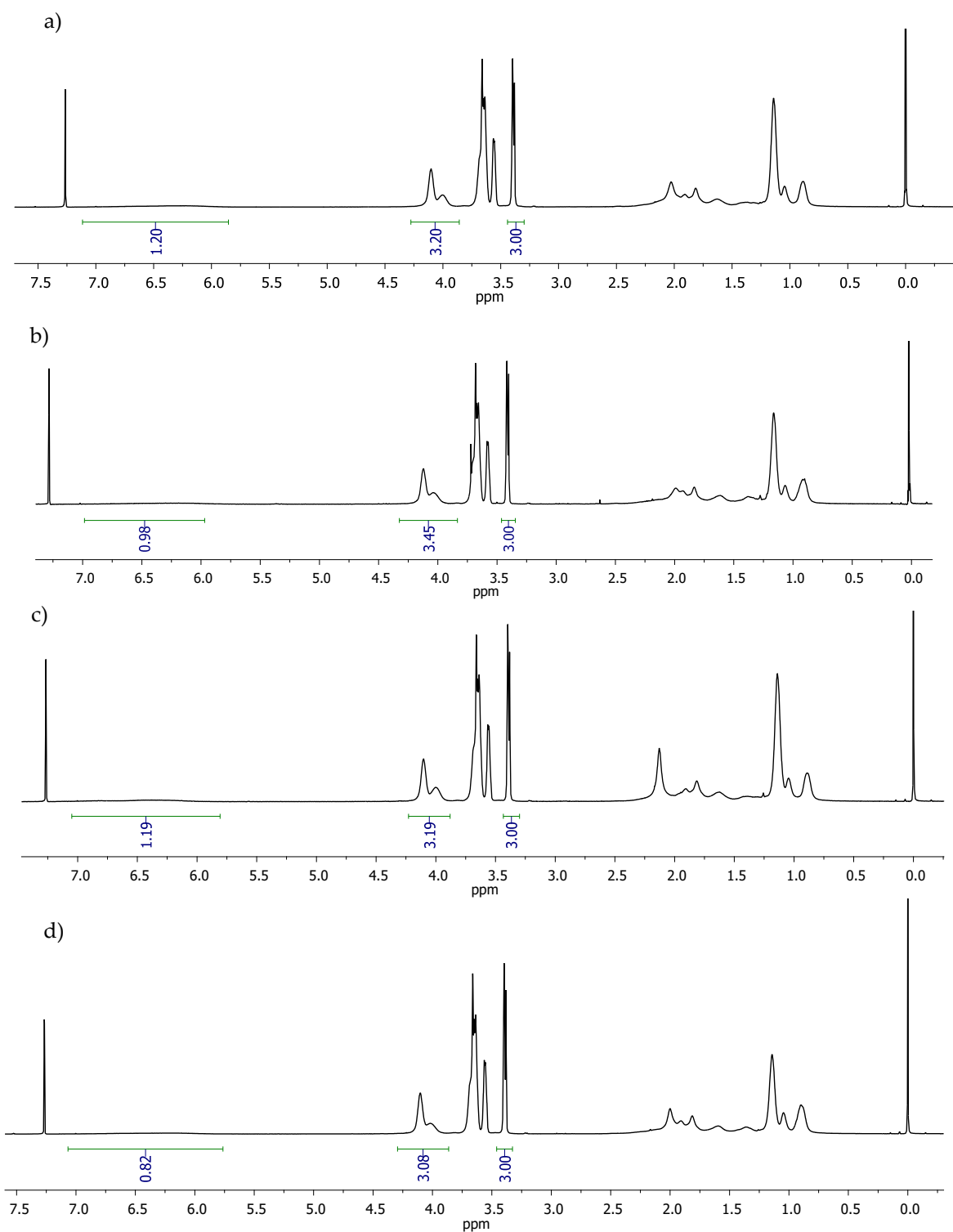


Figure S4. ^1H -NMR spectra (400 MHz) in CDCl_3 of block copolymers: a) P1-2, b) P1-3, c) P3-2, d) P3-3.

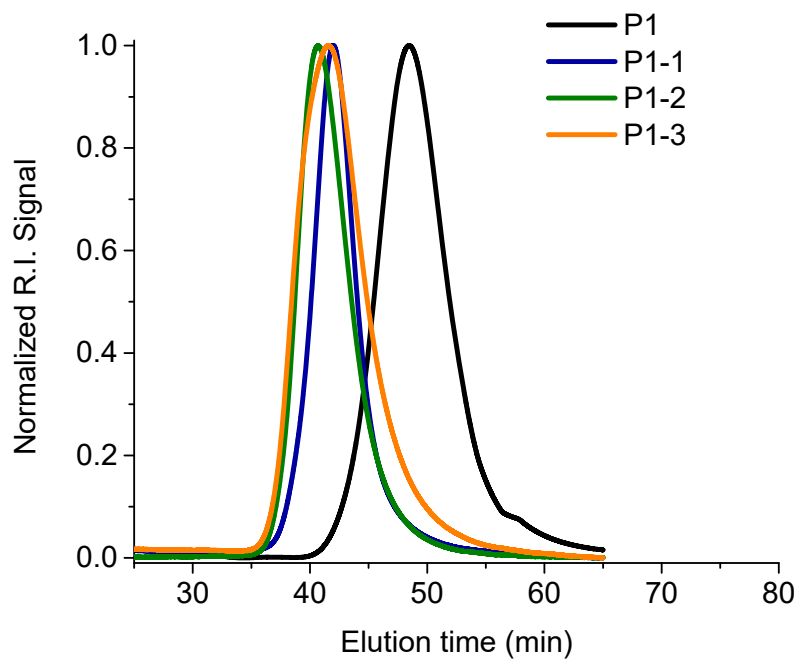


Figure S5. Normalized SEC traces (RI detector) in DMF of P(DEGMA-*co*-OEGMA)-*b*-PNIPAAm and P(DEGMA-*co*-OEGMA)-*b*-P(NIPAAm-*co*-BA) block copolymers.

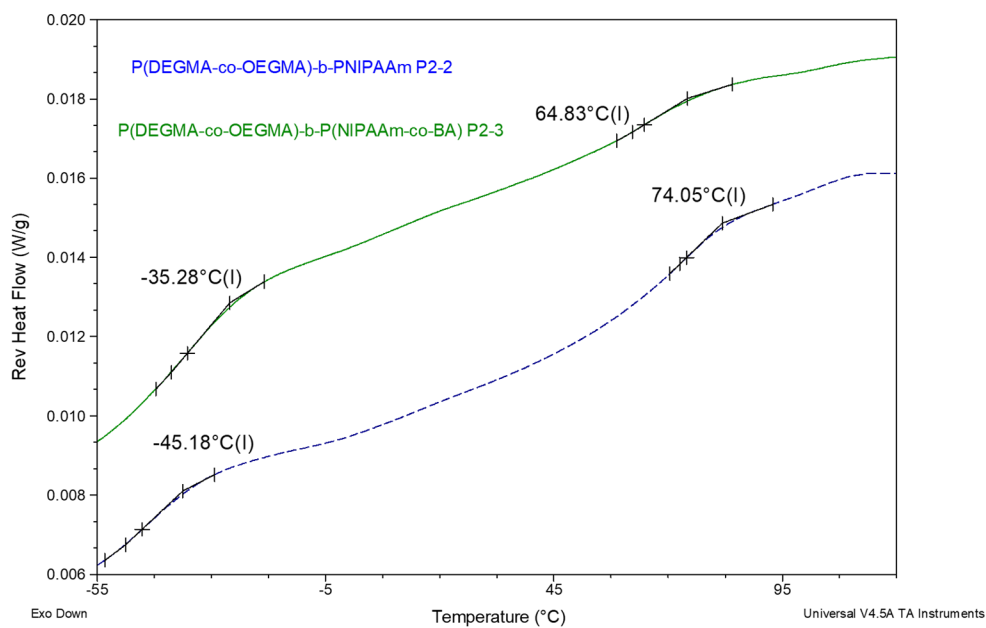


Figure S6. DSC thermograms of P(DEGMA-*co*-OEGMA)-*b*-PNIPAAm (P2-2) and P(DEGMA-*co*-OEGMA)-*b*-P(NIPAAm-*co*-BA) (P2-3) block copolymers.

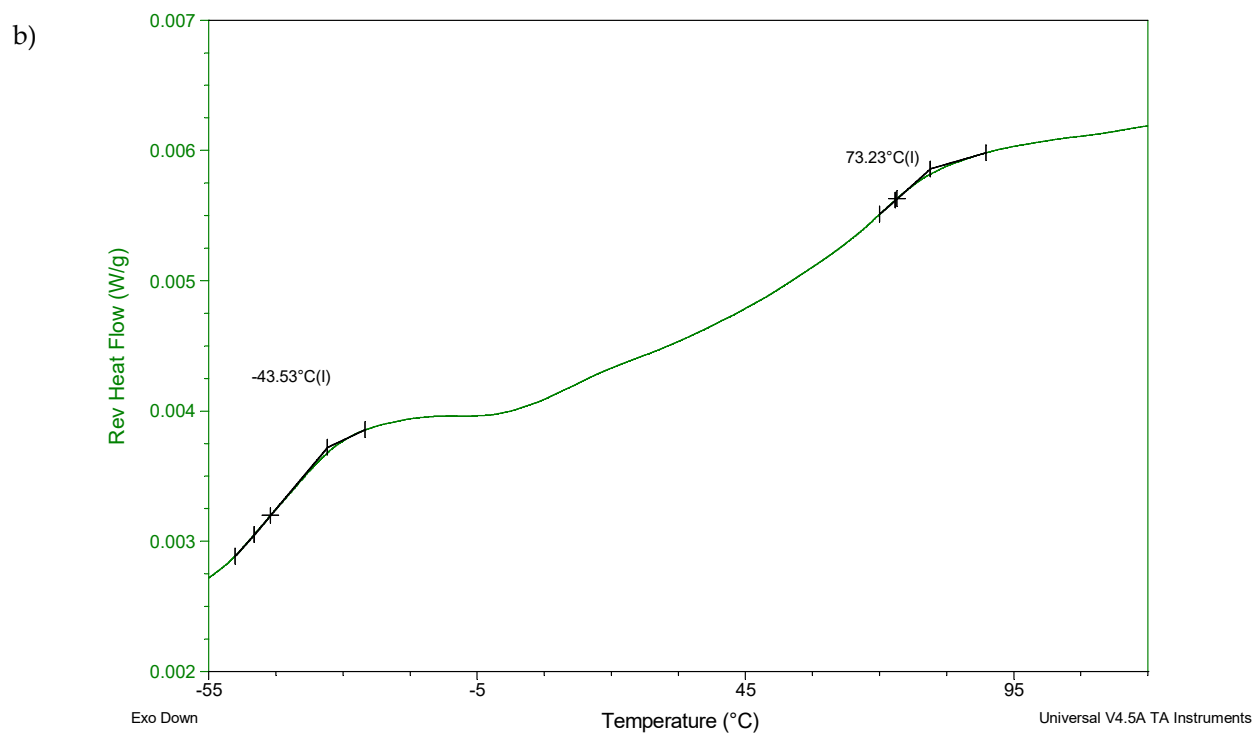
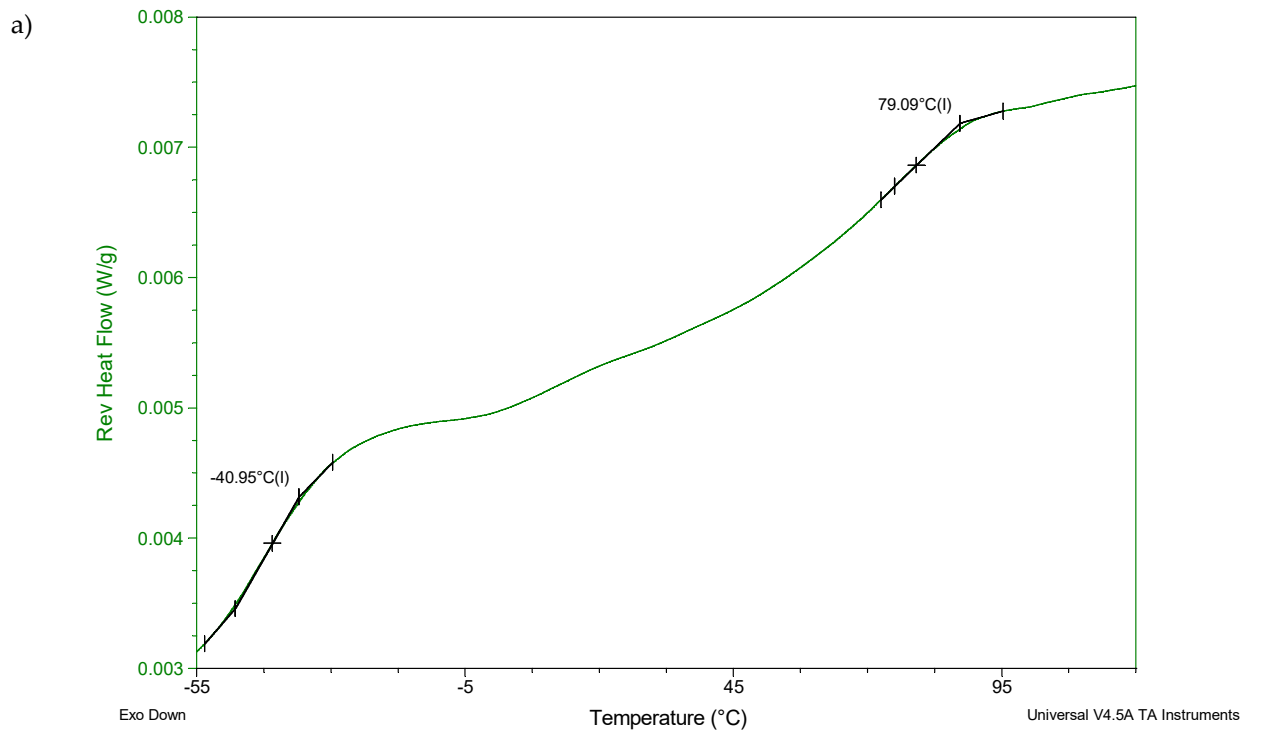


Figure S7. DSC thermograms of block copolymers: a) P1-2, b) P3-2.

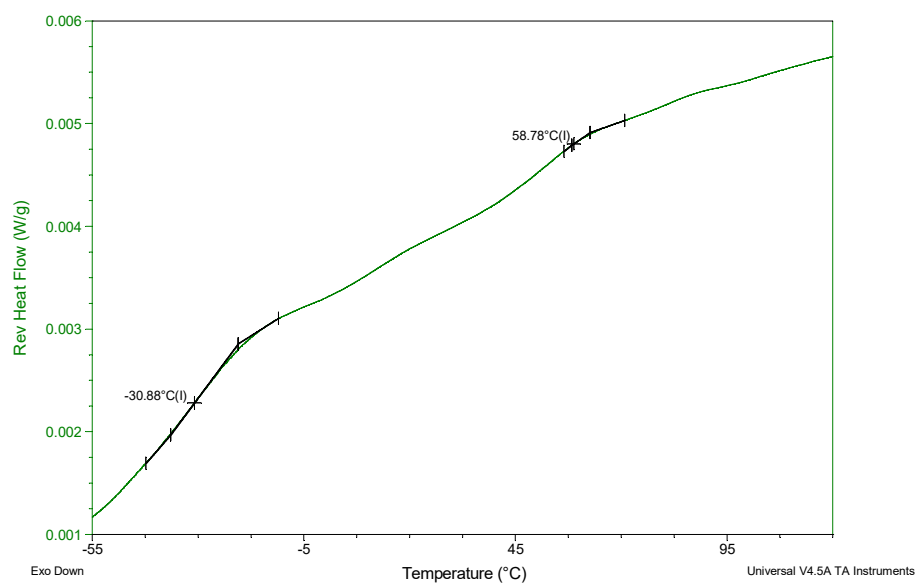


Figure S8. DSC thermograms of block copolymer P3-3.

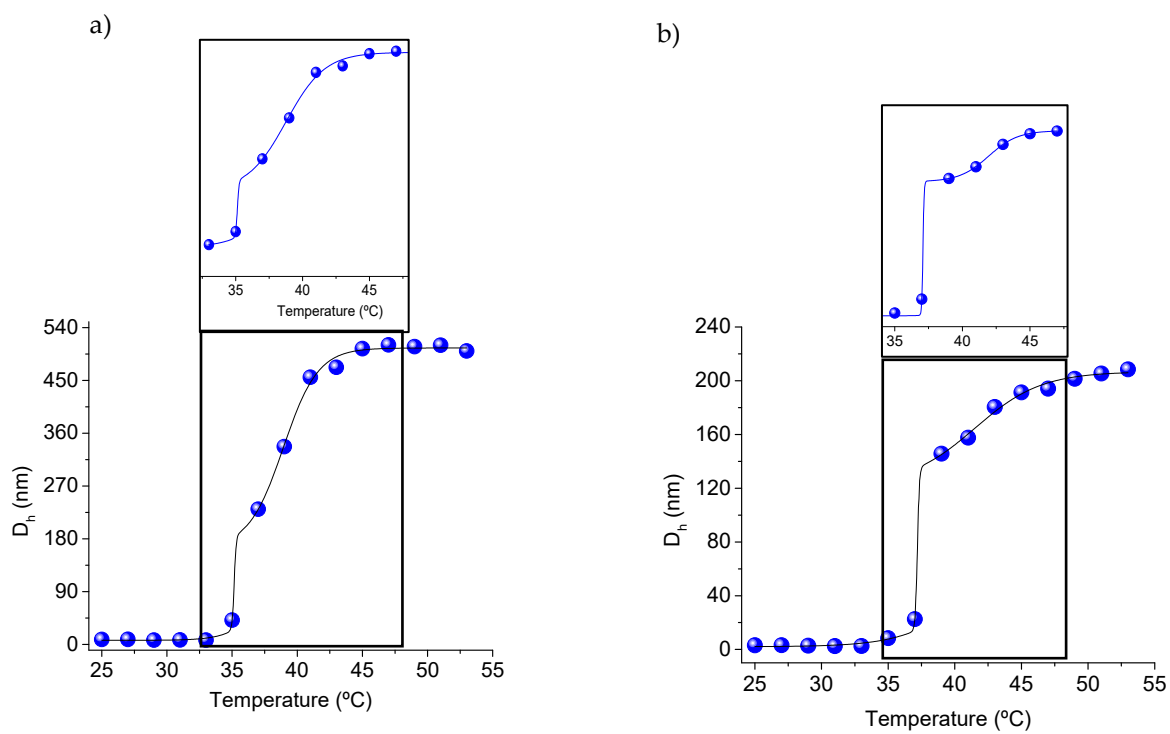


Figure S9. Determination of T_{cp} of block copolymers (1 mg mL⁻¹): a) P(DEGA-*co*-OEGMA)_{47%}-*b*-PNIPAAm_{53%}, b) P(DEGA-*co*-OEGMA)_{45%}-*b*-PNIPAAm_{55%}.

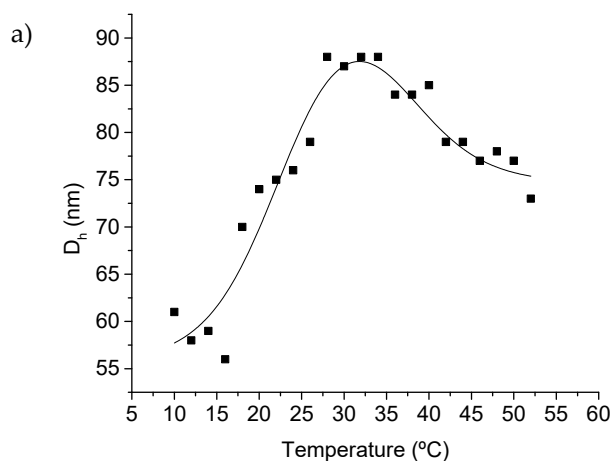


Figure S10. Determination of T_{cp} of block copolymers (1 mg mL^{-1}): a) P(DEGA-*co*-OEGMA)_{50%}-*b*-P(NIPAAm_{44%}-*co*-BA_{6%}).

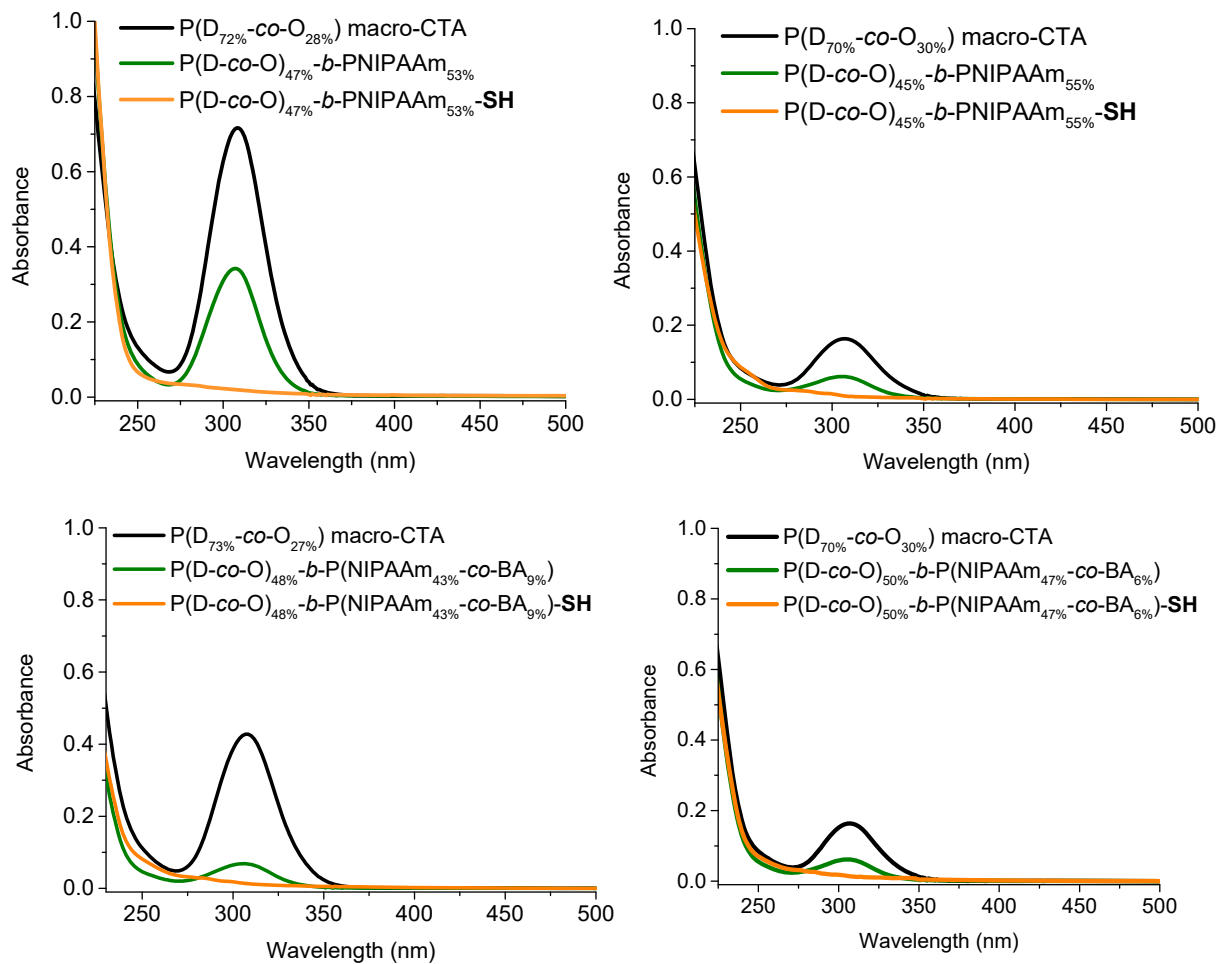


Figure S11. UV-Vis spectra ($c=1 \text{ mg mL}^{-1}$ in ethanol) of block copolymers and thiol-terminated block copolymers.

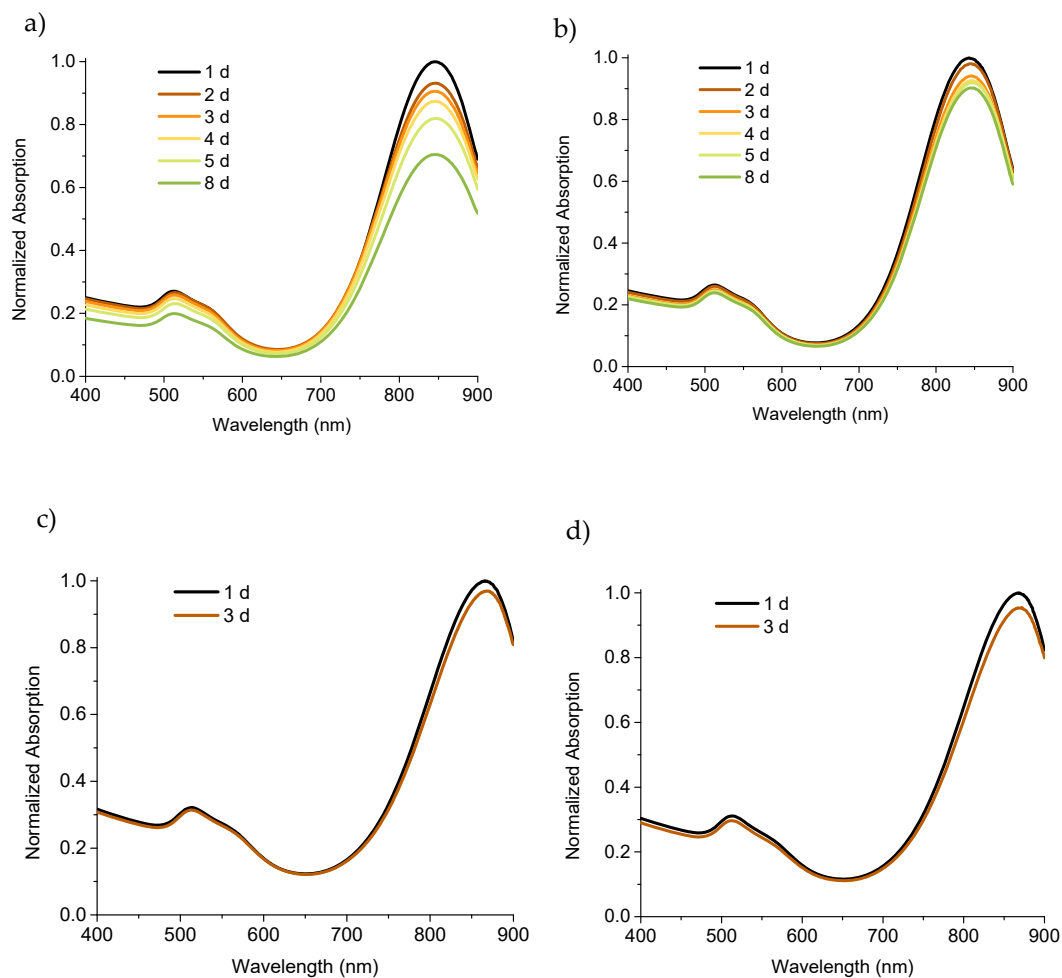
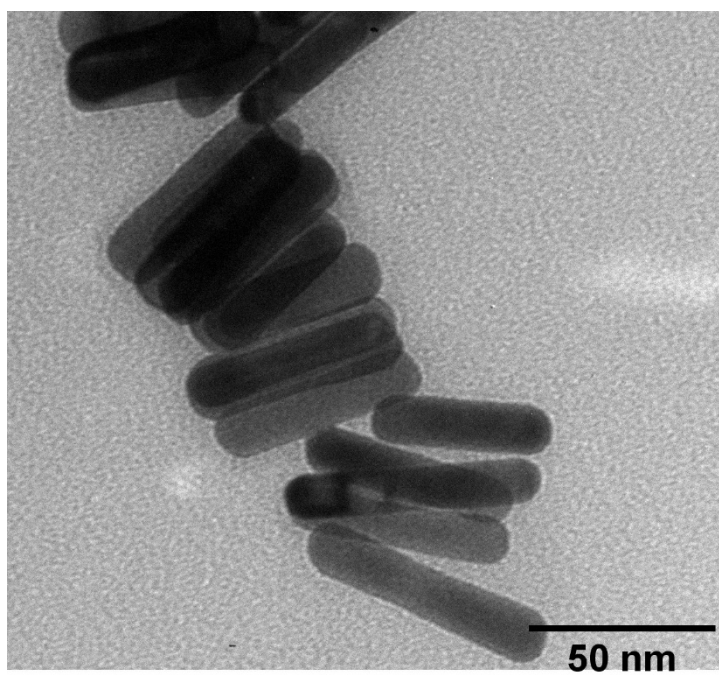


Figure S12. Optical stability against time: a) P(DEGMA-*co*-OEGMA)_{47%}-*b*-PNIPAAm_{53%}@GNRD, b) P(DEGMA-*co*-OEGMA)_{45%}-*b*-PNIPAAm_{55%}@GNRDs, c) P(DEGMA-*co*-OEGMA)_{48%}-*b*-P(NIPAAm_{43%}-*co*-BA_{9%})@GNRDs, d) P(DEGMA-*co*-OEGMA)_{50%}-*b*-P(NIPAAm_{44%}-*co*-BA_{6%})@GNRDs.

a)



b)

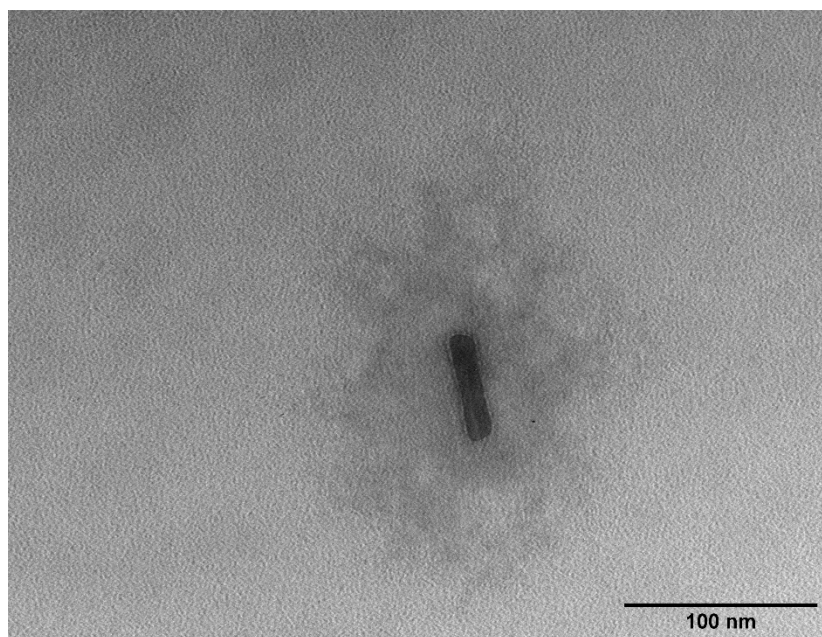


Figure S13. TEM micrographs of nanohybrids: a) $\text{P}(\text{DEGMA-}co\text{-OEGMA})_{45\%}\text{-}b\text{-PNIPAAm}_{55\%}\text{@GNRDs}$, b) $\text{P}(\text{DEGMA-}co\text{-OEGMA})_{50\%}\text{-}b\text{-P}(\text{NIPAAm}_{44\%}\text{-}co\text{-BA}_{6\%})\text{@GNRDs}$.

Table S1. Aggregation of sample P(D-co-O)_{37%}-*b*-PNIPAAm_{63%}@GNRDs at different temperatures.

Sample	T (°C)	D _h (nm)	PDI	St Dev (d.nm)
P(D-co-O) _{37%} - <i>b</i> -PNIPAAm _{63%} @GNRDs	25 °C	85 & 3	0.821	46.11 & 0.9881
	37 °C	165	0.203	60.58
	40 °C	198	0.146	75.56

Table S2. Aggregation data of block copolymers@GNRDs at 37 °C.

Sample	D _h (nm)	PDI	St Dev (d.nm)
P(D-co-O) _{47%} - <i>b</i> -PNIPAAm _{53%} @GNRDs	247	0.184	76.10
P(D-co-O) _{37%} - <i>b</i> -PNIPAAm _{63%} @GNRDs	165	0.203	60.58
P(D-co-O) _{45%} - <i>b</i> -PNIPAAm _{55%} @GNRDs	135 & 16.1	0.282	55.79
P(D-co-O) _{48%} - <i>b</i> -P(NIPAAm _{43%} -co-BA _{9%})@GNRDs	788	1.00	109.3
P(D-co-O) _{50%} - <i>b</i> -P(NIPAAm _{44%} -co-BA _{6%})@GNRDs	190	0.119	60.89

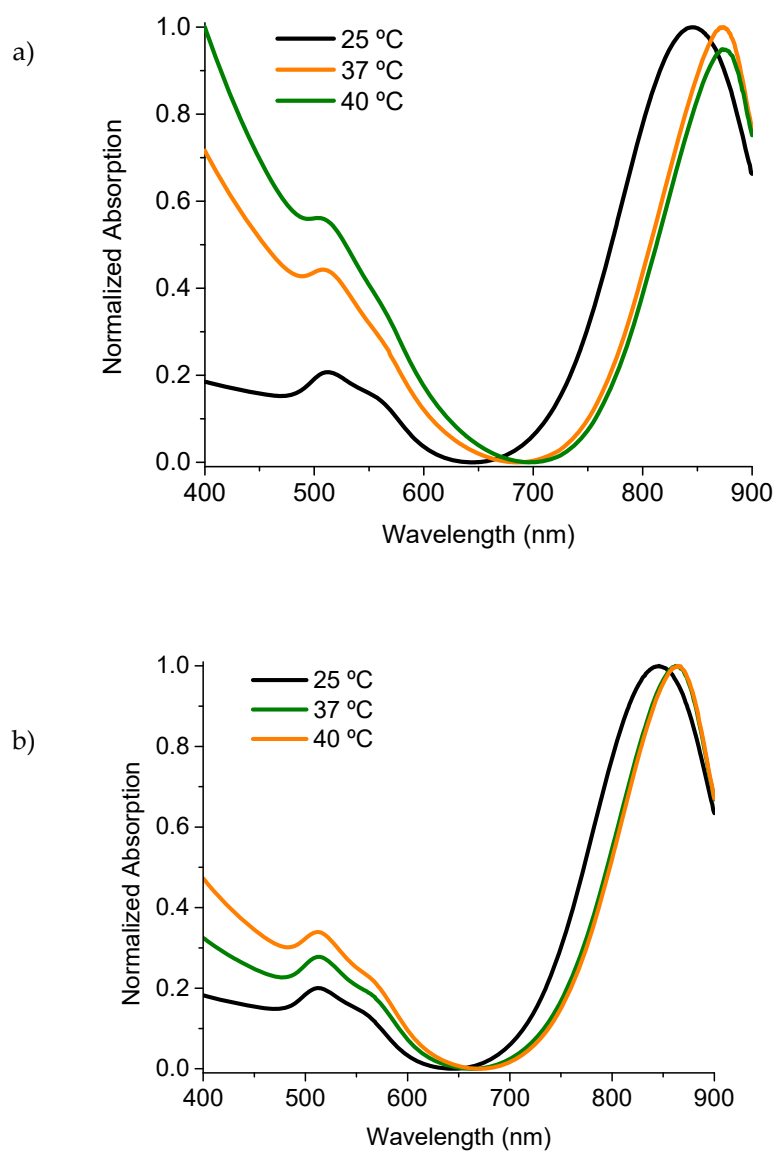


Figure S14. UV-Vis absorption spectra at 25 °C, 37 °C and 40 °C for nanohybrids: a) P(DEGMA-*co*-OEGMA)_{47%}-*b*-PNIPAAm_{53%}@GNRDs, b) P(DEGMA-*co*-OEGMA)_{45%}-*b*-PNIPAAm_{55%}@GNRDs.

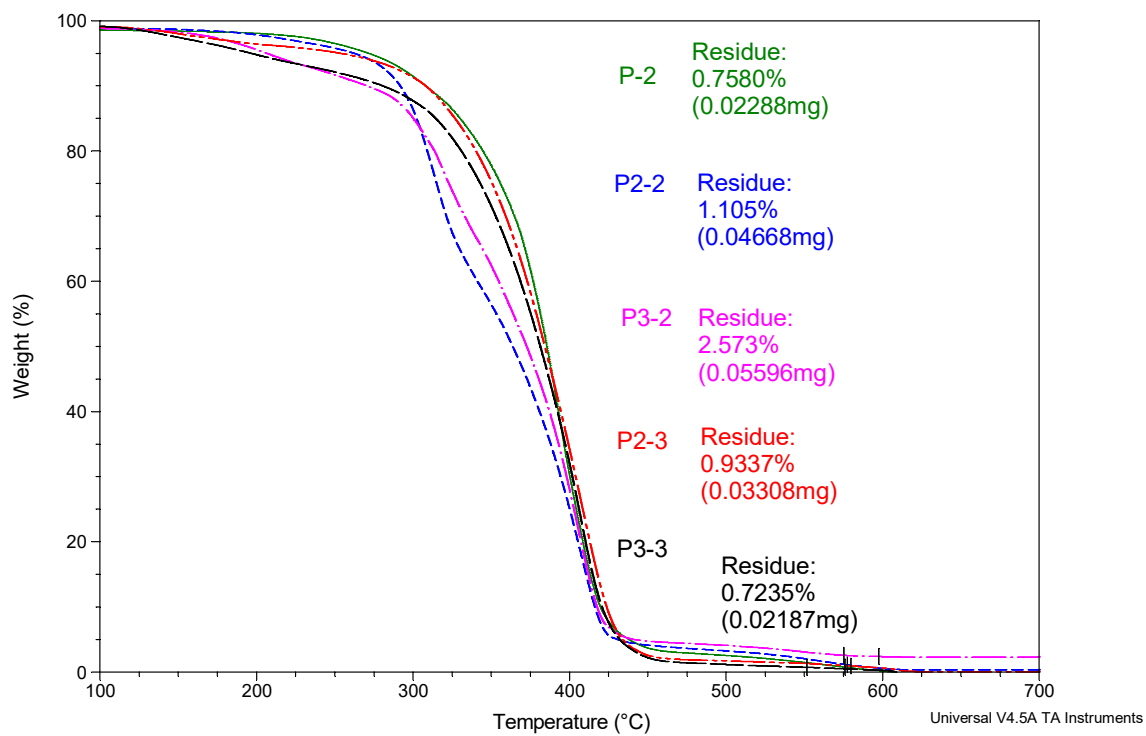


Figure S15. TGA-thermograms of block copolymers.