Electronic Supplementary Information

Double Thermoresponsive Di- and Triblock Copolymers Based on *N*-vinylcaprolactam and *N*-vinylpyrrolidone: Synthesis and Comparative Study of Solution Behavior.

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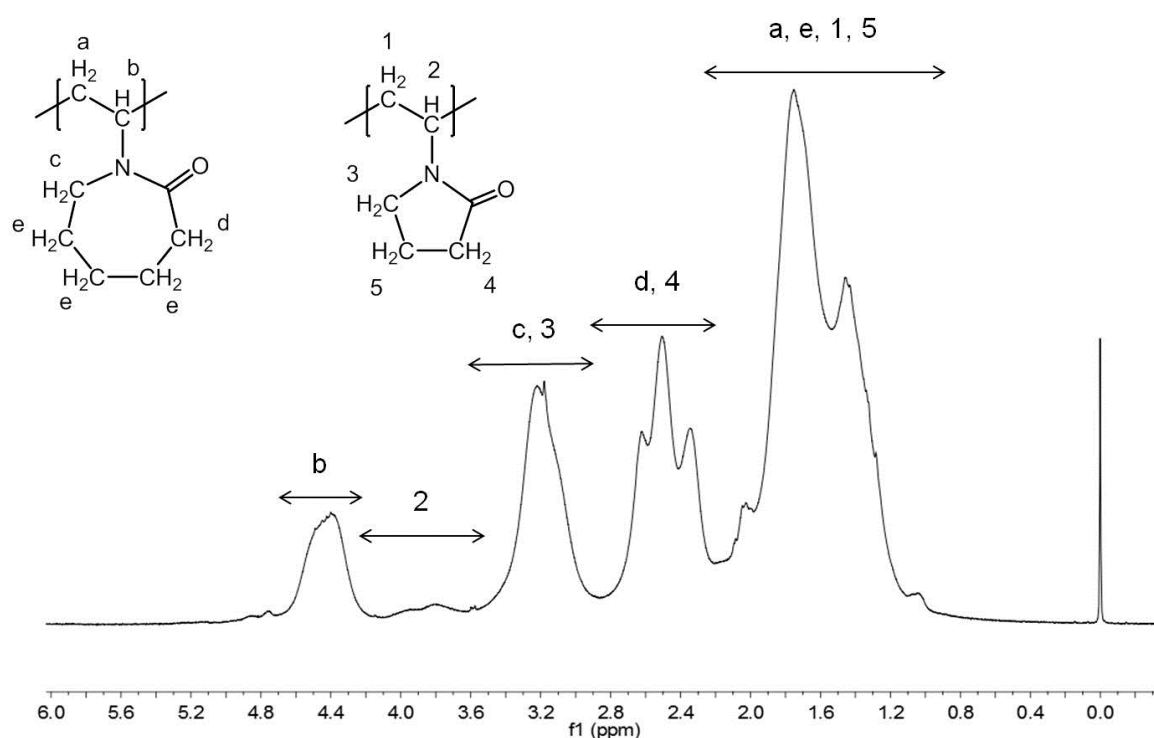

Figure S1. ¹H NMR spectra (CDCl₃ at 25 °C) of the P(*N*VCL-*stat*-*N*VP) statistical copolymers prepared by CMRP. (see entry 1 Table 1)

Table S1. Block copolymers synthesis by cobalt-mediated radical copolymerization of NVCL and NVP in bulk at 40 °C.

| | | PNVCL | | | PNVCL-*block*-P(NVCL-*stat*-NVP) | | | | | PNVCL-*block*-P(NVCL-*stat*-NVP)-*block*-PNVCL | |
| | | | | | | | | Conv. (%)[c] | | | |
Entry	[NVCL]/ [R-Co^{III}]	Time (h)	Conv. (%)	M_n (g/mol)[a] / Đ[b]	[NVP]/ [R-Co^{III}]	Time (h)	M_n (g/mol)[a] / Đ[b]	NVCL	NVP	M_n (g/mol)[a] / Đ[b]	In copolymer (mol %) PNVP/PNVCL[d]
1	359/1	2.5	16	9500 / 1.07	431/1	3	41400 / 1.13	30	23	64500 / 1.24	57/43
2	359/1	5	27	18400 / 1.05	430/1	2	43100 / 1.08	43	19	71900 / 1.24	50/50
3	719/1	1.5	15	32800 / 1.06	858/1	0.5	57500 / 1.06	21	18	110500 / 1.13	35/65
4	880/1	1	23	39200 / 1.06	2725/1	0.5[e]	76200/ 1.08	33	13	128000 / 1.13	50/50

[a] Determined by SEC-MALLS in DMF containing LiBr. [b] Determined by SEC in DMF containing LiBr (Calibration PS). [c] Total conversion of monomers determined by ^{1}H NMR 250 MHz in CDCl$_3$. [d] Molar composition of triblocks determined by ^{1}H NMR 400 MHz in CDCl$_3$. [e] reaction at 30 °C.
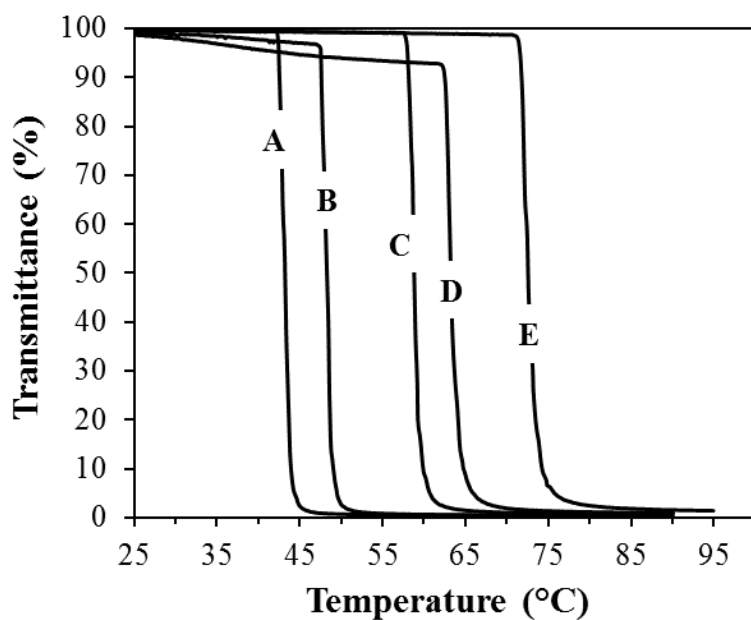
Figure S2.   Overlay of the turbidimetry curves for the P(*N*VCL-*stat*-*N*VP) statistical copolymers aqueous solutions (1 mg/mL) with various compositions (temperature ramp = 1 °C/min. (**A** $F_{NVP} = 0.18$, **B** $F_{NVP} = 0.27$, **C** $F_{NVP} = 0.42$, **D** $F_{NVP} = 0.49$, **E** $F_{NVP} = 0.57$)
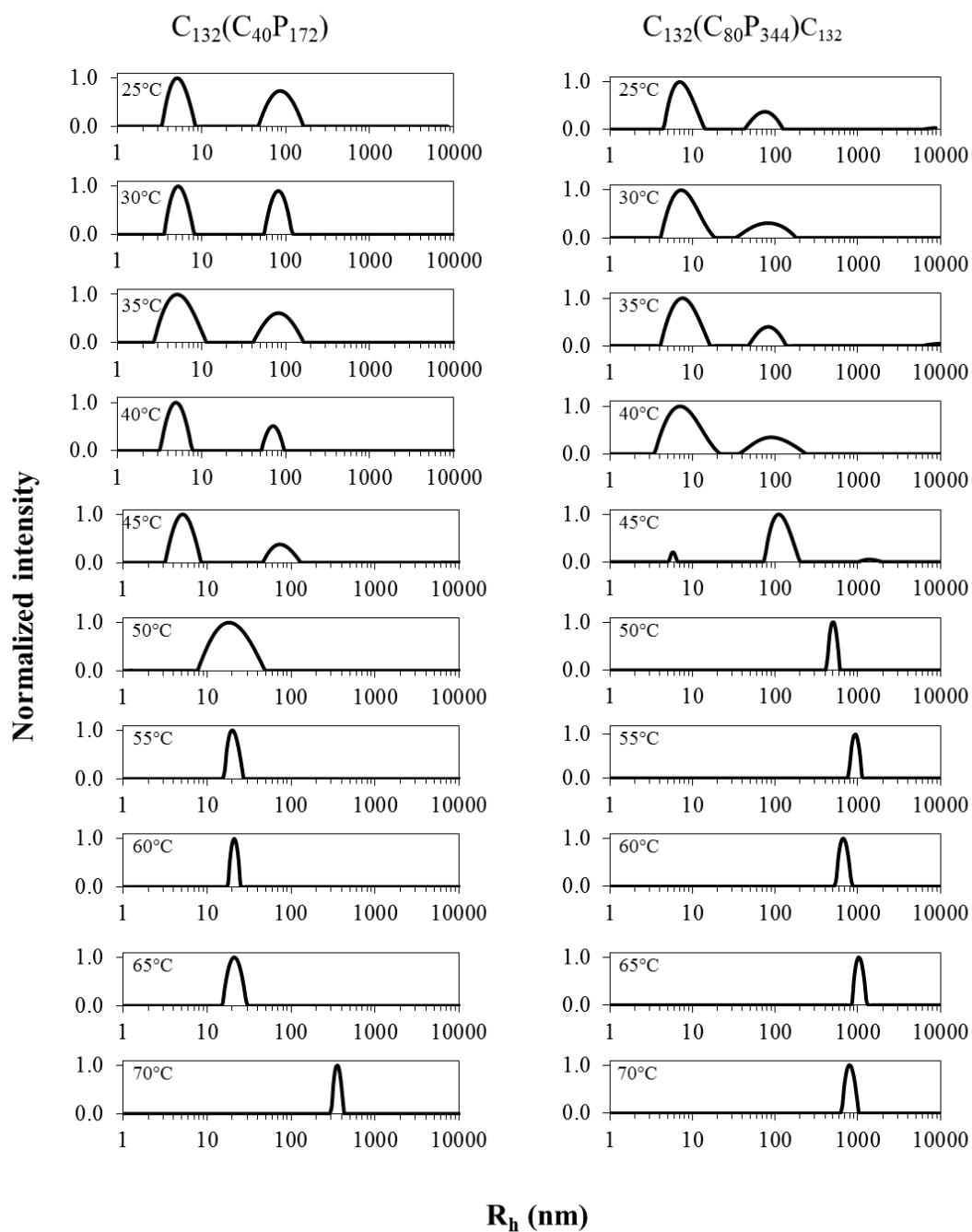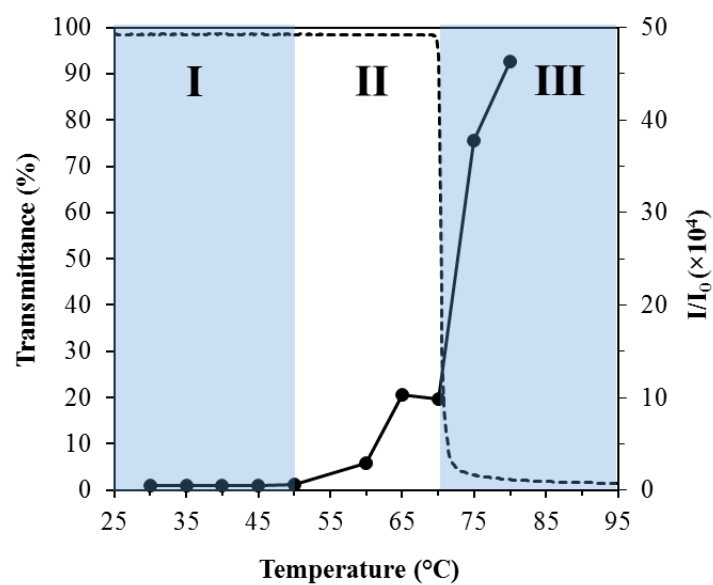
Figure S3. Intensity normalized CONTIN size distribution of $C_{132}(C_{40}P_{172})$ and $C_{132}(C_{80}P_{344})C_{132}$ in water (1 g L^{-1}) at various temperatures.

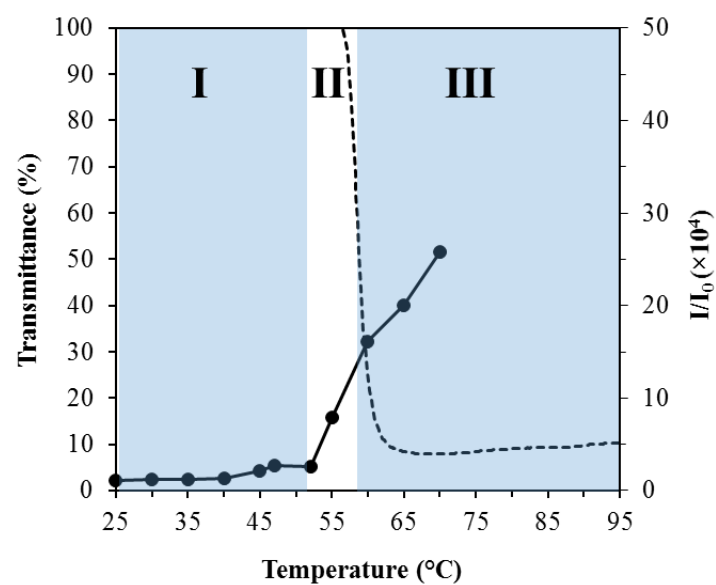**C$_{68}$(C$_{74}$P$_{191}$)**

C$_{68}$(C$_{148}$P$_{382}$)C$_{68}$

Figure S4. Transmittance (1 °C min^{-1}) (dotted line) and scattered intensity measured by DLS (full line) for the C$_{68}$(C$_{74}$P$_{191}$) diblock and the parent C$_{68}$(C$_{148}$P$_{382}$)C$_{68}$ triblock aqueous solutions (1 g L^{-1}) as a function of temperature.

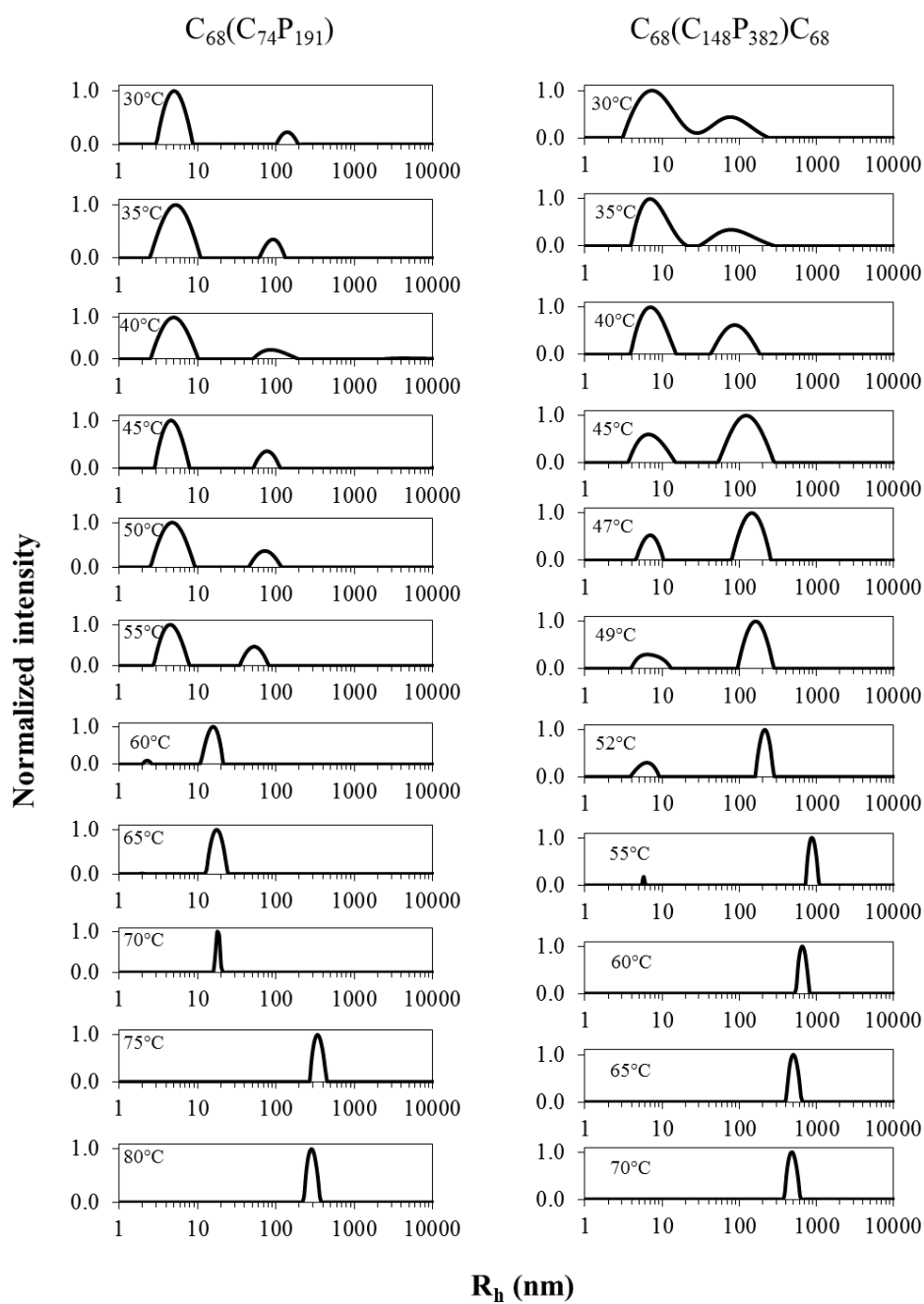$C_{68}(C_{74}P_{191})$ and $C_{68}(C_{148}P_{382})C_{68}$

Figure S5. Intensity normalized CONTIN size distribution of $C_{68}(C_{74}P_{191})$ and $C_{68}(C_{148}P_{382})C_{68}$ in water (1 g L^{-1}) at various temperatures.
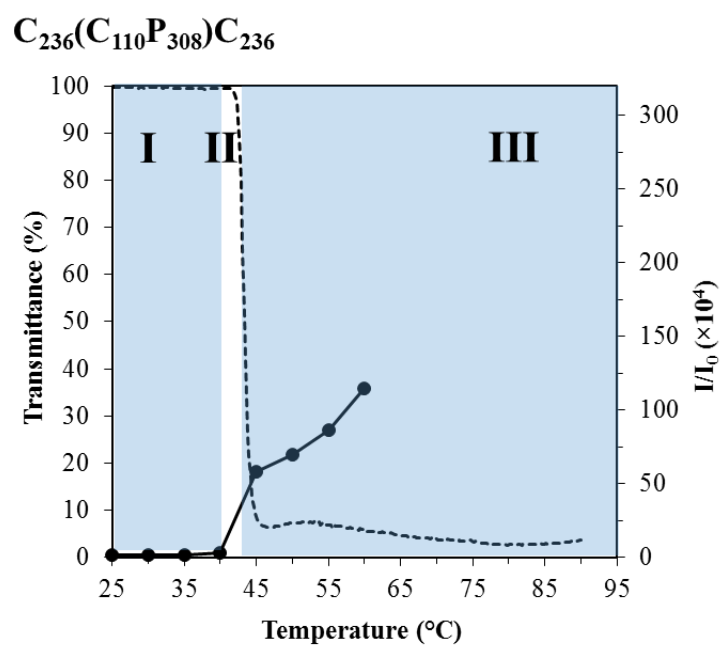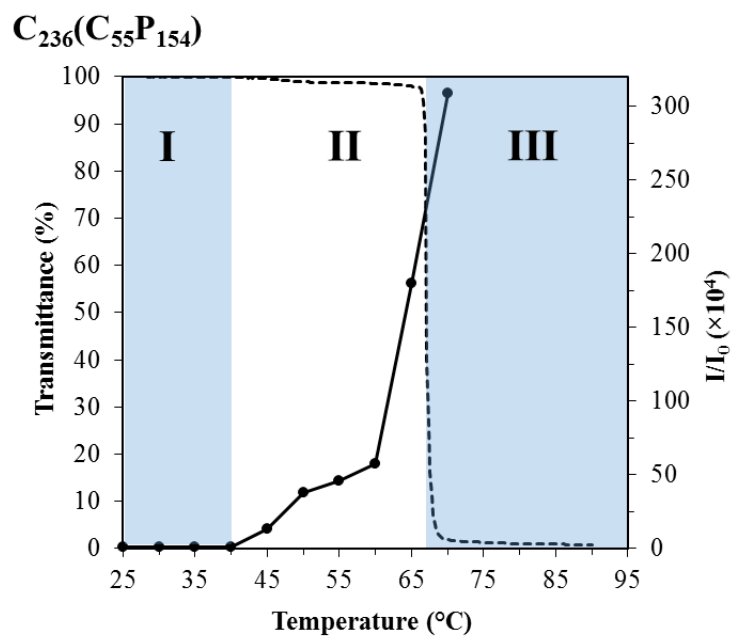
C$_{236}$(C$_{55}$P$_{154}$)

C$_{236}$(C$_{110}$P$_{308}$)C$_{236}$

Figure S6. Transmittance (1 °C min^{-1}) (dotted line) and scattered intensity measured by DLS (full line) for the C$_{236}$(C$_{55}$P$_{154}$) diblock and the parent C$_{236}$(C$_{110}$P$_{308}$)C$_{236}$ triblock aqueous solutions (1 g L^{-1}) as a function of temperature.
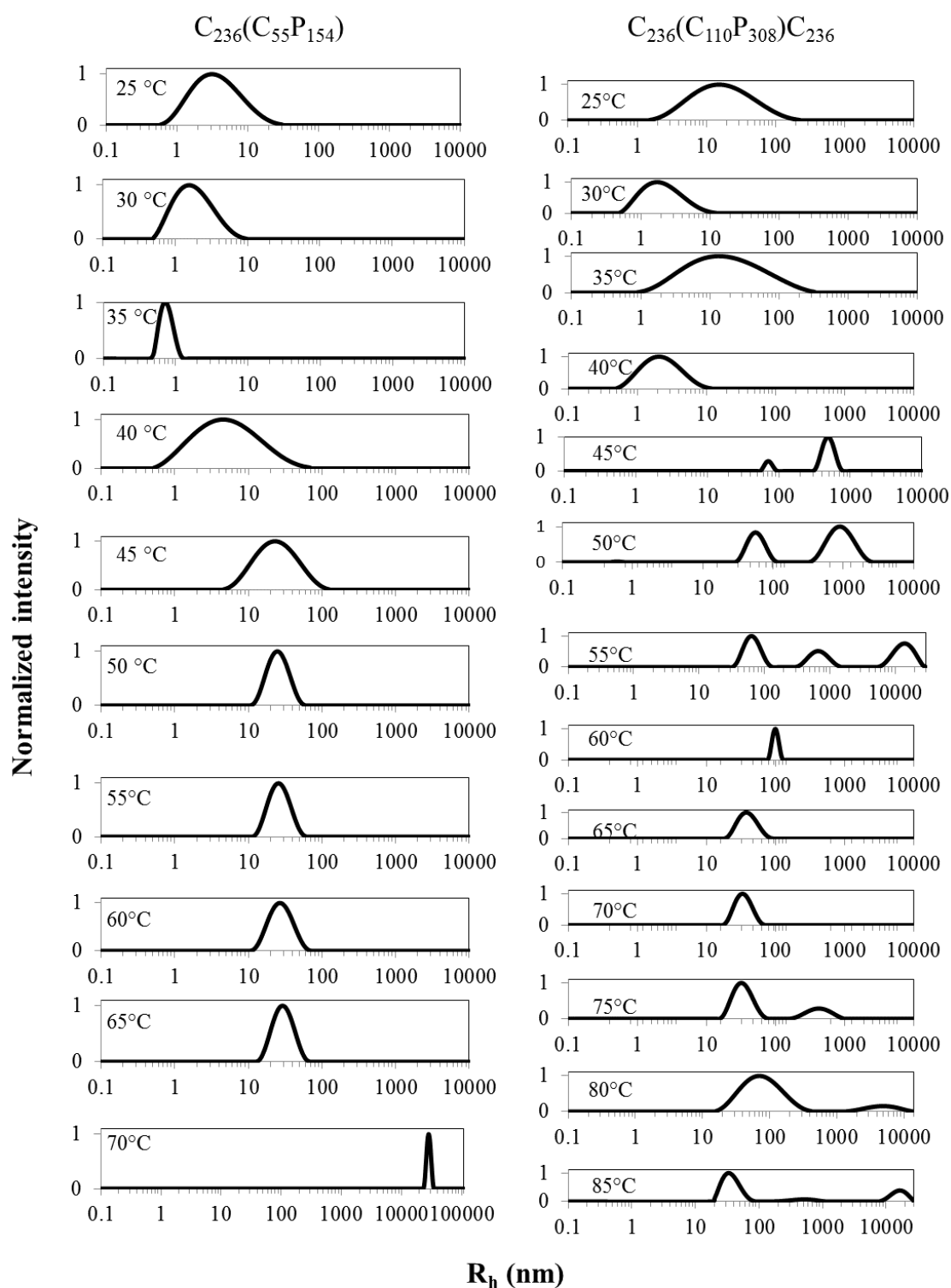
Figure S7. Intensity normalized CONTIN size distribution of $C_{236}(C_{55}P_{154})$ and $C_{236}(C_{110}P_{308})C_{236}$ in water (1 g L^{-1}) at various temperatures.
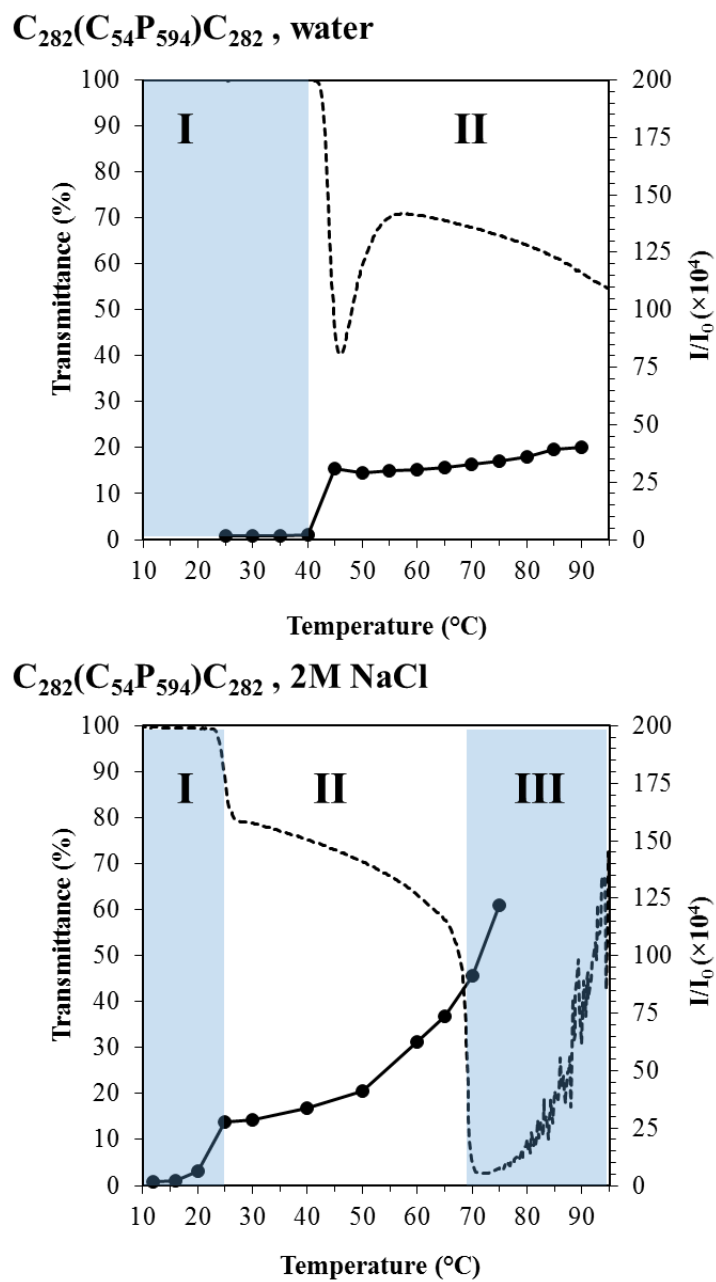
C_{282}(C_{54}P_{594})C_{282} , water

C_{282}(C_{54}P_{594})C_{282} , 2M NaCl

Figure S8. Transmittance (1 °C min^{-1}) (dotted line) and scattered intensity measured by DLS (full line) for the C$_{282}$(C$_{54}$P$_{594}$)C$_{282}$ triblock (1 g L^{-1}) in water and in 2M NaCl aqueous solutions as a function of temperature.
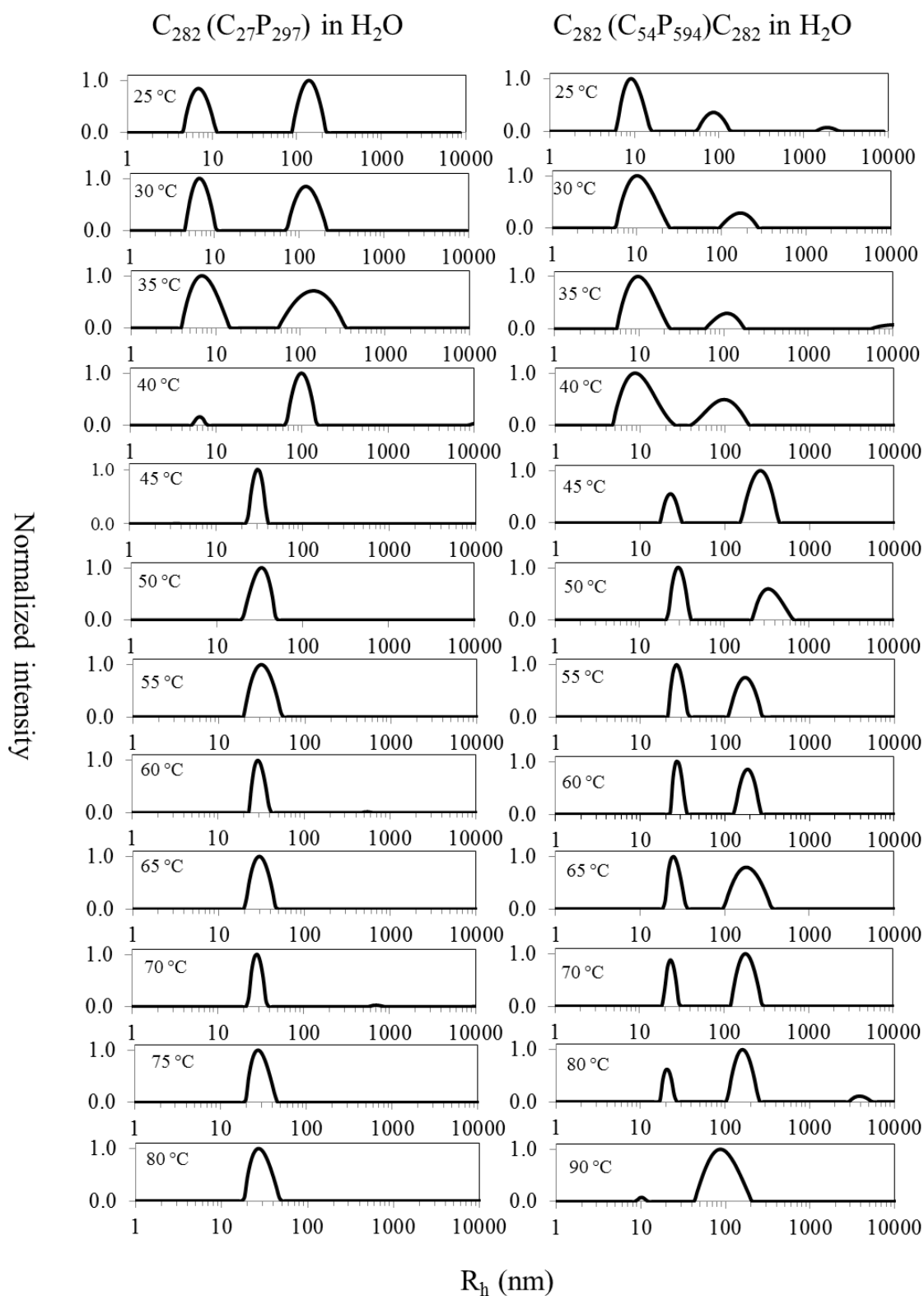
Figure S9. Intensity normalized CONTIN size distribution of $C_{282}(C_{27}P_{297})$ and $C_{282}(C_{54}P_{594})C_{282}$ in water (1 g L^{-1}) at various temperatures.
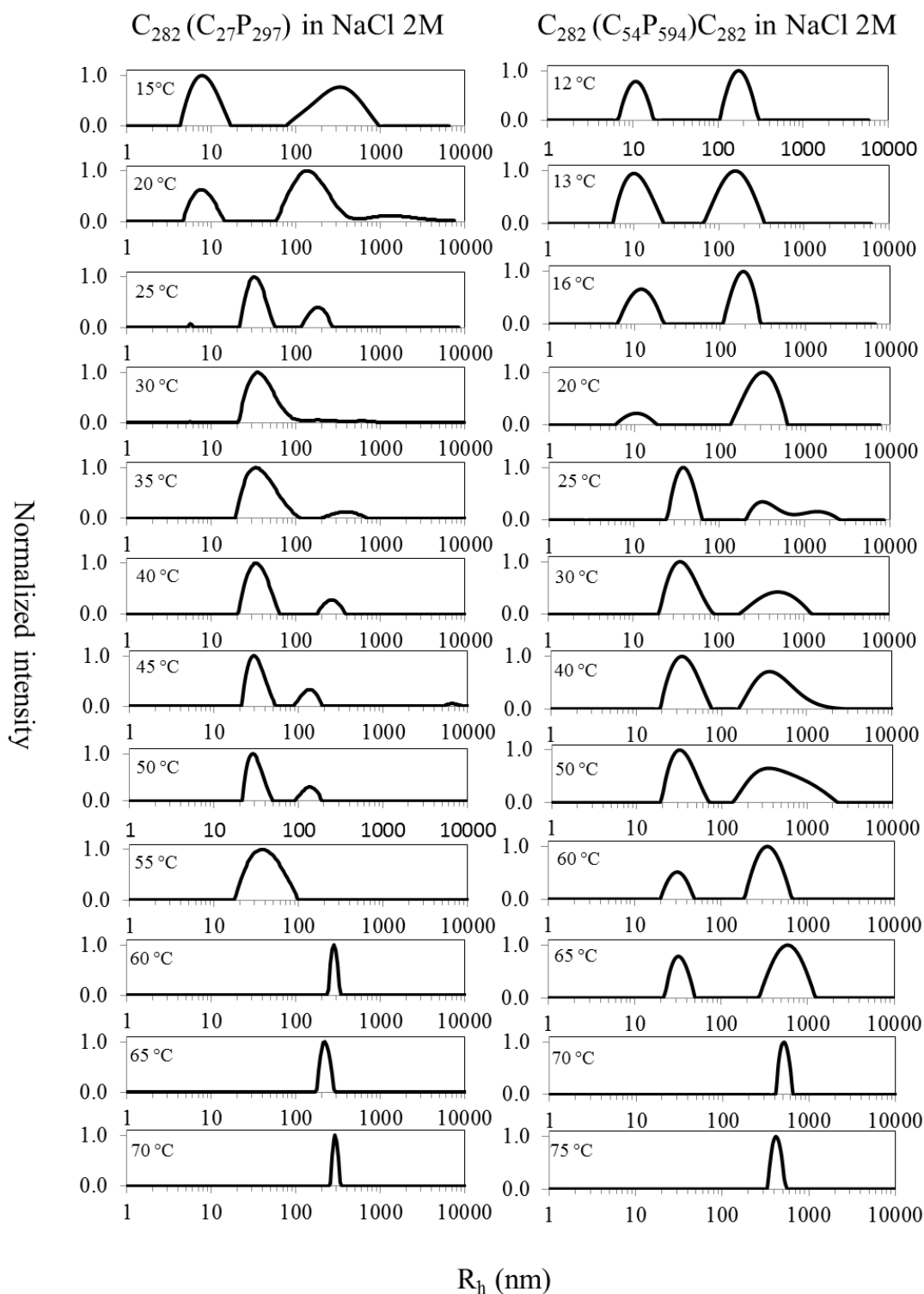
C$_{282}$ (C$_{27}$P$_{297}$) in NaCl 2M   C$_{282}$ (C$_{54}$P$_{594}$)C$_{282}$ in NaCl 2M

Normalized intensity

R$_h$ (nm)

Figure S10. Intensity normalized CONTIN size distribution of C$_{282}$(C$_{27}$P$_{297}$) and C$_{282}$(C$_{54}$P$_{594}$)C$_{282}$ in a 2 M NaCl aqueous solution (1 g L^{-1}) at various temperatures.
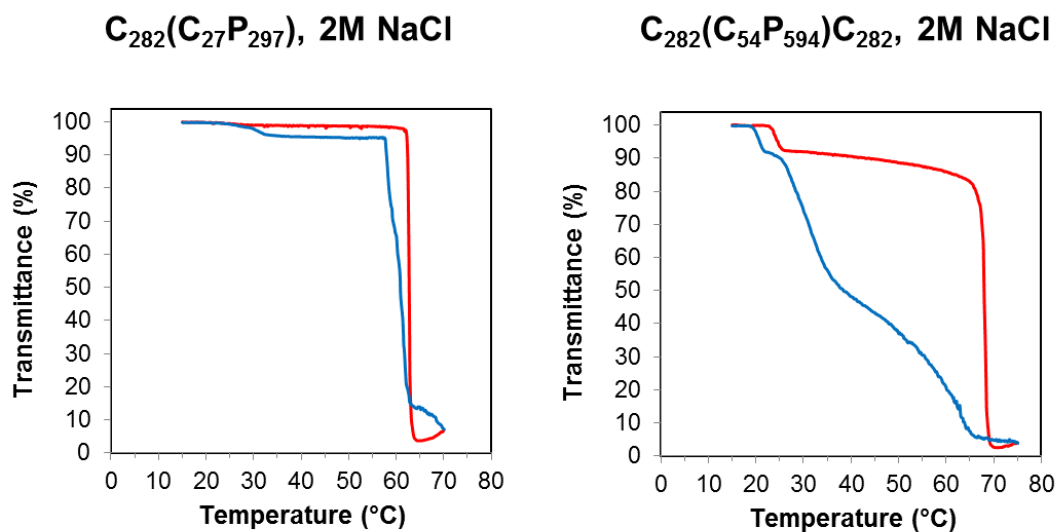
11

C$_{282}$(C$_{27}$P$_{297}$), 2M NaCl

C$_{282}$(C$_{54}$P$_{594}$)C$_{282}$, 2M NaCl

Figure S11. Transmittance (1 °C min^{-1}) for C$_{282}$(C$_{27}$P$_{297}$) diblock and C$_{282}$(C$_{54}$P$_{594}$)C$_{282}$ triblock in a 2 M NaCl aqueous solution (1 g L^{-1}) during a heating-cooling cycle. Measurements recorded when increasing the temperature are represented in red. Blue corresponds to the cooling phase.
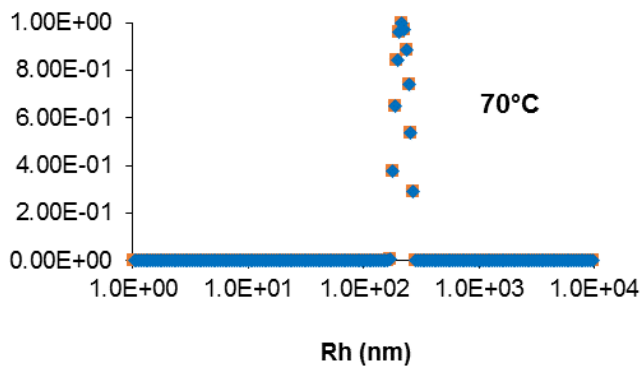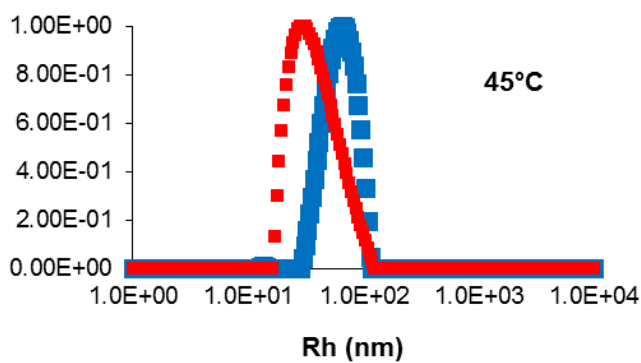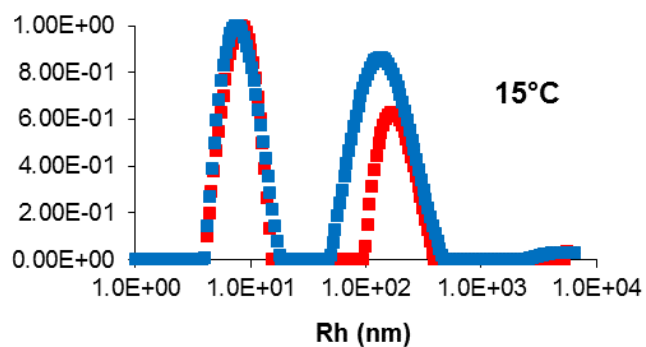
Figure S12. Intensity normalized CONTIN size distribution of $C_{282}(C_{27}P_{297})$ in a 2 M NaCl aqueous solution (1 g L^{-1}) at different temperatures during a heating-cooling cycle. DLS distributions obtained during the heating and the cooling phases are represented in red and blue, respectively.