Electronic Supplementary Material (ESI) for Soft Matter.

Doubly thermo-responsive copolymers in ionic liquid

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Contents

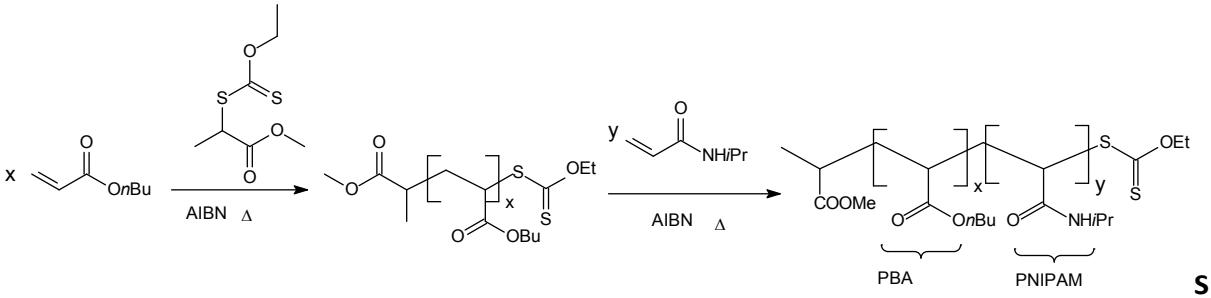
1. Synthesis of block copolymers

Table S1. Theoretical weight fractions (ω) of each block in the copolymers.

notation	C1 PBA-*b*-PNIPAM			C2 PBA-*b*-P(NIPAM$_{82\%}$-*stat*-NtBuAM$_{18\%}$)			C3 PBA-*b*-P(NIPAM$_{60\%}$-*stat*-NtBuAM$_{40\%}$)		
Block proportions	2k/8k	5k/5k	8k/2k	2k/8k	5k/5k	8k/2k	2k/8k	5k/5k	8k/2k
ω_{PBA}	0.2	0.5	0.8	0.2	0.5	0.8	0.2	0.5	0.8
ω_{PNIPAM}	0.8	0.5	0.2	0.66	0.412	0.165	0.474	0.296	0.118
ω_{PtBuAM}	0	0	0	0.14	0.088	0.035	0.326	0.204	0.082

1a. Synthesis of PBA-*b*-PNIPAM diblock copolymers (Series C1).

Copolymers of BA and NIPAM (Series C1) were synthesized and characterized according to previously reported procedures.[21]



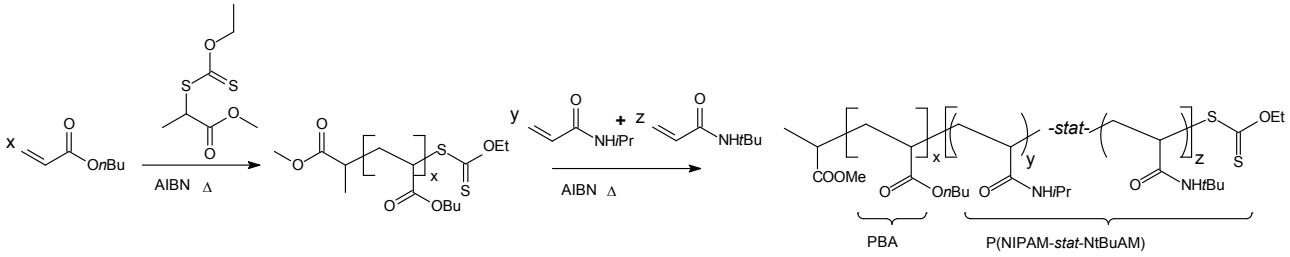
Scheme S1. Synthesis of poly(*n*-butyl acrylate)-*b*-poly(*N*-isopropyl acrylamide), PBA-*b*-PNIPAM by RAFT/MADIX polymerisation with theoretical $\bar{M}_n$ = 10000 g.mol^{-1}.

Table S2. Experimental conditions and polymerisation results for the synthesis of diblock copolymers (series C1)

Copolymers	m_{AIBN} (g)	$m_{xanthate}$ (g)	m_{BA} (g)	m_{PBA} (g)	m_{NIPAM} (g)	$m_{ethanol}$ (g)	Conv. %	$\bar{M}_n$ g.mol^{-1} [a]	Đ
PBA_{2k}	0.051	0.521	4.994			3.39	98.2	2200	1.19
C1 PBA_{2k}-*b*-$PNIPAM_{8k}$	0.187			3.873	15.556	16.446	100	10050	1.16
PBA_{5k}	0.051	0.214	4.931			2.235	98.3	5600	1.24
C1 PBA_{5k}-*b*-$PNIPAM_{5k}$	0.056			1.545	1.546	2.413	100	9400	1.25
PBA_{8k}	0.076	0.208	7.799			3.586	98.9	9150	1.21
C1 PBA_{8k}-*b*-$PNIPAM_{2k}$	0.192			4.001	1.076	3.615	100	10100	1.20

[a] SEC in THF with RI-MALS detection, 10 mg/mL, 1 mL/min

1.b. Synthesis of PBA-b-P(NIPAM-stat-NtBuAM) diblock copolymers (series C2 and C3).



Scheme S2. Synthesis of poly(*n*-butyl acrylate)-*b*-poly(*N*-isopropyl acrylamide-*stat*-*N*-tert-butylacrylamide), PBA-*b*-P(NIPAM-*stat*-NtBuAM) by MADIX polymerisation with theoretical $\bar{M}_n$ = 10000 g.mol^{-1}. Series C2: (w/w) ratio of NIPAM/NtBuAM = 82/18 Series C3: (w/w) ratio of NIPAM/NtBuAM = 40/60

Table S3. Experimental conditions and polymerisation results for the synthesis of modified block copolymers (series C2 and C3).

Copolymers	m_{AIBN} (g)	$m_{xanthate}$ (g)	m_{BA} (g)	m_{PBA} (g)	m_{NIPAM} (g)	$m_{N\text{-}tBuAA}$ (g)	$m_{ethanol}$ (g)	Conv. (%)	$\bar{M}_n$ g.mol^{-1} [a]	Đ
PBA_{2k}	0.052	0.531	5.105				2.450	99	2100	1.20
C2 PBA_{2k}-*b*-P($NIPAM_{82\%}$-*stat*-$NtBuAM_{18\%}$)$_{8k}$	0.098			2.974	6.585	1.433	9.605	100	9950	1.33
PBA_{5k}	0.055	0.266	6.419				3.068	98	5400	1.22
C2 PBA_{5k}-*b*-P($NIPAM_{82\%}$-*stat*-$NtBuAM_{18\%}$)$_{5k}$	0.194			5.810	3.300	0.724	6.825	100	10000	1.18
PBA_{8k}	0.105	0.338	12.78				7.160	99	8700	1.23
C2 PBA_{8k}-*b*-P($NIPAM_{82\%}$-*stat*-$NtBuAM_{18\%}$)$_{2k}$	0.384			12.21	1.648	0.407	14.645	100	9700	1.27
PBA_{2k}	0.052	0.537	5.165				2.247	98.4	2200	1.19
C3 PBA_{2k}-*b*-P($NIPAM_{60\%}$-*stat*-$NtBuAM_{40\%}$)$_{2k}$	0.096			2.000	4.755	3.265	8.962	100	12700	1.16
PBA_{5k}	0.052	0.232	5.351				2.562	98.7	5100	1.23
C3 PBA_{5k}-*b*-P($NIPAM_{60\%}$-*stat*-$NtBuAM_{40\%}$)$_{5k}$	0.192			3.999	2.372	1.647	7.826	100	10250	1.21
PBA_{8k}	0.110	0.268	10.02				4.797	99.4	7900	1.21
C3 PBA_{8k}-*b*-P($NIPAM_{60\%}$-*stat*-$NtBuAM_{40\%}$)$_{2k}$	0.385			2.001	1.186	0.815	7.131	100	8600	1.23

[a] SEC in THF with RI-MALS detection, 10 mg/mL, 1 mL/min

2. Size Exclusion Chromatography (SEC)

dn/dc of P(A/B) diblock copolymers was calculated according to the following equation 1:

$$dn/dc_{(A/B)} = W_A*(dn/dc)_A + W_B*(dn/dc)_B \quad \text{(Eq. 1)}$$

where W_A and W_B are the mass fractions of blocks A and B in the copolymer, respectively. $(dn/dc)_{PBA}$=0.065 mL.g^{-1} (S. Podzimek, M. Kaska, J. Snuparek*, Macromol. Symp.* **2000**, *151*, 543-548) and $(dn/dc)_{PNIPAm}$=0.107 mL.g^{-1} (S. Zhou, S. Fan, S.C.F. Au-Yeung, C. Wu, *Polymer* **1995,** *7*, 1341-1346).

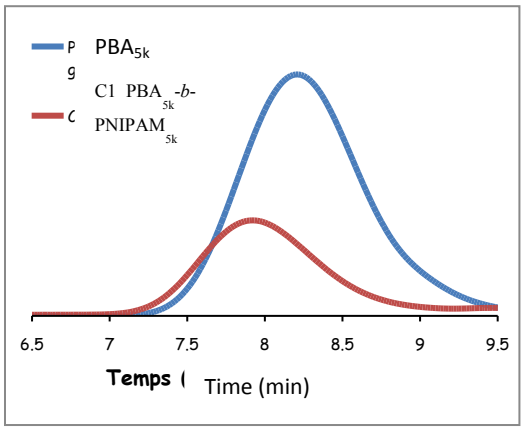


Figure S1. Size exclusion chromatograms (RI response) in THF of PBA_{5k} and of PBA_{5k}-b-$PNIPAM_{5k}$

3. Viscosity measurements of [C_2mim][NTf_2]

Viscosity was measured on an Advanced Rheometer TA Instruments type AR1000 with thermostatic control. The analysis was performed by using a cone-plan geometry with a diameter of 60 mm and a truncation of 61 µm with a 1°59'54'' angle. The velocity gradient was between 0.5 and 1000 s^{-1}.

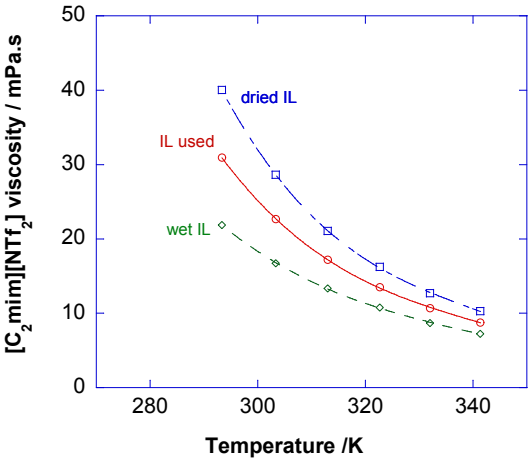


Figure S2. Viscosity of [C_2mim][NTf_2] versus temperature. Dried IL under reduce pressure at 50°C for 24 h with constant stirring: 14.5 ppm, wet IL (saturated in water): 15300 ppm, used IL (commercial without supplementary drying): 3575 ppm of water.

4.c. Phase transition temperatures of PNIPAM homopolymers

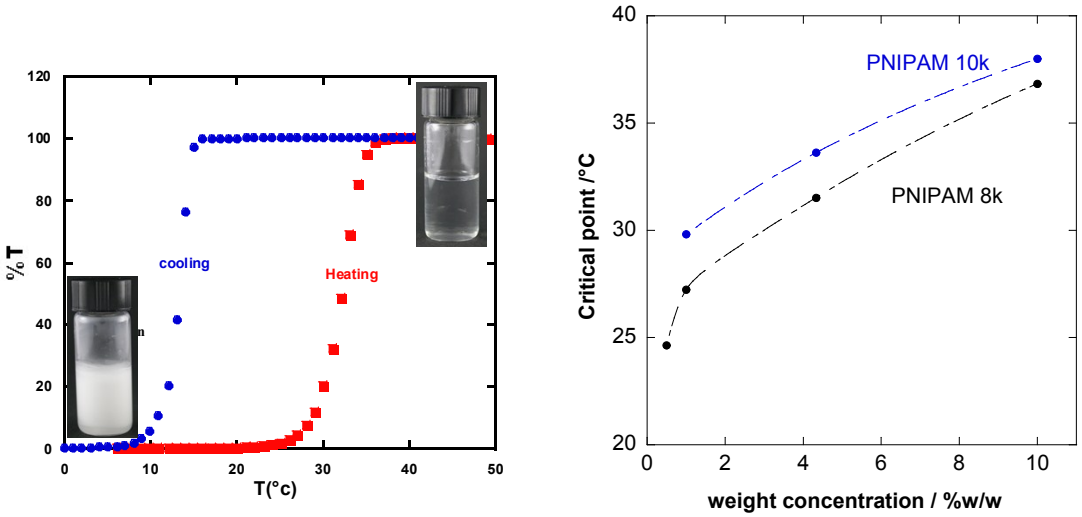


Figure S3. (A) Turbidity curves for PNIPAM 8k in [C_2mim][NTf_2] at a concentration of 1.0 wt.% with cooling and heating rates at 5°C/min. (B) Clarification point for PNIPAM 8k and 10k in [C_2mim][NTf_2] as a function of polymer concentrations (0.5, 1, 4.3, 10%). These points were calculated by the extrapolation to 0°C/min of the transition temperatures obtained from the inflection point of transmittance vs temperature curves measured at different rates.

4.d. Phase transition temperatures of PBA homopolymers

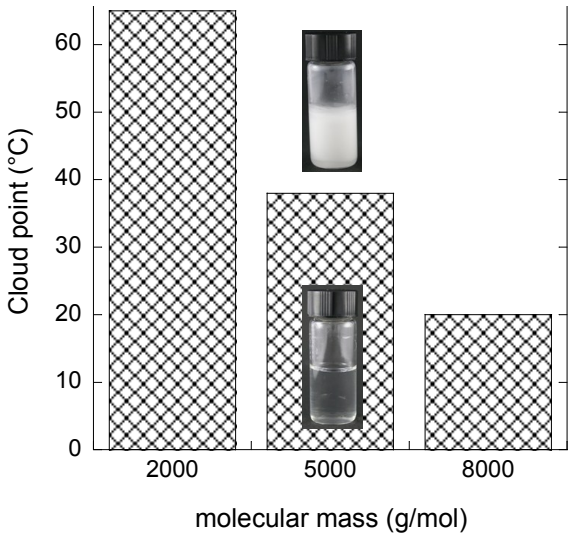


Figure S4. Cloud points determined by DLS measurements for PBA2k, 5k and 8k homopolymers in IL (1wt.%) on heating and cooling processes.

4.e. Phase transition temperatures of block copolymers

Table S4. Transition temperatures of PBA-b-PNIPAM and PBA-*b*-P(NIPAM-*stat*-NtBuAM) copolymer solutions in [C_2mim][NTf_2] (with 3575 ppm of water) at a concentration of 1.0 wt.%. Determination of Critical Points by turbidimetry: Transmittance of copolymer solutions was recorded with a Cary spectrophotometer with increasing temperature (from 0 to 50°C) at different heating rates (0.2, 0.5, 1, 2, 5°C/min). The transition temperature were then calculated by the extrapolation to 0 °C/min of the transition temperatures obtained from the inflection point of each transmittance curve.

Series	copolymer	Transition temperature (°C)	by turbidimetry		by DLS
			On heating	On cooling	
C1	2/8	Clarification point Cloud point	31.3	30.7	26 >65
	5/5	Clarification point Cloud point	18.8	17.2	16 53
	8/2	Clarification point Cloud point	7.5	 29.5	7.5 38
C2	2/8	Clarification point	27	25.2	25
	5/5	Clarification point Cloud point	16.5	15.7	16 51
	8/2	Clarification point Cloud point	 30.2	 31.9	9 30
C3	2/8	Clarification point Cloud point	28.8	28.4	31
	5/5	Clarification point Cloud point	22.7	21.7	26 56
	8/2	Clarification point Cloud point	 28.2	 25.2	7 63

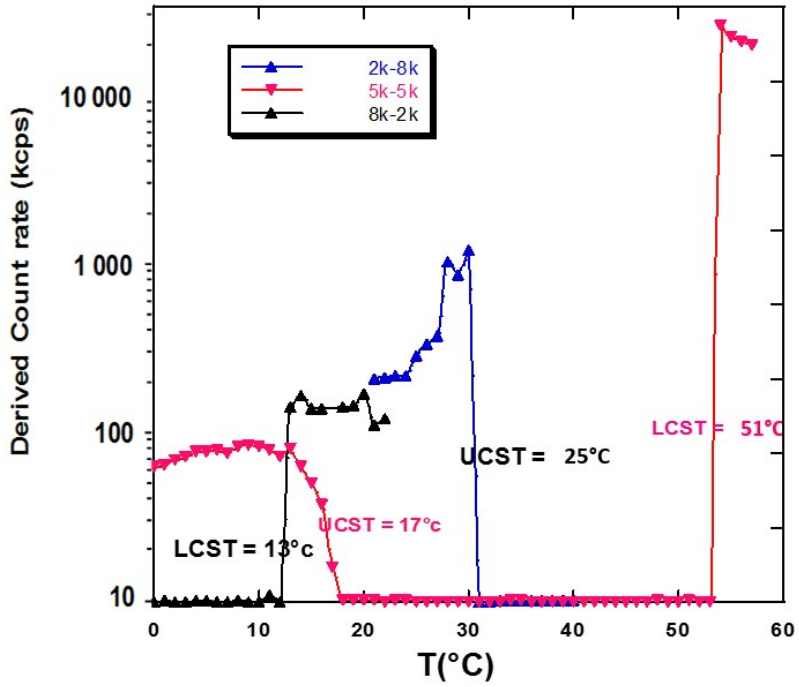


Figure S5. Temperature dependence of the derived count rate of the scattered light for C2 PBA-*b*-P(NIPAM-*stat*-NtBuAM) polymer solutions in [C_2mim][NTf_2] at a concentration of 1.0 wt.%.

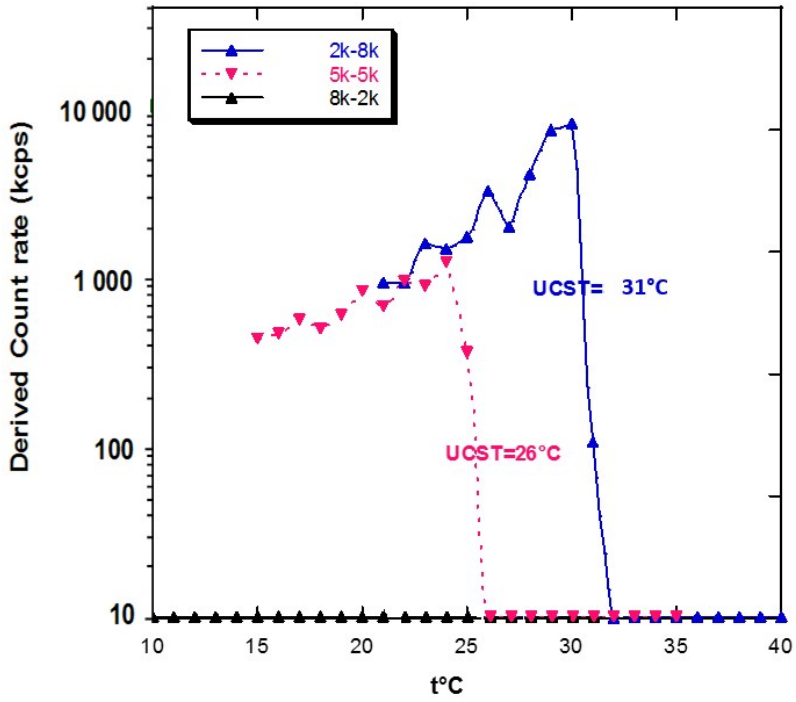


Figure S6. Temperature dependence of the derived count rate of the scattered light for C3 PBA-*b*-P(NIPAM-*stat*-NtBuAM) polymer solutions in [C_2mim][NTf_2] at a concentration of 1.0 wt.%.

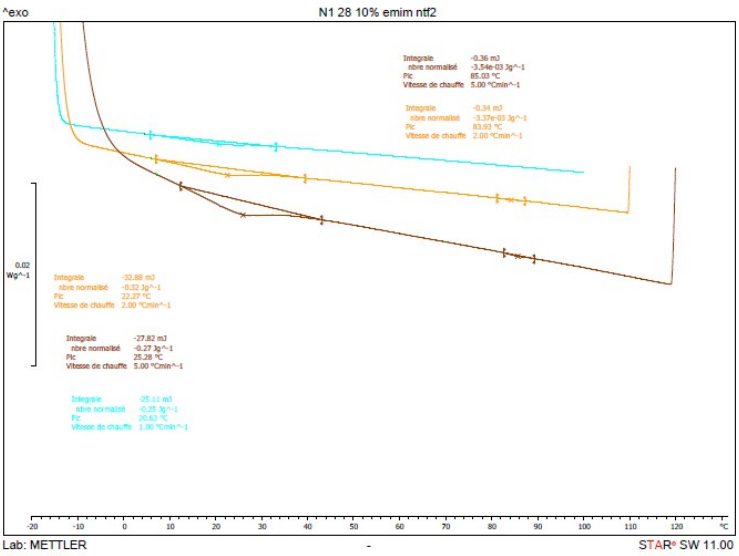


Figure S7. DSC thermogram for C1 2/8 PBA-*b*-PNIPAM polymer solutions in [C_2mim][NTf_2] at a concentration of 10 wt.% at 1, 2 and 5°C/min. (Temperature of transitions: 20.26°C and 83.20°C)

5. Size of aggregates in IL

5.a. Analysis by DLS

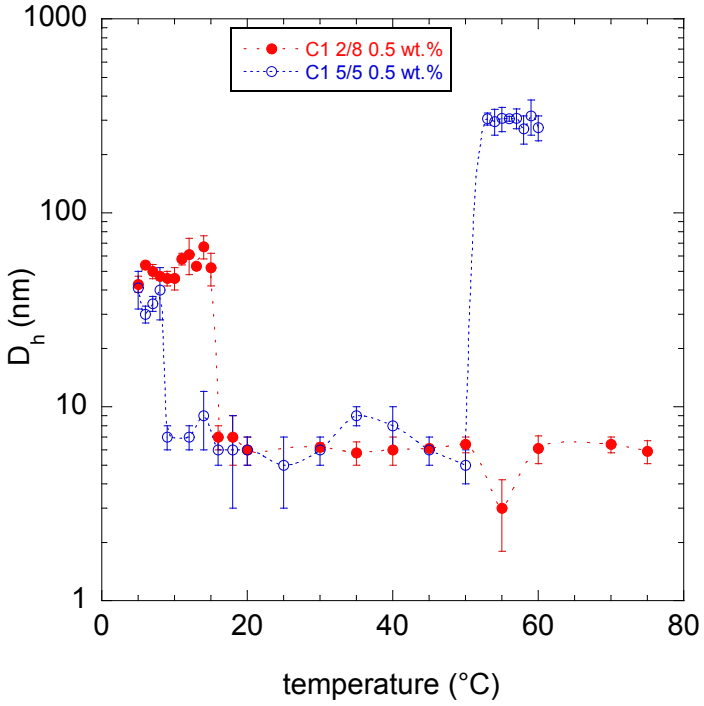


Figure S8. Mean hydrodynamic diameter (D_h) obtained from DLS measurements for a 0.5 wt.% solutions of C1 2/8 and of C1 5/5 in function of temperature.

5.b. Analysis by Cryo-Scanning Electron Microscopy (Cryo-SEM)

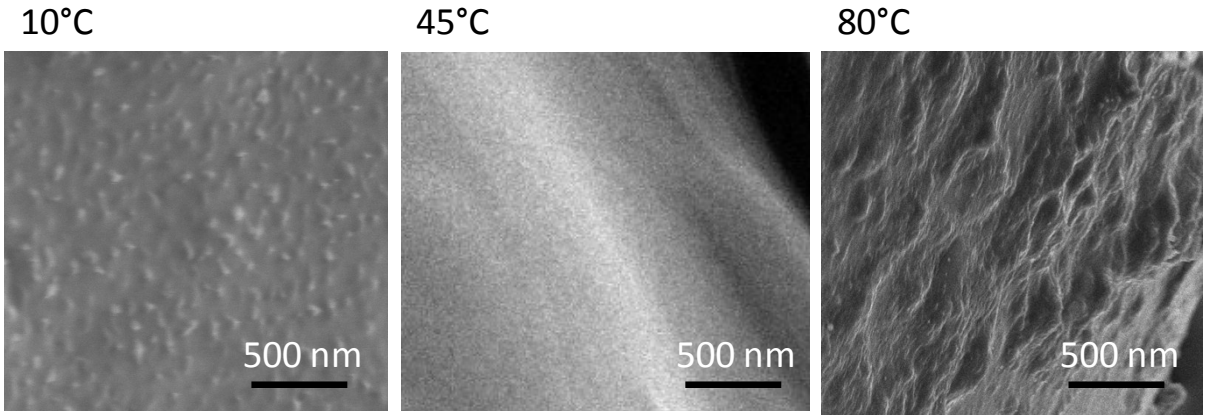


Figure S9. Cryo-SEM images of PBA-b-PNIPAM C1 5/5 at three different temperatures (10°C, 45°C and 80°C)