

Supporting Information for

Dual, orthogonal switching of the “schizophrenic” self-assembly of diblock copolymers

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Structural parameters from model fitting of the SANS curves

Tables S1-S7 give all parameters from the fits of the models in Eqs. 1 and 2 in the main text to the small-angle neutron scattering curves of the PSBP₈₀-*b*-PNIPAM₁₀₀ and PSBP₈₀-*b*-PNIPAM₁₁₅ solutions. Figure S1 gives IR spectra of the polymers. Figure S2 gives SEC elugrams of the polymers.

Table S1. Best fit parameters of Eq. 1 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPAM₁₀₀ solution in D₂O in regime I.

	10 °C	20 °C	30 °C
r_{avg} [nm]	14.4 ± 1.4	13.8 ± 1.3	13.8 ± 1.3
p	0.22 ± 0.02	0.24 ± 0.02	0.28 ± 0.03
R_{HS} [nm]	26 ± 3	24 ± 2	24 ± 2
η	0.15 ± 0.01	0.10 ± 0.01	0.04 ± 0.01
I_P	$(8.6 \pm 0.8) \times 10^{-9}$	$(1.2 \pm 0.1) \times 10^{-9}$	$(3.2 \pm 0.3) \times 10^{-9}$
α	3.9 ± 0.2	4.1 ± 0.3	4.1 ± 0.3
I_{OZ} [cm ⁻¹]	1.4 ± 0.1	3.4 ± 0.2	8.3 ± 0.7
ξ_{OZ} [nm]	1.5 ± 0.2	2.4 ± 0.2	3.6 ± 0.3
SLD_{sphere} [nm ⁻²]		$(7.7 \pm 0.4) \times 10^{-5}$	

Table S2. Best fit parameters of Eq. 1 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPAM₁₀₀ solution in D₂O in regime III.

	40 °C	50 °C
r_{avg} [nm]	10.6 ± 1.0	11.9 ± 1.2
L [nm]	23 ± 2	36 ± 4
b [nm]	10 ± 1	16 ± 2
p	0.21 ± 0.02	0.16 ± 0.02
R_{HS} [nm]	19 ± 2	22 ± 3
η	0.44 ± 0.02	0.52 ± 0.03
I_P	$(4.9 \pm 0.4) \times 10^{-10}$	$(7.0 \pm 0.6) \times 10^{-10}$
α	4.9 ± 0.3	4.8 ± 0.3
C [cm ⁻¹]	1.7 ± 0.1	1.5 ± 0.1
ξ_{solv} [nm]	4.7 ± 0.4	7.9 ± 0.8
m	1.36 ± 0.12	0.94 ± 0.10
d_0 [nm]	15 ± 2	15 ± 2
$SLD_{cylinder}$ [nm ⁻²]	$(7.7 \pm 0.4) \times 10^{-5}$	

Table S3. Best fit parameters of Eq. 1 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPMAM₁₁₅ solution in D₂O in regime I.

	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
r_{avg} [nm]	12.7 ± 1.3	12.3 ± 1.2	12.1 ± 1.2	11.7 ± 1.1	11.5 ± 1.2	11.5 ± 1.2
p	0.25 ± 0.02	0.27 ± 0.03	0.27 ± 0.03	0.27 ± 0.03	0.22 ± 0.02	0.10 ± 0.01
R_{HS} [nm]	24 ± 2	23 ± 2	23 ± 2	23 ± 2	24 ± 2	19 ± 2
η	0.11 ± 0.01	0.09 ± 0.01	0.07 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.09 ± 0.01
$I_P \times 10^{-8}$	10.0 ± 1.0	1.3 ± 0.1	8.4 ± 0.9	8.6 ± 0.9	1.6 ± 0.2	14.7 ± 1.2
α	4.0 ± 0.2	3.9 ± 0.2	3.5 ± 0.1	3.5 ± 0.1	3.7 ± 0.1	4.1 ± 0.2
I_{OZ} [cm ⁻¹]	7 ± 1	10 ± 1	17 ± 2	25 ± 2	46 ± 3	46 ± 3
ξ_{OZ} [nm]	3.5 ± 0.2	3.9 ± 0.3	4.8 ± 0.4	5.6 ± 0.5	7.3 ± 0.7	6.9 ± 0.5
SLD_{sphere} [nm ⁻²]	(7.1 ± 0.3) × 10 ⁻⁵					

Table S4. Best fit parameters of Eq. 1 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPMAM₁₁₅ solution in D₂O in regime III.

	50 °C	55 °C	60 °C	65 °C
r_{avg} [nm]	10.1 ± 1.0	13.1 ± 1.1	13.5 ± 1.2	13.5 ± 1.2
L [nm]	25 ± 2	29 ± 3	34 ± 3	54 ± 5
b [nm]	16 ± 2	18 ± 2	18 ± 2	18 ± 2
p	0.50 ± 0.05	0.20 ± 0.02	0.16 ± 0.01	0.16 ± 0.2
R_{HS} [nm]	21 ± 2	22 ± 2	22 ± 2	22 ± 2
η	0.34 ± 0.02	0.35 ± 0.03	0.36 ± 0.03	0.37 ± 0.03
$I_P \times 10^{-9}$	2.2 ± 0.2	0.8 ± 0.1	0.9 ± 0.1	1.2 ± 0.1
α	4.7 ± 0.3	4.9 ± 0.3	4.9 ± 0.3	4.9 ± 0.3
C [cm ⁻¹]	3.2 ± 0.2	1.6 ± 0.1	1.5 ± 0.1	1.6 ± 0.2
ξ_{solv} [nm]	4.2 ± 0.2	3.9 ± 0.2	5.5 ± 0.3	5.8 ± 0.4
m	1.59 ± 0.21	1.53 ± 0.13	1.13 ± 0.10	1.16 ± 0.11
d_0 [nm]	17 ± 2	15 ± 2	14 ± 1	14 ± 1
$SLD_{cylinder}$ [nm ⁻²]	$(7.1 \pm 0.3) \times 10^{-5}$			

Table S5. Best fit parameters of Eq. 1 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPMAM₁₁₅ solution in 0.004 M NaBr in D₂O in regimes I and II.

	Regime I			Regime II		
	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
r_{avg} [nm]	11.8 ± 1.2	11.1 ± 1.0	10.0 ± 1.0	2.9 ± 0.3	2.3 ± 0.2	2.3 ± 0.2
p	0.26 ± 0.03	0.27 ± 0.03	0.29 ± 0.03	0.85 ± 0.08	0.80 ± 0.07	0.53 ± 0.05
R_{HS} [nm]	22 ± 2	21 ± 2	20 ± 2	17 ± 2	17 ± 2	18 ± 2
η	0.10 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.08 ± 0.01	0.08 ± 0.01	0.11 ± 0.01
$I_P \times 10^{-9}$	11.1 ± 1.1	2.1 ± 0.2	1.4 ± 0.1	0.5 ± 0.1	62 ± 2	460 ± 60
α	3.8 ± 0.1	4.0 ± 0.1	4.1 ± 0.2	3.8 ± 0.2	3.4 ± 0.1	3.2 ± 0.1
I_{OZ} [cm ⁻¹]	21 ± 2	31 ± 3	36 ± 4	26 ± 3	23 ± 3	23 ± 3
ξ_{OZ} [nm]	6.2 ± 0.4	6.8 ± 0.5	7.0 ± 0.6	5.8 ± 0.5	5.3 ± 0.4	5.4 ± 0.5
SLD_{sphere} [nm ⁻²]	(7.1 ± 0.3) × 10 ⁻⁵					

Table S6. Best fit parameters of Eq. 2 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPMAM₁₁₅ solution in 0.004 M NaBr in D₂O in regime II.

	35 °C	40 °C	45 °C
$I_P \times 10^{-7}$	1.8 ± 0.1	3.9 ± 0.2	19 ± 2
α	3.3 ± 0.1	3.1 ± 0.1	2.8 ± 0.1
C [cm ⁻¹]	40 ± 3	27 ± 2	22 ± 2
ξ_{solv} [nm]	8.6 ± 0.6	6.2 ± 0.4	5.1 ± 0.3
m	1.93 ± 0.13	1.99 ± 0.13	2.05 ± 0.15
d_0 [nm]	85 ± 7	90 ± 8	105 ± 10

Table S7. Best fit parameters of Eq. 1 for the SANS data of a 50 g L⁻¹ PSBP₈₀-*b*-PNIPMAM₁₁₅ solution in 0.004 M NaBr in D₂O in regime III.

	50 °C	55 °C	60 °C	65 °C
r_{avg} [nm]	12.3 ± 1.2	12.6 ± 1.1	13.3 ± 1.2	13.8 ± 1.3
L [nm]	20 ± 2	25 ± 3	30 ± 4	45 ± 5
b [nm]	10 ± 1	17 ± 2	17 ± 2	19 ± 2
p	0.27 ± 0.02	0.16 ± 0.01	0.14 ± 0.01	0.13 ± 0.01
R_{HS} [nm]	21 ± 2	21 ± 3	22 ± 2	22 ± 2
η	0.32 ± 0.02	0.34 ± 0.03	0.35 ± 0.03	0.35 ± 0.03
$I_P \times 10^{-9}$	4.3 ± 0.2	0.7 ± 0.1	0.9 ± 0.1	0.7 ± 0.1
α	4.5 ± 0.3	4.8 ± 0.3	4.9 ± 0.3	4.9 ± 0.3
C [cm ⁻¹]	3.8 ± 0.3	1.6 ± 0.1	1.5 ± 0.1	1.4 ± 0.2
ξ_{solv} [nm]	4.8 ± 0.3	4.2 ± 0.3	7.0 ± 0.61	8.0 ± 0.7
m	1.49 ± 0.13	1.50 ± 0.11	1.10 ± 0.11	1.13 ± 0.12
d_0 [nm]	17 ± 2	15 ± 2	13 ± 1	13 ± 1
$SLD_{cylinder}$ [nm ⁻²]	$(7.1 \pm 0.3) \times 10^{-5}$			

Molecular characterization of the polymers

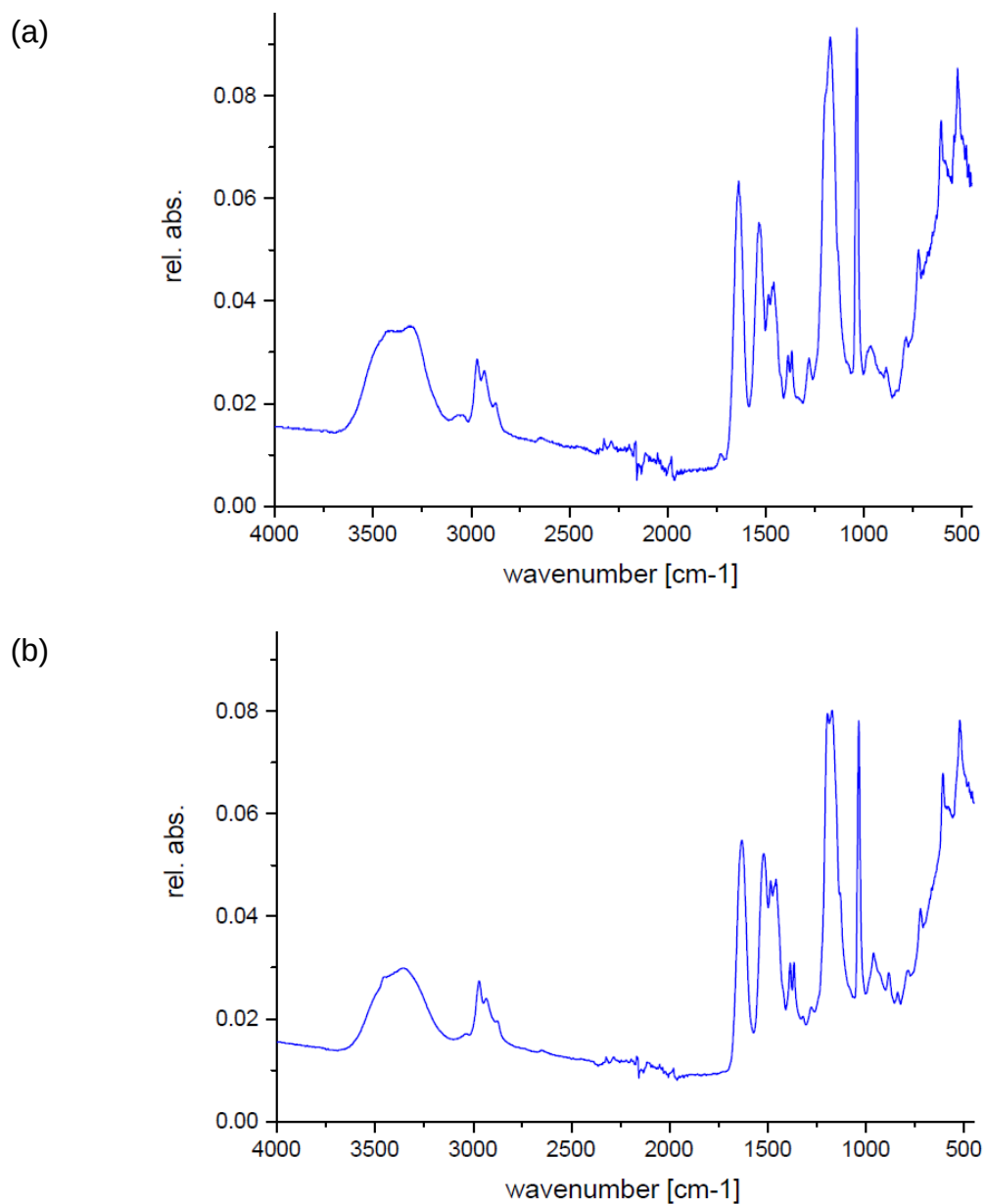


Figure S1. Infrared spectra (neat, ATR-FTIR) of the block copolymers:

(a) PSBP₈₀-*b*-PNIPAM₁₀₀ and (b) PSBP₈₀-*b*-PNIPMAM₁₁₅.

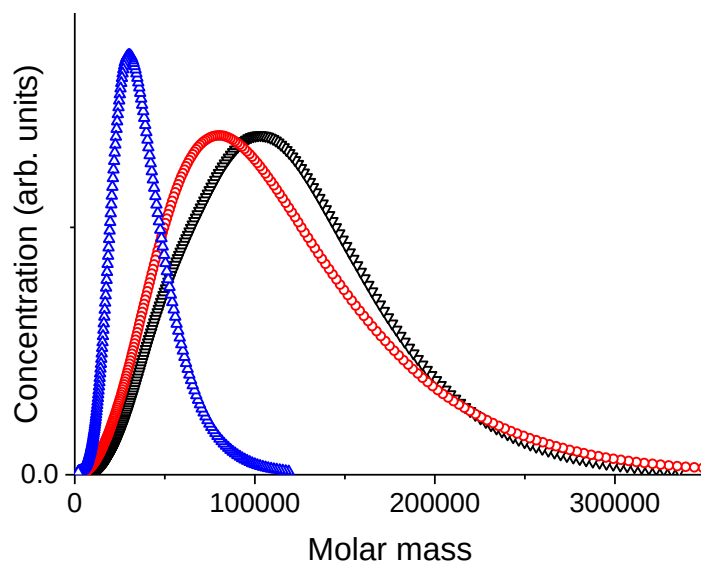


Figure S2. SEC elugrams of macro RAFT agent PSBP₈₀ (blue ▲), and of the derived block copolymers PSBP₈₀-*b*-PNIPAM₁₀₀ (red ○) and PSBP₈₀-*b*-PNIPMAM₁₁₅ (black ▼). Conditions: eluent hexafluoroisopropanol (HFIP) containing 50 mM CF₃COONa, 40 °C, calibration with narrowly distributed poly(methyl methacrylate) standards 500 - 520,000 D.