Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Phase Transitions in Concentrated Solution Self-Assembly of Globular Protein-Polymer Block Copolymers

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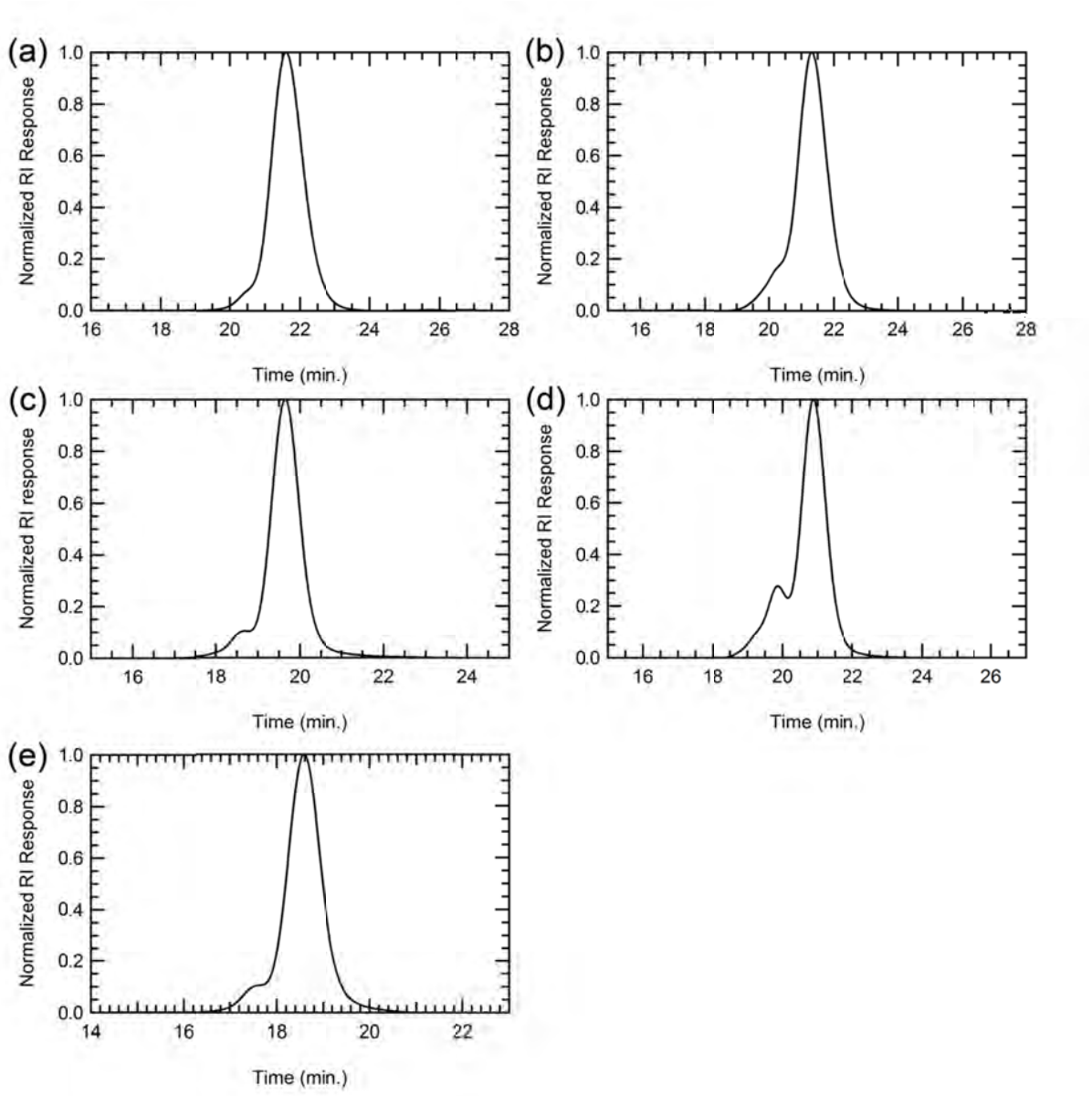

Figure S1. Gel permeation chromatography of (a) PNIPAM8k: M_n = 8,190 g/mol; M_w = 9,640 g/mol; PDI = 1.18 (b) PNIPAM17k: M_n = 17,200 g/mol; M_w = 19,300 g/mol; PDI = 1.12 (c) PNIPAM27k: M_n = 27,000; M_w = 29,400; PDI = 1.09. (d) PNIPAM30k: M_n = 29,700; M_w = 37100; PDI = 1.25 (e) PNIPAM57k: M_n = 57,100 g/mol; M_w = 60,700 g/mol; PDI = 1.06

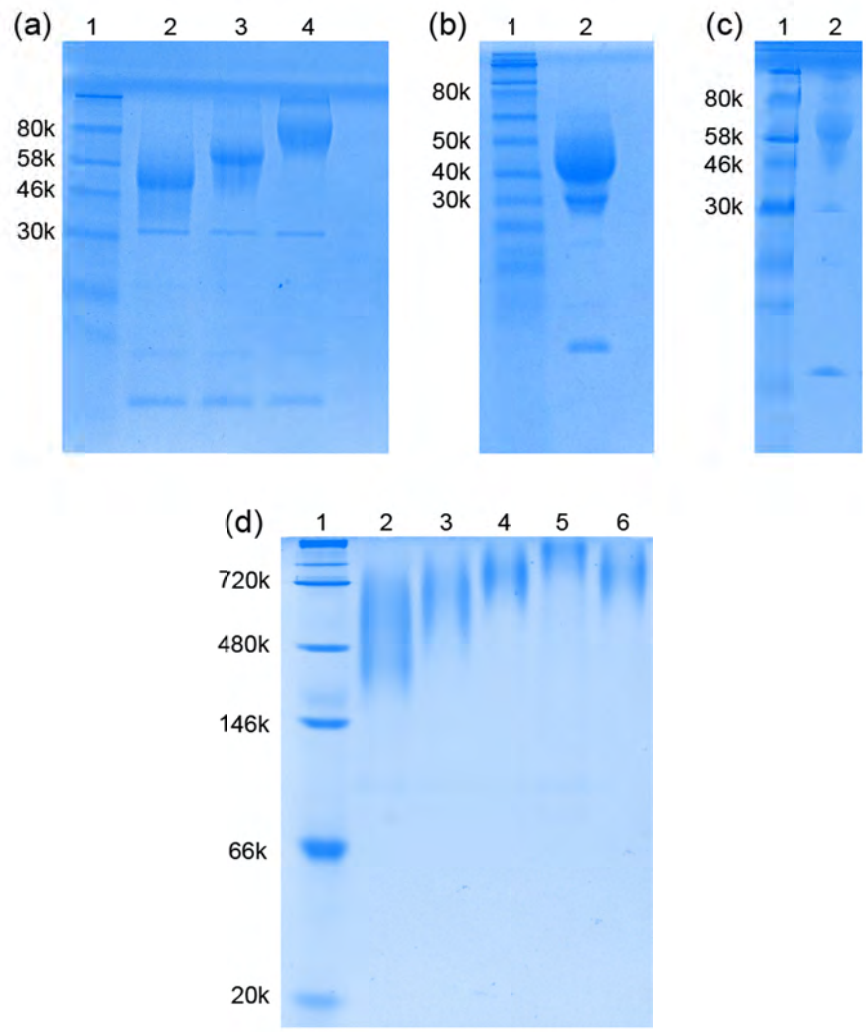

Figure S2. Denaturing protein gels of mCherryS131C-*b*-PNIPAM bioconjugates are shown in (a) – (c); a native protein gel of the bioconjugates is shown in (d). Lanes 1-4 in (a) represent ladder, mChP17, mChP30, mChP57, respectively. Lanes 1-2 in (b) represent ladder and mChP8, respectively. Lanes 1-2 in (c) represent ladder and mChP27, respectively. Lane 1 in (d) represents the native gel ladder, and lanes 2 – 6 correspond to mChP8, mChP17, mChP30, mChP57, and mChP27. Bands at 30k in the denaturing gels are unconjugated mCherry impurity, and smaller molar mass bands correspond to mCherry fragments resulting from breaking of the chromophore acylimine bond during gel sample preparation. The primary source of impurity in SDS-PAGE is cleavage of polymer and protein during gel boiling due to hydrolysis of the ester bond linking the two blocks. Native PAGE, which does not involve a harsh boiling step, shows undetectable levels of impurity, suggesting that the conjugates are > 98% pure.

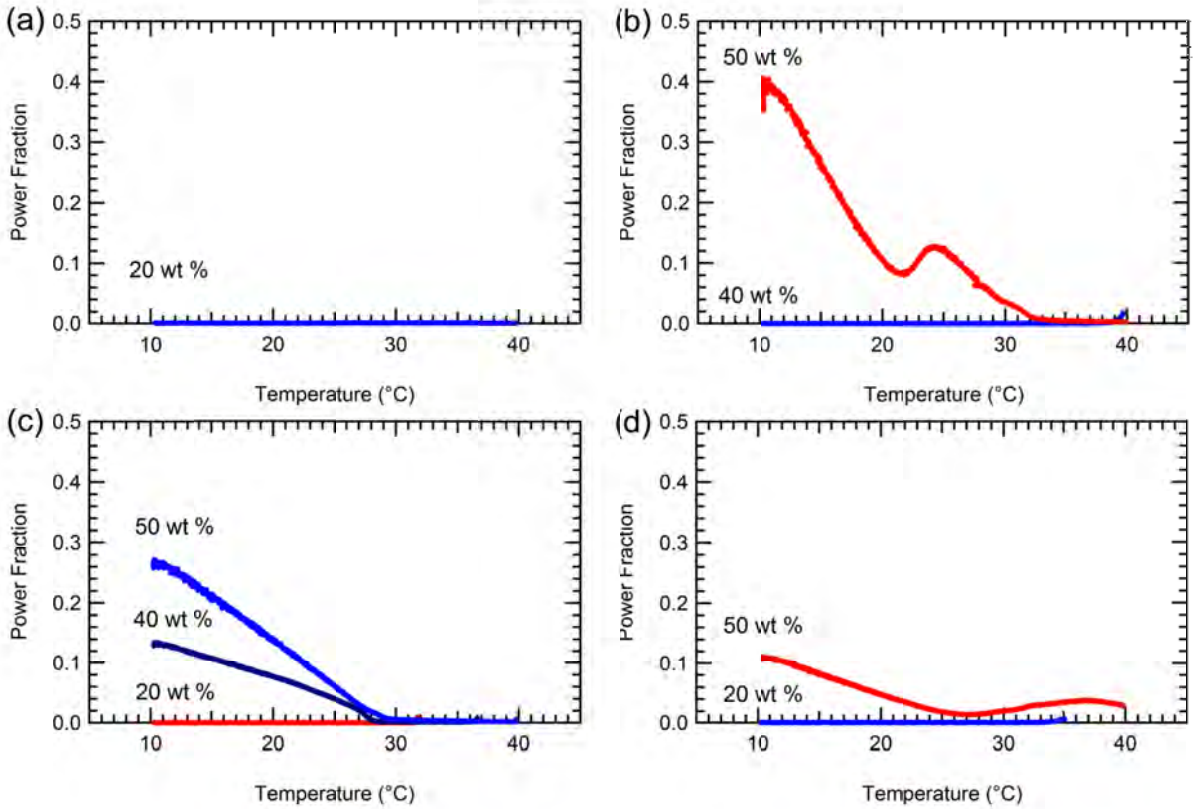

Figure S3. Representative depolarized light scattering (DPLS) measurements for (a) mChP8 (b) mChP17 (c) mChP30, and (d) mChP57. DPLS was measured from 10 to 40 °C and corrected for transmissive and reflective losses. Macrophase separation and a subsequent loss in transmission at high temperatures results in an artificially high power fraction after correction for transmissive losses; therefore, data has been omitted in mChP30 and mChP57 in the 20 wt.% curves beyond their macrophase separation transitions.

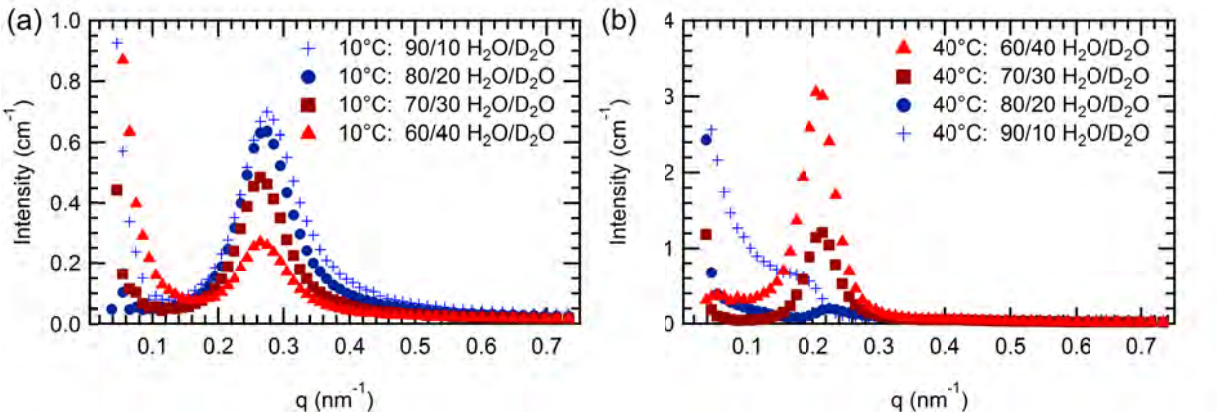

Figure S4. Small-angle neutron scattering of mCherryS131C-*b*-PNIPAM27k in different H_2O/D_2O blend compositions at (a) T = 10 °C and (b) T = 40 °C. At 40 °C, higher scattering intensity with increasing D_2O content is observed as water favorably partitions into the protein block as the polymer domain collapses above the thermal transition temperature.

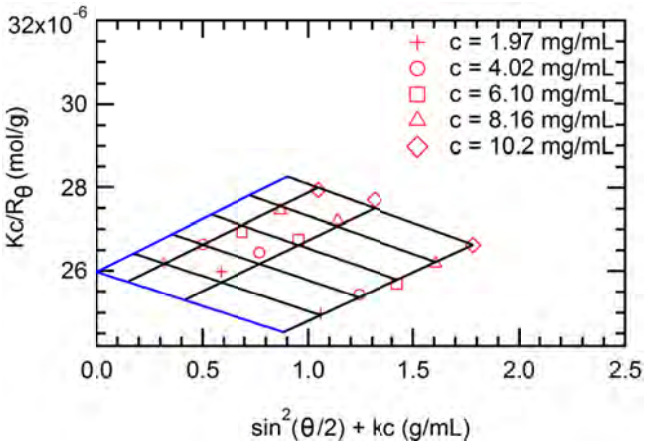

Figure S5. Zimm plot of mCherry. From extrapolation to zero concentration, the weight-average molar mass is determined to be 3.8e4 g/mol, somewhat larger than the expected value of 2.8e4 g/mol. mCherry is observed to exert weak self-repulsion in solution. The second virial coefficient was determined to be A_2 = 1.1e-4 mol mL g^{-2}.

Table S1. The concentration and temperature conditions corresponding to each representative SAXS pattern in Figure 3 are listed below.

Sample	Phase	Conc. (wt.%)	T (°C)
mChP8	Hex	50	30
	NB Lam	40	15
	DM	20	40
	Dis	20	10
mChP17	HPC	50	10
	Hex	40	30
	NB Lam	40	10
	DM	20	40
	Dis	20	10
mChP30	PL	50	30
	Lam	40	10
	NB Lam	33	10
	DM	20	40
	Dis	20	10
mChP57	Lam	50	10
	NB Lam	40	10
	DM	35	40
	Dis	25	10

Table S2. Scattering length densities (SLDs) of molecules. SLDs were computed using the Scattering Length Density Calculator from the NIST Center for Neutron Research: http://www.ncnr.nist.gov/resources/sldcalc.html

Molecule	Density (g/cm^3)	Molecular formula	SLD ($Å^{-2}$)
mCherryS131C	1.19	$C_{1250}H_{1915}N_{341}O_{377}S_{12}$	1.67e-6
PNIPAM	1.05	$C_6H_{11}NO$	7.8e-7
H_2O	1.00	H_2O	-5.6e-7
D_2O	1.107	D_2O	6.37e-6