frontiers

Supplementary Material

1 CALCULATED ATOMIC PARTIAL CHARGES OF MOLECULAR ENTITIES

Table S1. Atomic partial charges (e) used in this study. The PNIPAM and PDEA head, middle, and tail monomers are custom-calculated RESP charges under the influence of the polarizable continuum model that are replaced in the GROMACS topology files consistent with the OPLS/AA force field. The glycerol and water atomic charges are the standard values included in the OPLS/AA and SPC/E force fields, respectively. Atoms names are consistent with Figure 1 of the main manuscript.

	PNIPAM			PDEA				
atom	head	middle	tail	head	middle	tail	glycerol	water
C1	-0.1315	-0.1304	-0.1315	-0.1789	-0.1759	-0.1792	0.1450	—
C2	-0.0634	-0.0629	-0.0634	-0.0804	-0.0791	-0.0806	0.1450	—
C3	0.6392	0.6443	0.6390	0.5749	0.5842	0.5738	0.1450	—
C4	0.6191	0.6239	0.6188	0.0993	0.1009	0.0991	—	—
C5	-0.5042	-0.5002	-0.5044	-0.2240	-0.2202	-0.2244	—	—
C6	-0.5042	-0.5002	-0.5044	0.0993	0.1009	0.0991	—	—
C7	—	—	—	-0.2240	-0.2202	-0.2244	—	—
O1	-0.5948	-0.5900	-0.5950	-0.5686	-0.5591	-0.5697	-0.7300	-0.8476
O2	—	—	—	—	—	—	-0.7300	—
O3	—	—	—	—	—	—	-0.7300	—
N1	-0.7511	-0.7451	-0.7515	-0.3694	-0.3633	-0.3702	—	—
H1	0.0404	0.0407	0.0404	0.0529	0.0537	0.0528	0.4650	0.4328
H2	0.0404	0.0407	0.0404	0.0529	0.0537	0.0528	0.4650	0.4328
H3	0.0427	0.0430	0.0426	0.0594	0.0603	0.0593	0.4650	—
H4	0.3757	0.3787	0.3756	0.0573	0.0582	0.0572	0.0600	—
H5	-0.0138	-0.0137	-0.0138	0.0573	0.0582	0.0572	0.0600	—
H6	0.1275	0.1285	0.1275	0.0707	0.0719	0.0706	0.0600	—
H7	0.1275	0.1285	0.1275	0.0707	0.0719	0.0706	0.0600	—
H8	0.1275	0.1285	0.1275	0.0707	0.0719	0.0706	0.0600	—
H9	0.1275	0.1285	0.1275	0.0573	0.0582	0.0572	—	—
H10	0.1275	0.1285	0.1275	0.0573	0.0582	0.0572	—	—
H11	0.1275	0.1285	0.1275	0.0707	0.0719	0.0706	—	—
H12	—	—	—	0.0707	0.0719	0.0706	—	—
H13	—	—	—	0.0707	0.0719	0.0706	—	—
H_{cap}	0.0404	—	0.0426	0.0529	—	0.0593	—	—

2 VERIFICATION OF THE GLYCEROL FORCE FIELD

Several NPT-MD simulations were performed to assess the glycerol model density as a function of temperature, with results displayed in Figure S1. The 50:50 and 90:10 glycerol:water liquid mixtures contained 1110:5651 and 2350:1326 molecules of each liquid. The pure glycerol system contained 2383 glycerol molecules. All values were averaged over the last 3 ns of the NPT MD trajectories, have standard deviations of approximately 0.3 %, and are within 1 % of experimental measurements.

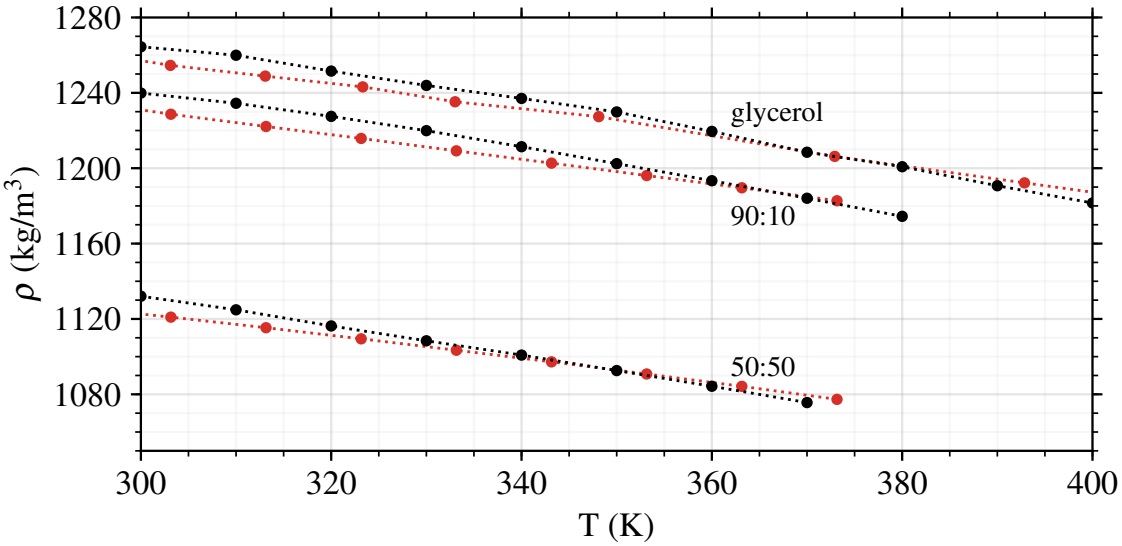

Figure S1. MD simulated densities of pure glycerol and two glycerol:water mixtures of 90:10 and 50:50 (depicted black) are compared to experimental measurements (depicted red) from *Gregory, S. R. (1963). Physical Properties of Glycerine and its Solutions (Glycerine Producers' Association).*

3 SUPPLEMENTARY DATA ON THE MOLECULAR DYNAMICS SIMULATIONS

Table S2 provides a summary of the eight system models developed in this study with their corresponding densities equilibrated though NPT-MD simulations at 101.325 kPa and the temperature listed in the table.

Structural and energetic properties of each oligomer were calculated and reported in Table 1 of the main manuscript, while Figures S2 and S3 give their time evolution along the last 200 ns of the full 1.0 μs MD trajectories.

As described in the main manuscript, a principal component analysis (PCA) of the cartesian coordinates of the 60 oligomer backbone atoms along the MD trajectories was performed. Additionally, a dihedral principal component analysis (dPCA) was performed considering the 57 oligomer contiguous dihedral angles along the oligomer backbone. The projection of the input data onto the two most prominent principal components of the PCA and the dPCA were termed PC_1, PC_2, and dPC_1, dPC_2, respectively. Their time evolution along the final 200 ns of the full MD trajectory are given in Figures S4 and S5. Meanwhile, Figure S6 provides a scatter plot between PC_1 and PC_2 that represent approximately 60% of the variance.

Table S2. Model systems used in the MD simulations: $N_{glycerol}$, N_{water} are the number of molecules of each solvent in each system. C_{olig} (wt%) identifies the mass concentration of polymer and ρ (kg/m^3) the NPT-equilibrated density of each system at two listed temperatures and 101.325 kPa.

oligomer	solvent	$N_{glycerol}$	N_{water}	C_{olig} (wt%)	T (K)	ρ (kg/m^3)
30-PNIPAM (572 atoms)	water	0	10980	1.69	290 300	1004 ± 2 1000 ± 3
	50:50	1110	5651	1.64	310 320	1125 ± 3 1116 ± 3
	90:10	2350	1326	1.40	360 370	1193 ± 3 1184 ± 3
	glycerol	2383	0	1.52	370 380	1209 ± 3 1199 ± 3
30-PDEA (662 atoms)	water	0	10964	1.90	290 300	1005 ± 2 1000 ± 2
	50:50	1110	5603	1.84	330 340	1110 ± 3 1101 ± 3
	90:10	2350	1279	1.57	360 370	1194 ± 3 1185 ± 3
	glycerol	2372	0	1.72	380 390	1199 ± 3 1190 ± 3

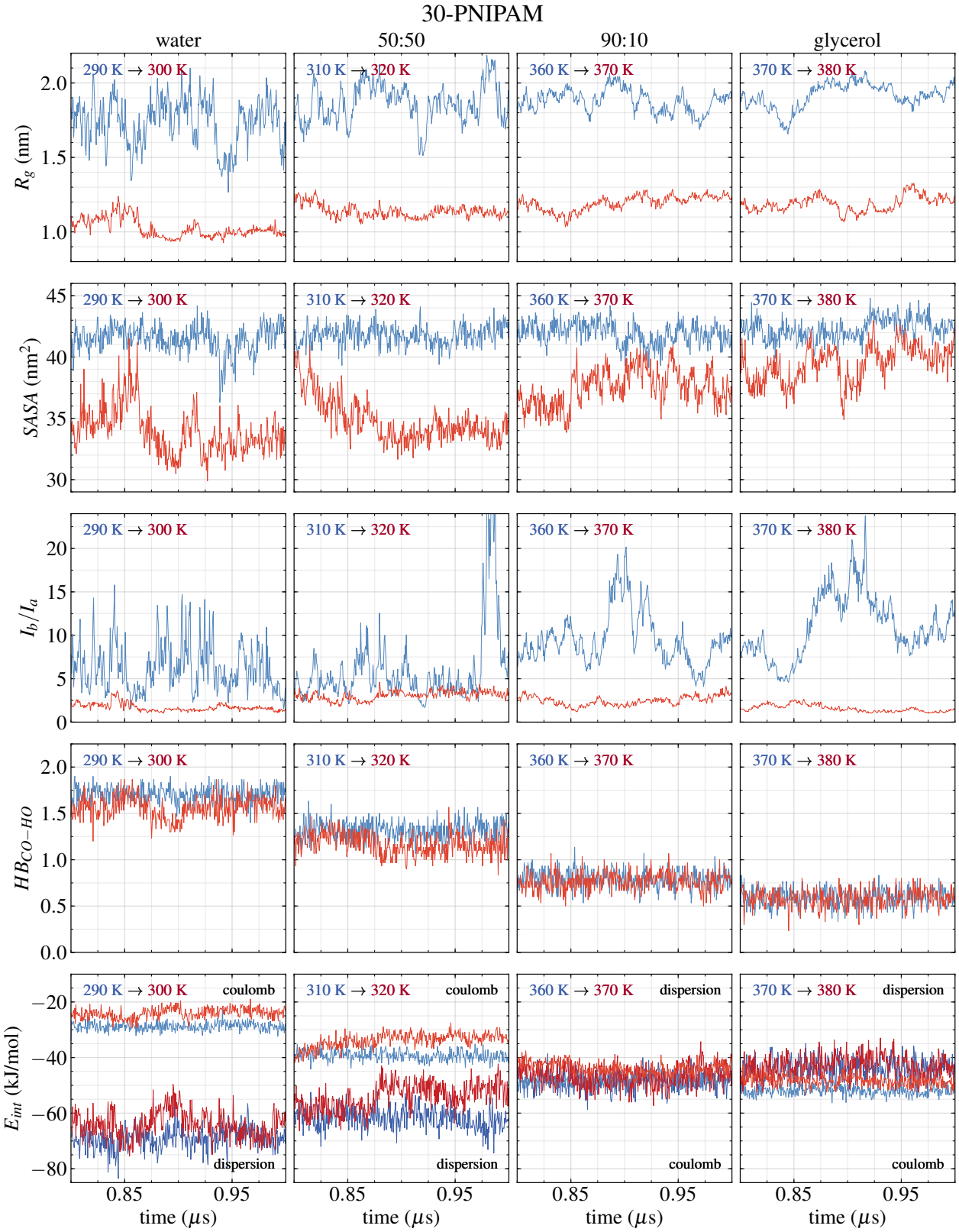

Figure S2. MD time profile of 30-PNIPAM properties in pure water, 50:50 and 90:10 glycerol:water mixtures, and in pure glycerol at two temperatures, below (blue) and above (red) the LCST of the system. Values are presented over the final 200 ns of each the 1.0 μs simulations.

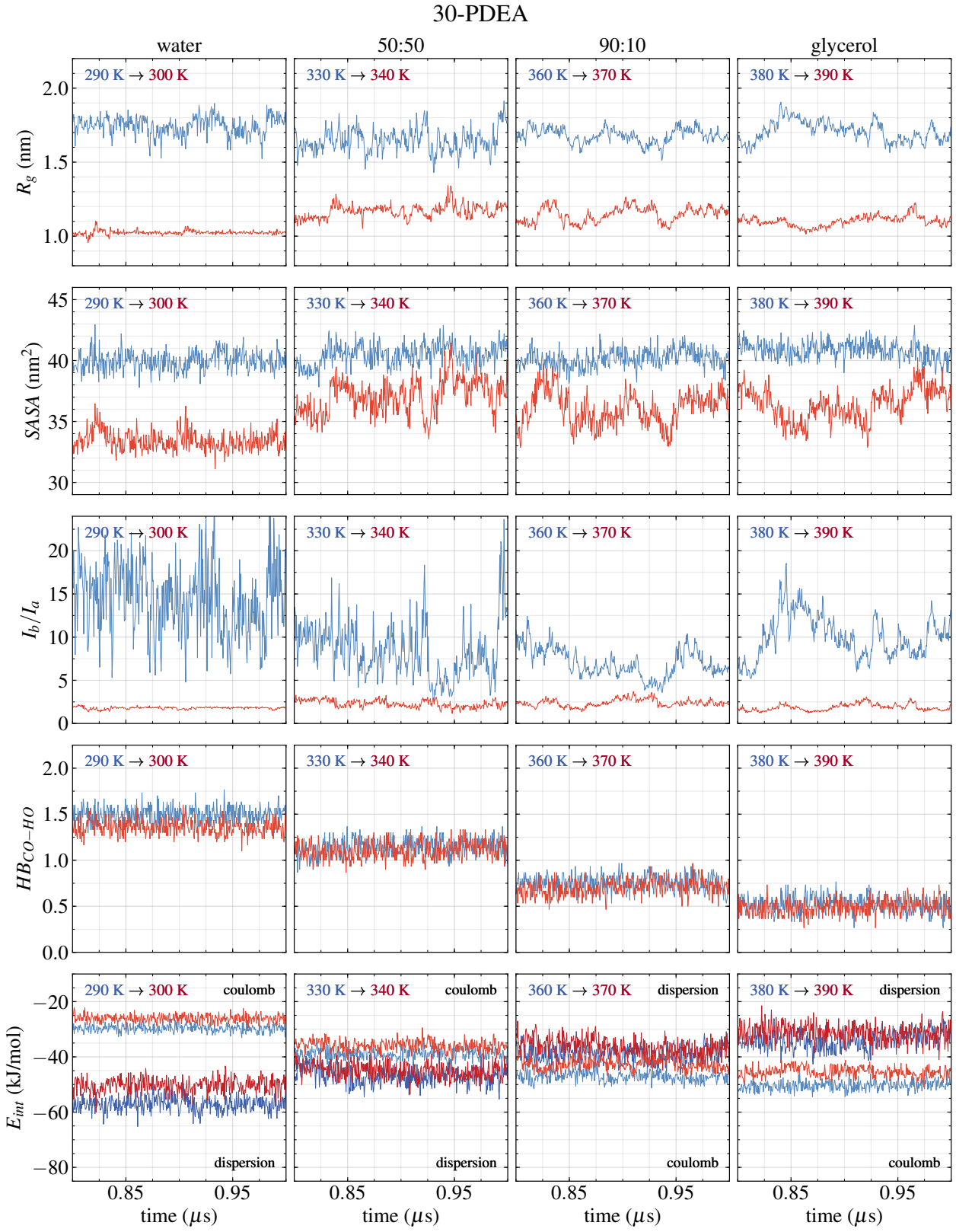

Figure S3. MD time profile of 30-PDEA in pure water, 50:50 and 90:10 glycerol:water mixtures, and in pure glycerol at two temperatures, below (blue) and above (red) the LCST of the system. Values are presented over the final 200 ns of each the 1.0 μs simulations.

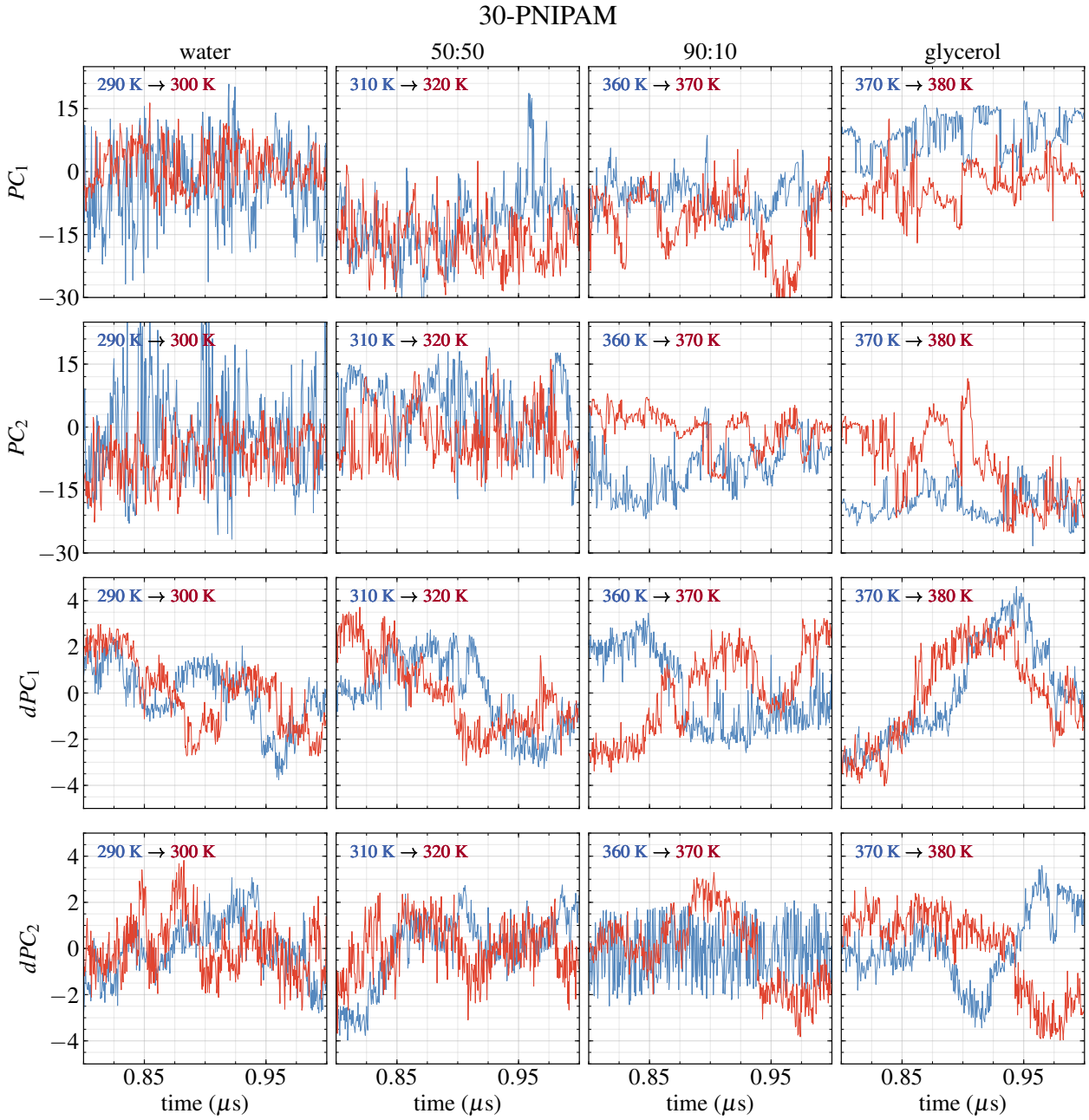

Figure S4. Time dependence of the input data projected onto the two principal components PC_1, PC_2 and dPC_1, dPC_2 of 30-PNIPAM in pure water, 50:50, 90:10 glycerol:water mixtures, and pure glycerol at two temperatures, below (blue) and above (red) the LCST of each oligomer in its liquid environment. Values are presented over the final 200 ns of each 1.0 μs simulations.

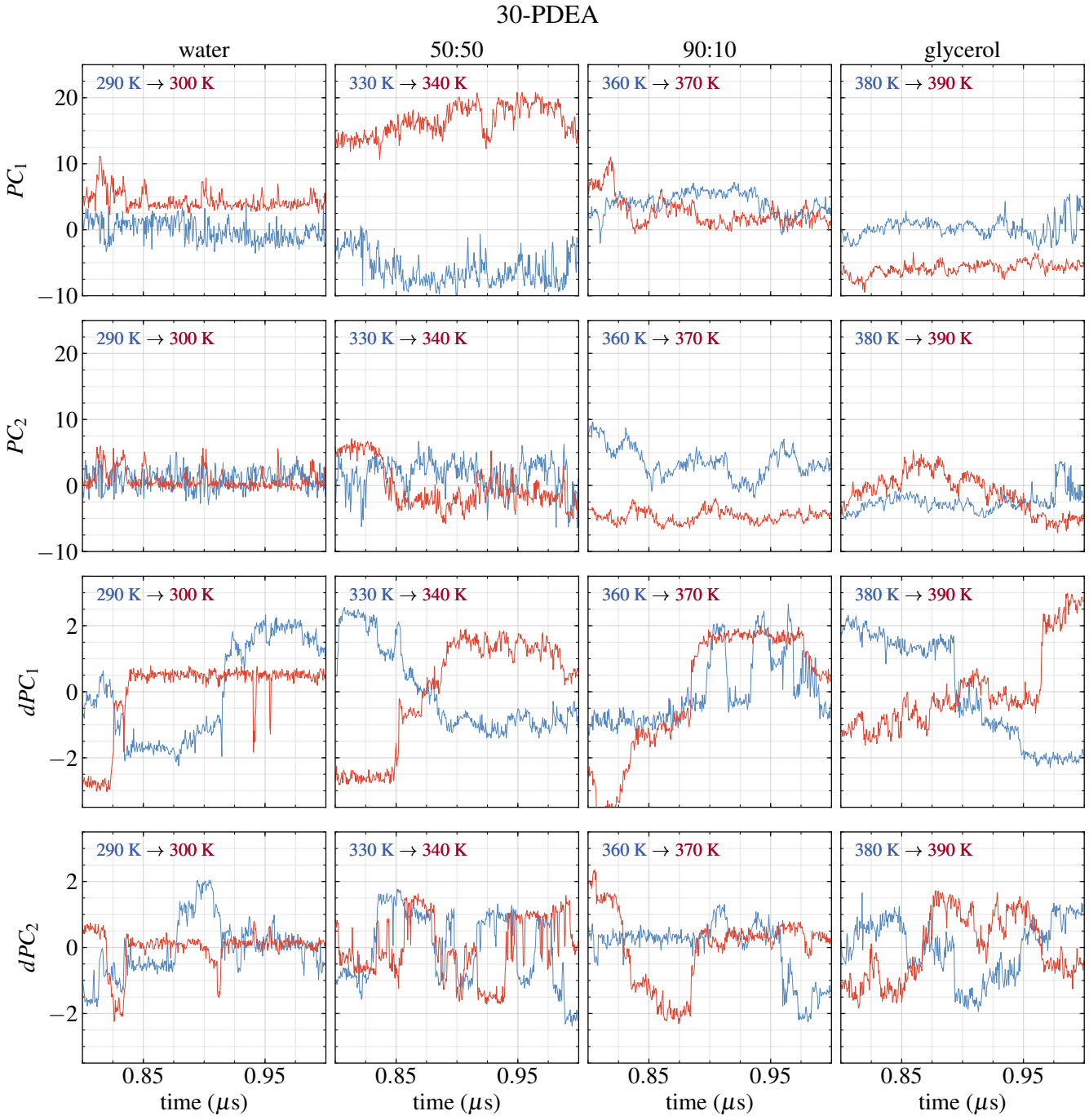

Figure S5. Time dependence of the input data projected onto the two principal components PC_1, PC_2 and dPC_1, dPC_2 of 30-PDEA in water, 50:50 and 90:10 glycerol:water mixtures, and glycerol, both before (blue) and after (red) the LCST of each solvent. Values are presented over the final 200 ns of each 1.0 μs simulations.

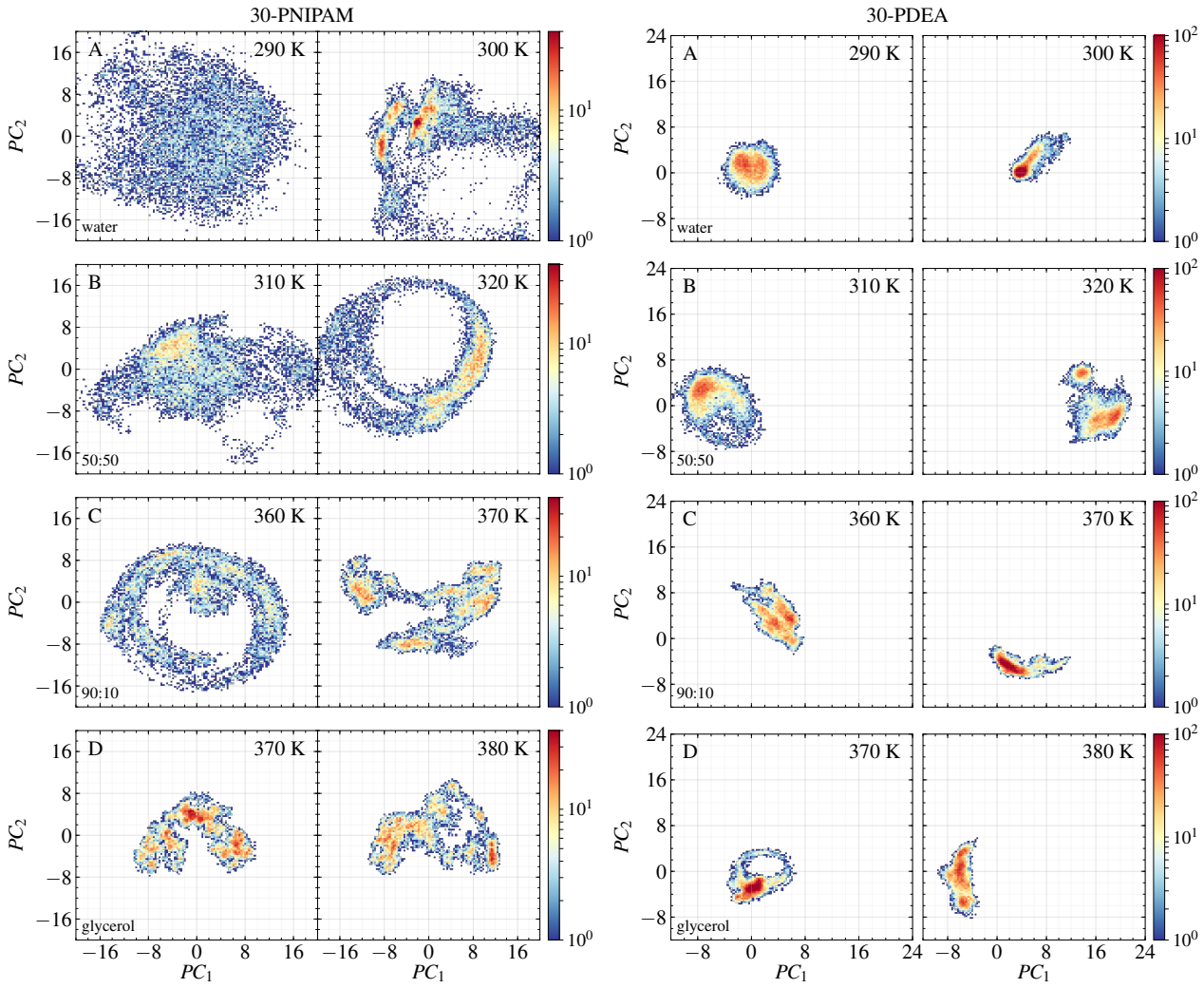

Figure S6. Scatter plots between input data projected onto the PC_1 and PC_2 for 30-PNIPAM and for 30-PDEA in (A) water, (B) 50:50 and (C) 90:10 glycerol:water mixtures, and (D) glycerol systems.