Supporting Information:

Effect of temperature and hydrophilic ratio on the structure of poly(N-vinylcaprolactam)-block-poly(dimethylsiloxane)-block-poly(N-vinylcaprolactam) polymersomes

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Table S1. Number-Average Molecular Weights (M_n), Polydispersity (Đ) of the Block Copolymers via GPC (Linear polystyrene samples were used as standards for GPC calibration)

Hydrophobic block	**Hydrophilic block**	M_n**, Da**	**Đ**
$PDMS_{65}$	$PMOXA_{14}$	5091	1.17
	$PVCL_{10}$	5034	1.13
	$PVCL_{15}$	5209	1.15
	$PVCL_{21}$	6092	1.15
$PDMS_{47}$	$PVCL_7$	3967	1.10
$PDMS_{30}$	$PVCL_5$	3312	1.17

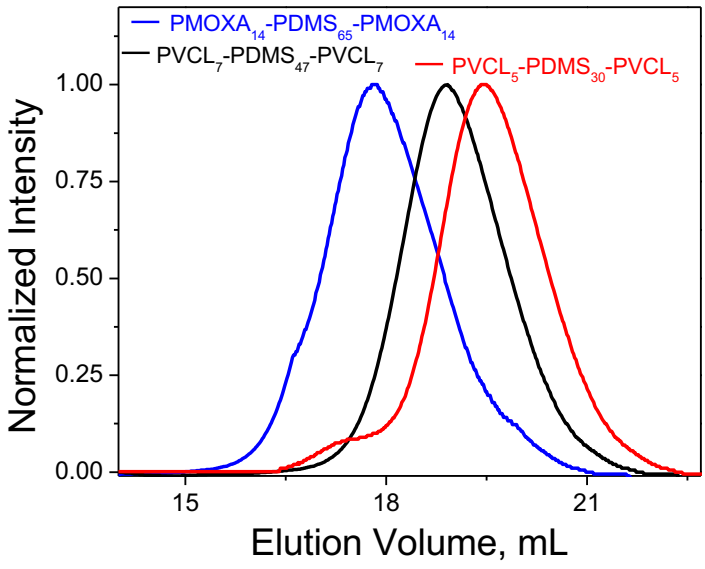

Figure S1. GPC traces of $PMOXA_{14}$-$PDMS_{65}$-$PMOXA_{14}$, $PVCL_7$-$PDMS_{47}$-$PVCL_7$, and $PVCL_5$-$PDMS_{30}$-$PVCL_5$ triblock copolymers.

Table S2. Fit Parameters Obtained from the Poly Core−Shell Model Deduced from SANS Curves.

Hydrophobic block	Hydrophilic block	Temperature	scale	avg core rad (A)	shell thickness (A)	polydisp (0,1)	SLD core (A^{-2})	SLD shell (A^{-2})	SLD solvent (A^{-2})
PDMS65	PMOXA14	25℃	6.01E-08	670.351	126.931	0.47573771	2.34E-06	1.90E-06	6.34E-06
		55℃	6.01E-08	663.234	130.539	0.61605592	2.34E-06	1.90E-06	6.34E-06
	PVCL10	25℃	2.45E-06	1619.478	141.523	0.2925268	2.84E-06	1.90E-06	6.34E-06
		55℃	2.45E-06	1293.459	117.239	0.30235111	2.84E-06	2.46E-06	6.34E-06
	PVCL15	25℃	2.46E-06	870.372	160.92	0.29346286	2.44E-06	1.90E-06	6.34E-06
		55℃	2.46E-06	760.231	130.169	0.47597947	2.44E-06	2.14E-06	6.34E-06
	PVCL21	25℃	2.18E-05	724.792	191.917	0.48731764	2.65E-06	1.82E-06	6.34E-06
		55℃	2.18E-05	704.539	136.212	0.65981751	2.65E-06	1.90E-06	6.34E-06
PDMS47	PVCL7	25℃	0.15147485	1496.145	103.427	0.37675478	4.80E-06	4.73E-06	4.17E-06
		55℃	0.15147485	1274.938	87.545	0.21274795	4.73E-06	4.19E-06	4.24E-06
PDMS30	PVCL5	25℃	0.02248607	1398.922	85.587	0.81811423	5.32E-06	2.09E-06	2.83E-06
		55℃	0.12868921	1099.901	80.099	0.70329481	4.73E-06	3.90E-06	4.24E-06

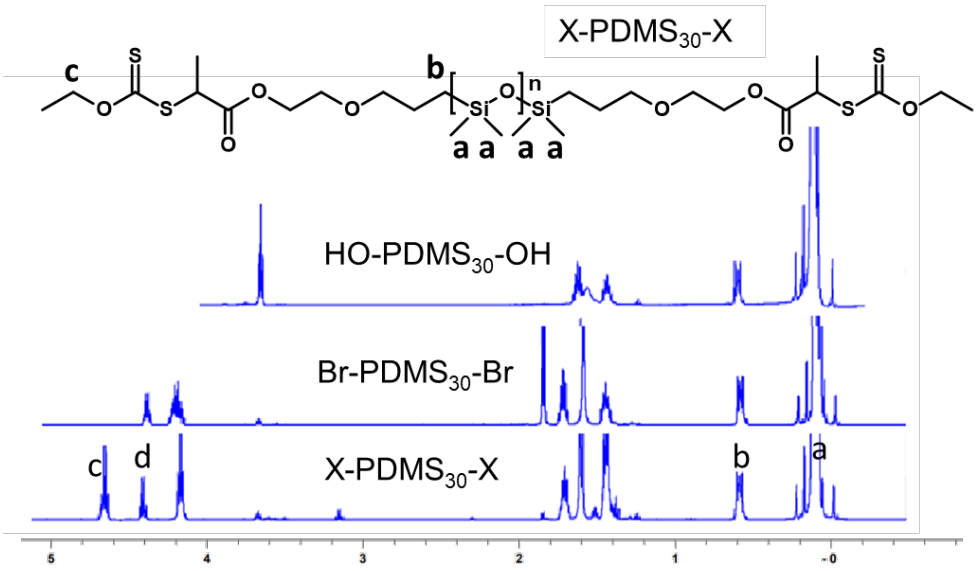

Figure S2. NMR spectra of bis(hydroxyethyl)-oxypropyl poly(dimethylsiloxane) (HO-$PDMS_{30}$-OH), the product of end group decoration (Br-$PDMS_{30}$-Br), and the final macro initiator (X-$PDMS_{30}$-X) and its chemical structure. According to the integration values, 97% of the hydroxy groups from $PDMS_{30}$-OH were modified to incorporate the CTA.

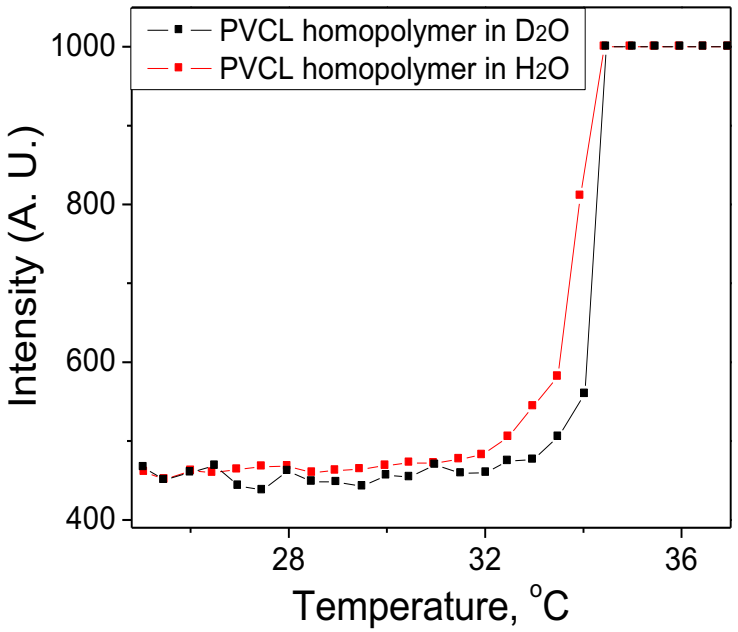

Figure S3. Temperature-dependent turbidity of PVCL homopolymer in H_2O and D_2O. Temperature-dependent scattering intensity of polymer solutions was determined with a fluorescence spectrophotometer (Varian, Cary Eclipse). The scattering intensity of 2 mL of PVCL homopolymer solutions with the concentration of 0.5 mg mL^{-1} was measured at λ=700 nm from 24 °C to 40 °C at the rate of 0.2 °C per minute.

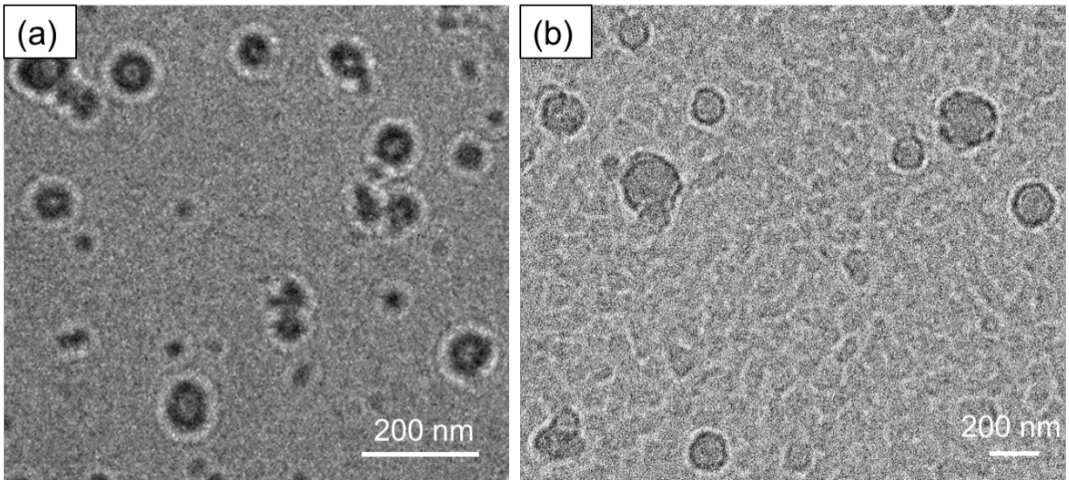

Figure S4. Cryo-TEM images of (a) $PVCL_{10}$-$PDMS_{65}$-$PVCL_{10}$ and (b) $PVCL_{5}$-$PDMS_{30}$-$PVCL_{5}$.

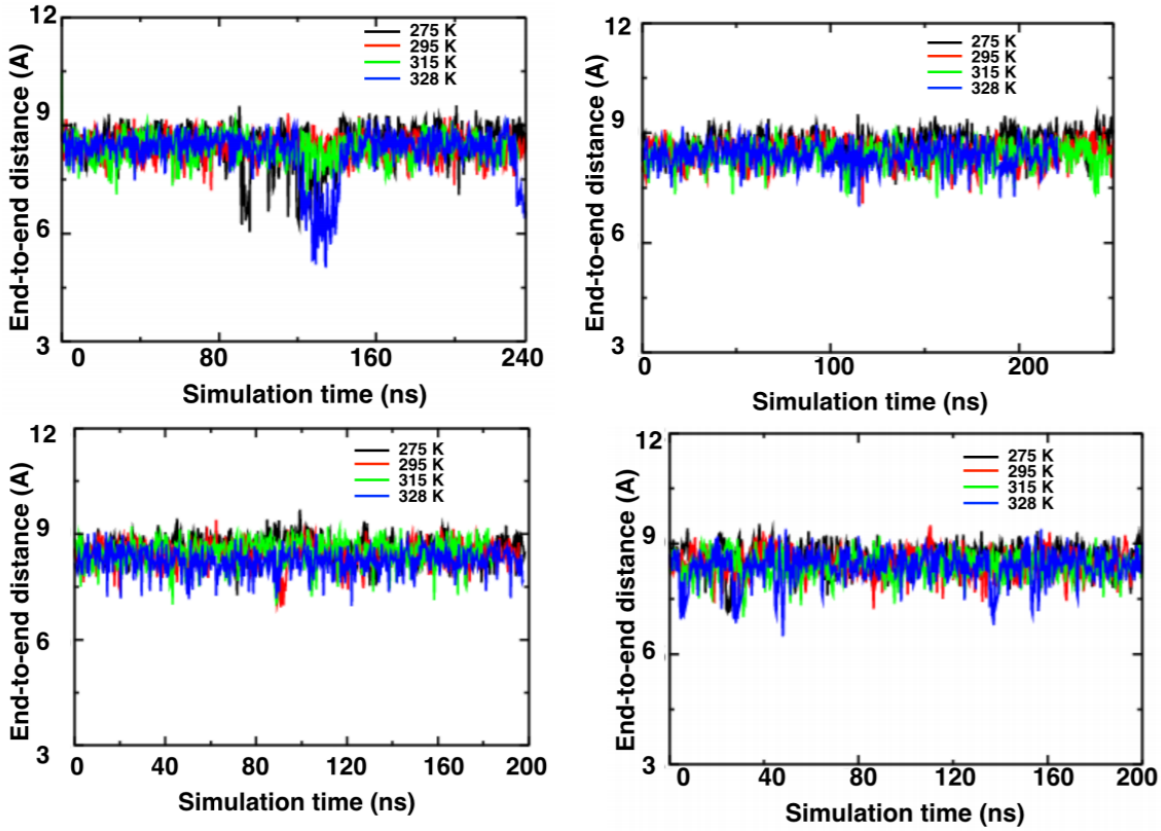

Figure S5. Simulated end-to-end distance of $PVCL_5$ at four temperature conditions. Each panel corresponds to an independent simulation replica.

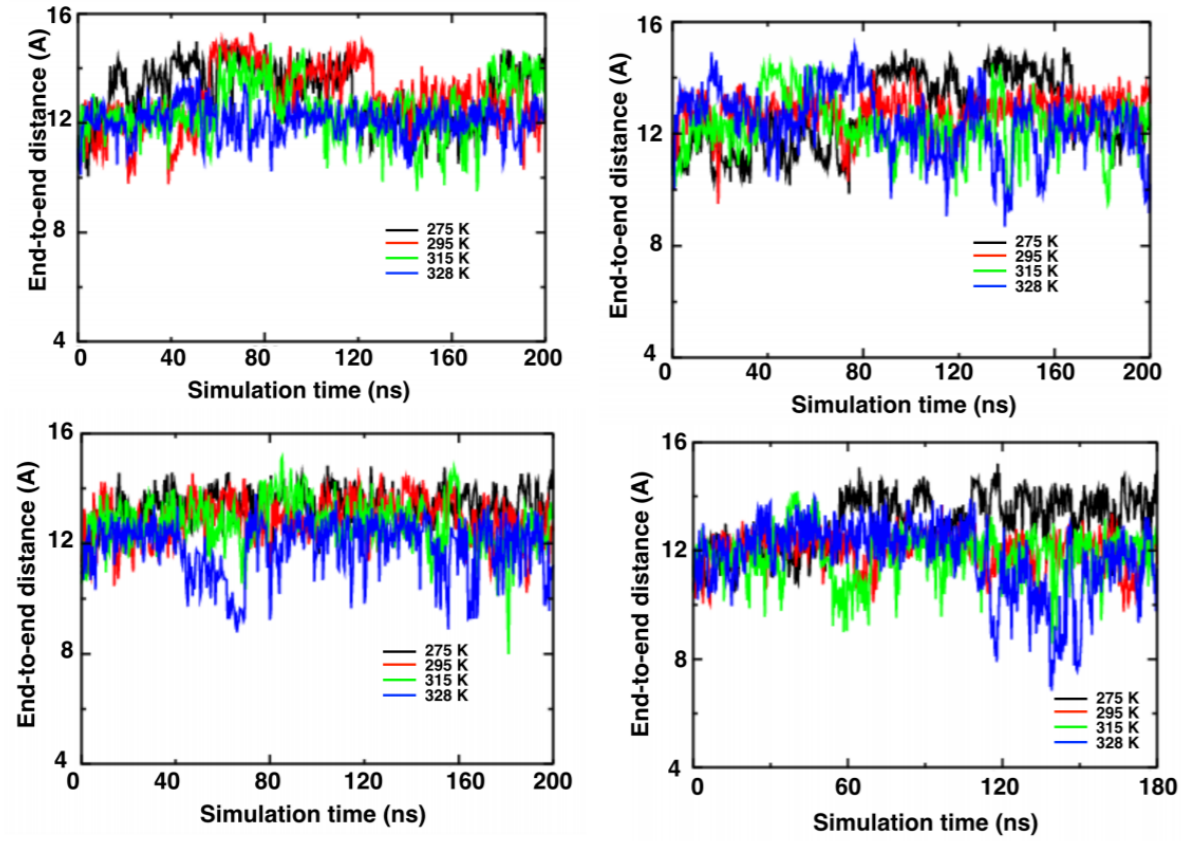

Figure S6. Simulated end-to-end distance of $PVCL_7$ at four temperature conditions. Each panel corresponds to an independent simulation replica.

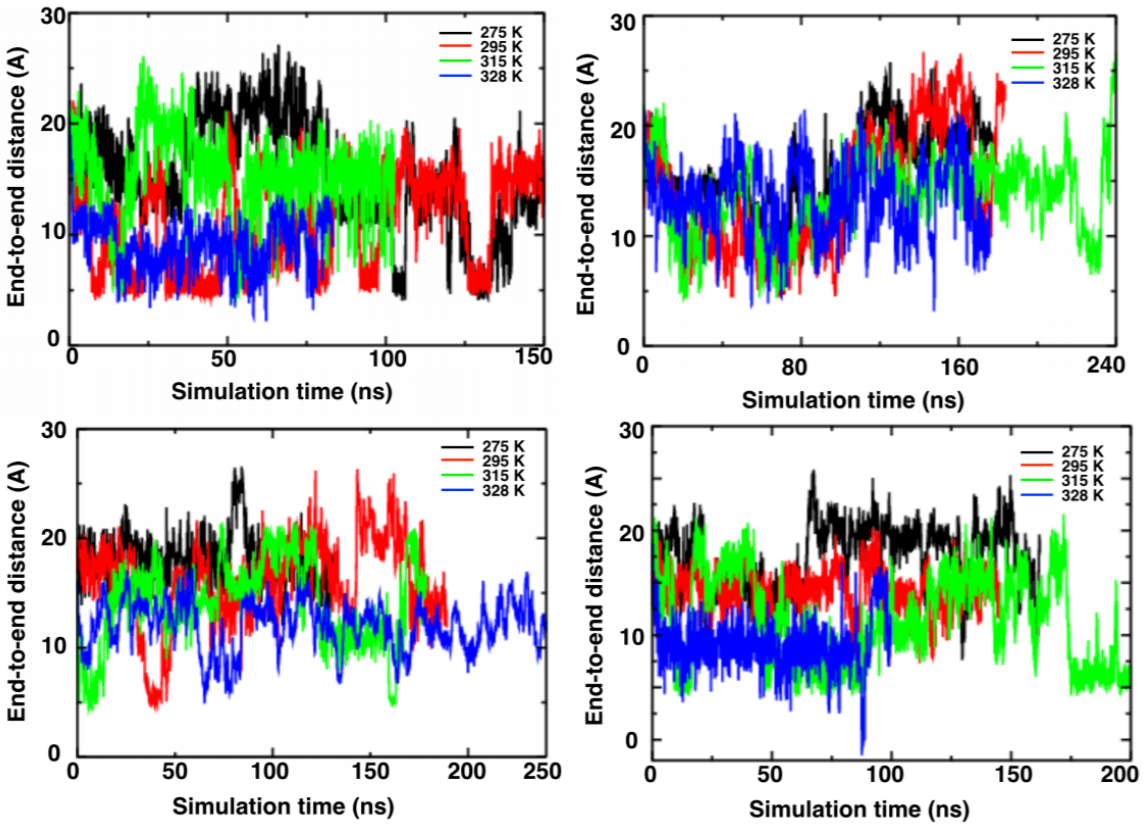

Figure S7. Simulated end-to-end distance of $PVCL_{10}$ at four temperature conditions. Each panel corresponds to an independent simulation replica.

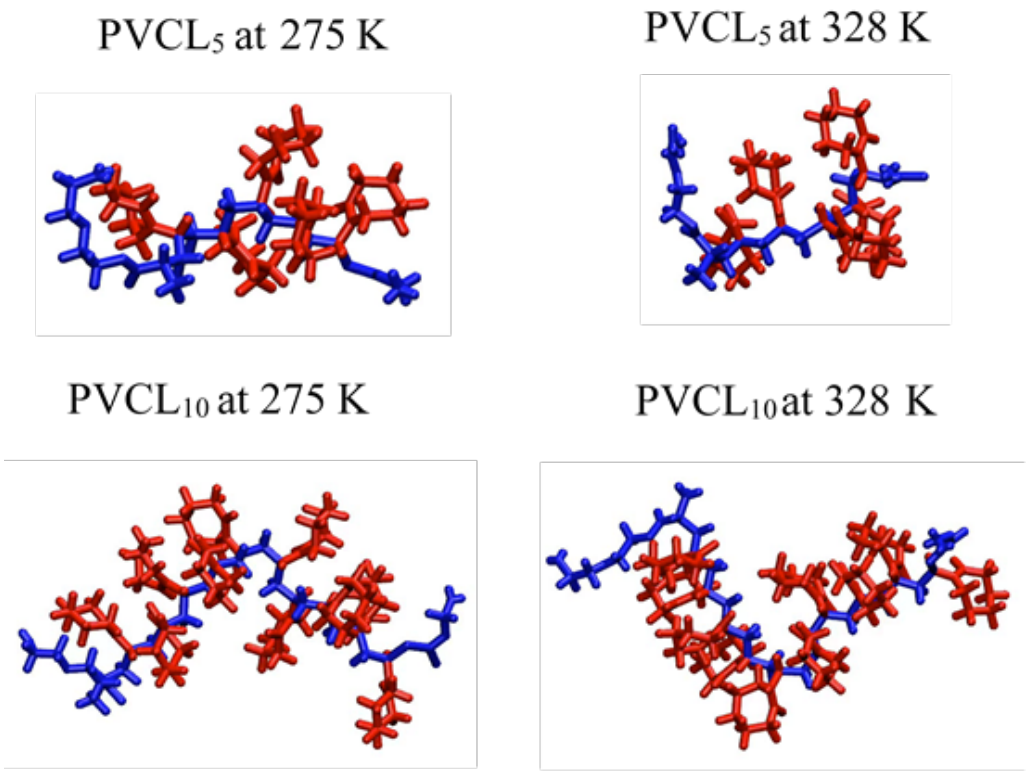

Figure S8. Snapshots of animations of MD trajectories illustrating the behavior of a $PVCL_5$ polymer at 275 K and at 238 K; and of a $PVCL_{10}$ polymer at 275 K and at 328 K. The backbone and side chains of each polymer are shown in blue and red, respectively, water and ions are not shown for clarity.