Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for Reduction of water-mediated repulsion drives poly(N-vinylcaprolactam) collapse upon heating

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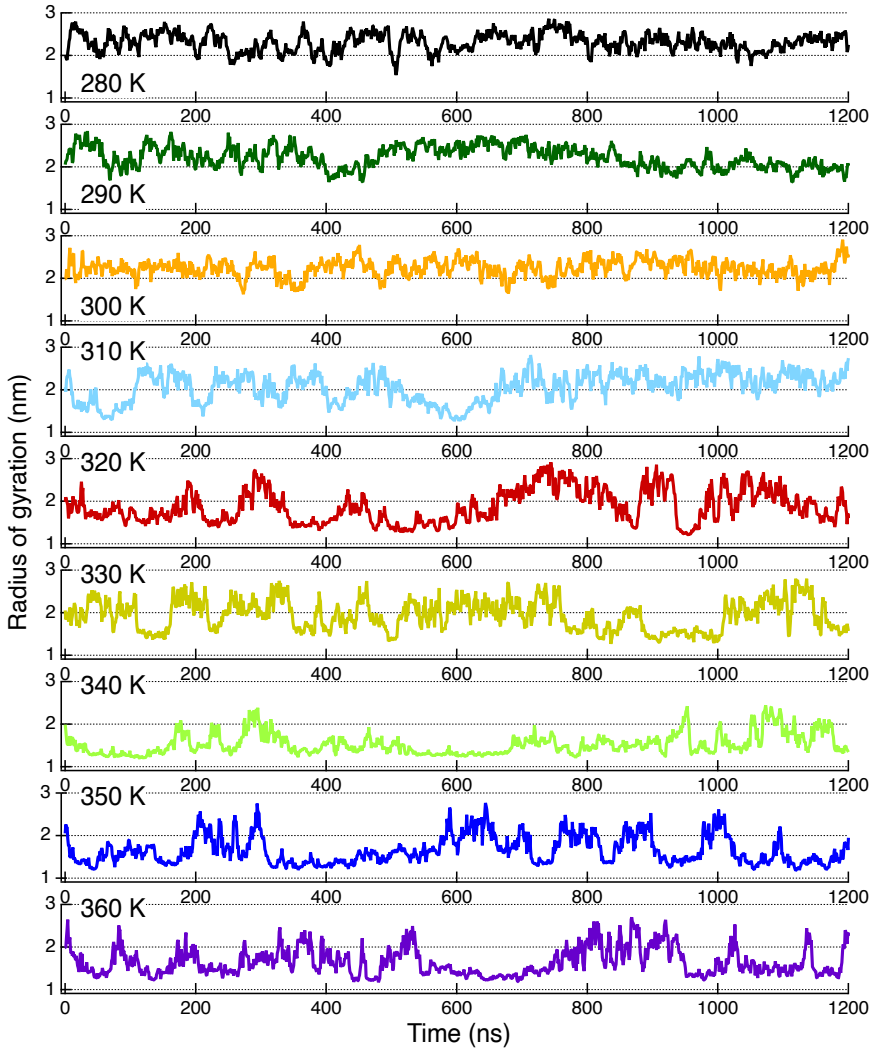

Figure S1. Time evolution of R_g for the PVCL 50-mer chain in water at various temperatures.

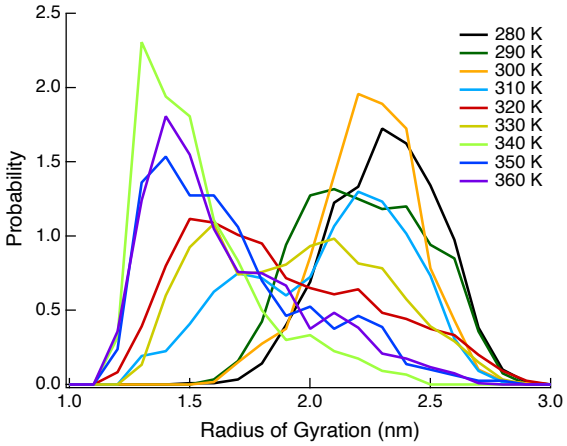

Figure S2. Probability distribution of R_g for the PVCL 50-mer chain in water at various temperatures.

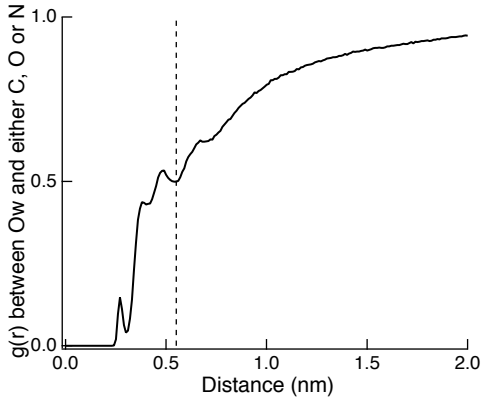

Figure S3. Radial distribution function $g(r)$ as a function of the distance r between water oxygen (Ow) and heavy atoms (C, O, and N) in PVCL computed for the PVCL 50-mer solution at 320 K. The peak at r=0.38 nm results from the water molecules bound to the carbonyl group of the caprolactam side chain. The dashed line indicates the minimum at 0.55 nm corresponding to the threshold for defining the PVCL hydration shell.

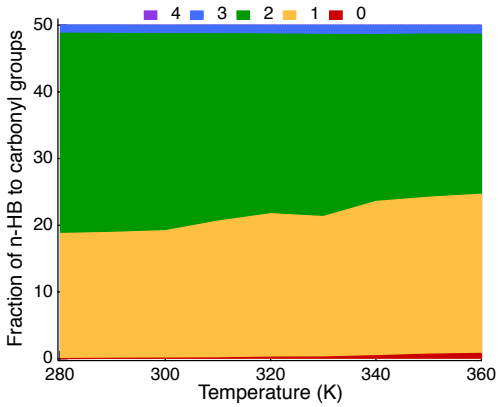

Figure S4. Cumulative stacked description of the number of CO groups with zero-to-four hydrogen bounds.

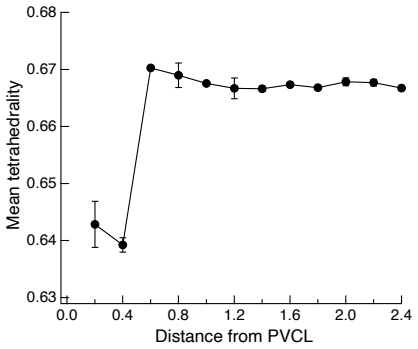

Figure S5. The mean tetrahedrality as a function of the distance from the PVCL surface, computed for the 50-mer solution at 300 K.

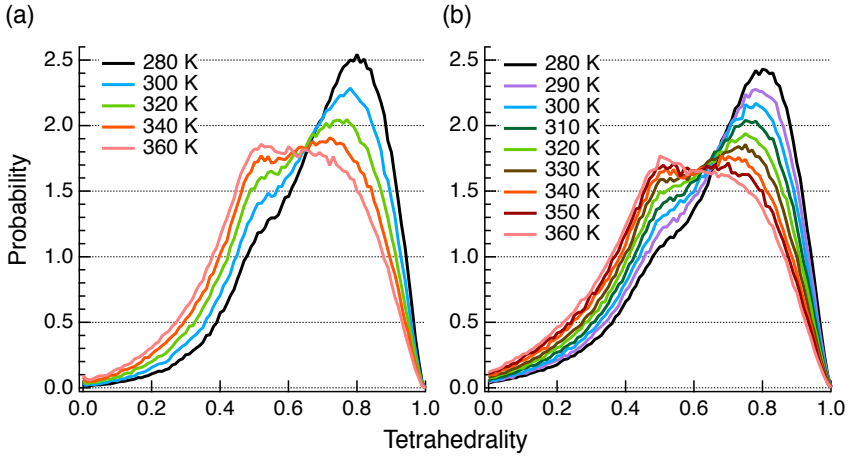

Figure S6. Tetrahedrality probability distributions of water molecules (a) in the bulk and (b) in the PVCL hydration shell at various temperatures.

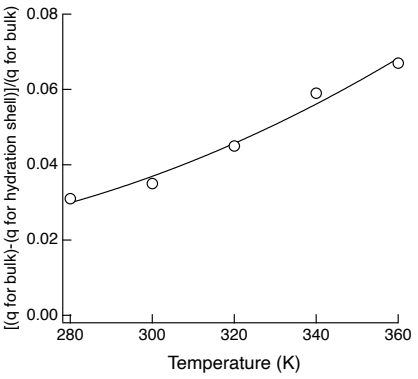

Figure S7. Temperature dependence of the difference in mean tetrahedrality between the hydration shell and the bulk regions. The value is computed by $[(\overline{q}$ for bulk)$-(\overline{q}$ for hydration shell)$]/(\overline{q}$ for bulk), where $\overline{q}$ represents the mean tetrahedrality.

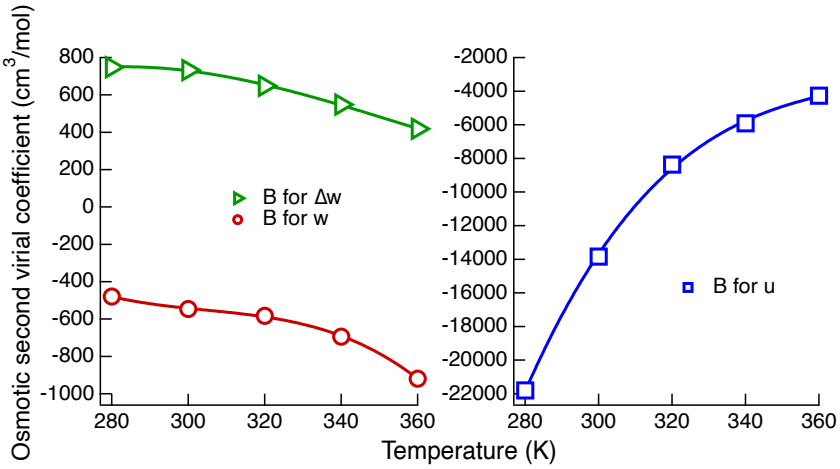

Figure S8. Temperature dependence of the osmotic second virial coefficient B for PVCL monomer in water, which is computed from the potential of mean force $w(r)$ via $B = -2\pi \int_0^\infty [e^{-w(r)/k_B T} - 1] r^2 dr$ (red circles on the left panel). The B value computed from the direct solute-solute interaction $u(r)$ and from the water-mediated interaction $\Delta w(r)$ are depicted as green triangles on the left and blue squares on the right, respectively. Negative and positive B values indicate attractive and repulsive interactions between two particles, respectively.