Supporting information for

LCST Behavior is Manifested in a Single Molecule: Elastin-like polypeptide $(VPGVG)_n$

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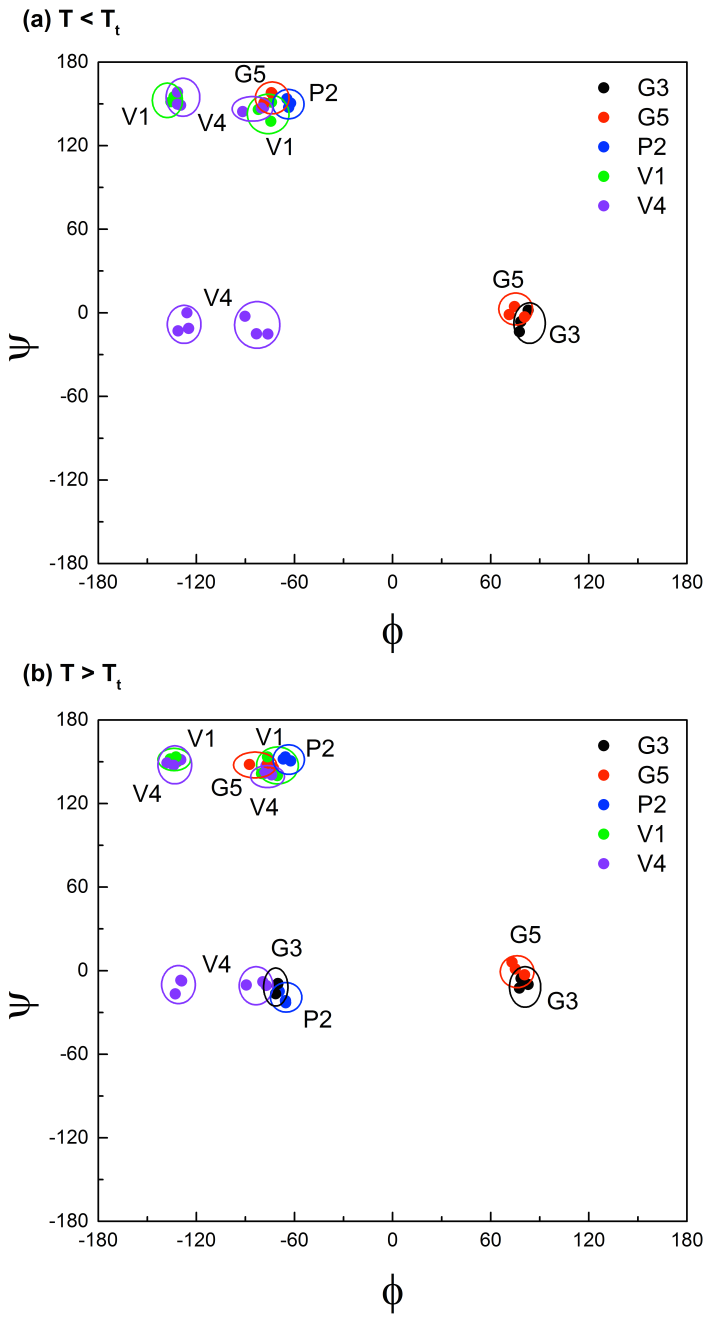


Figure. S1. Ramachandran plot showing peak values for ELP $(VPGVG)_n$ of 3 different lengths, L=10, 18, 30 at temperature (a) $T<T_t$ and (b) $T>T_t$. Each region has been circled with colors corresponding to residues on different positions. Ramachandran plots of L=10 and 30 have the same intensity change as $(VPGVG)_{18}$ in previous report by Li (39).

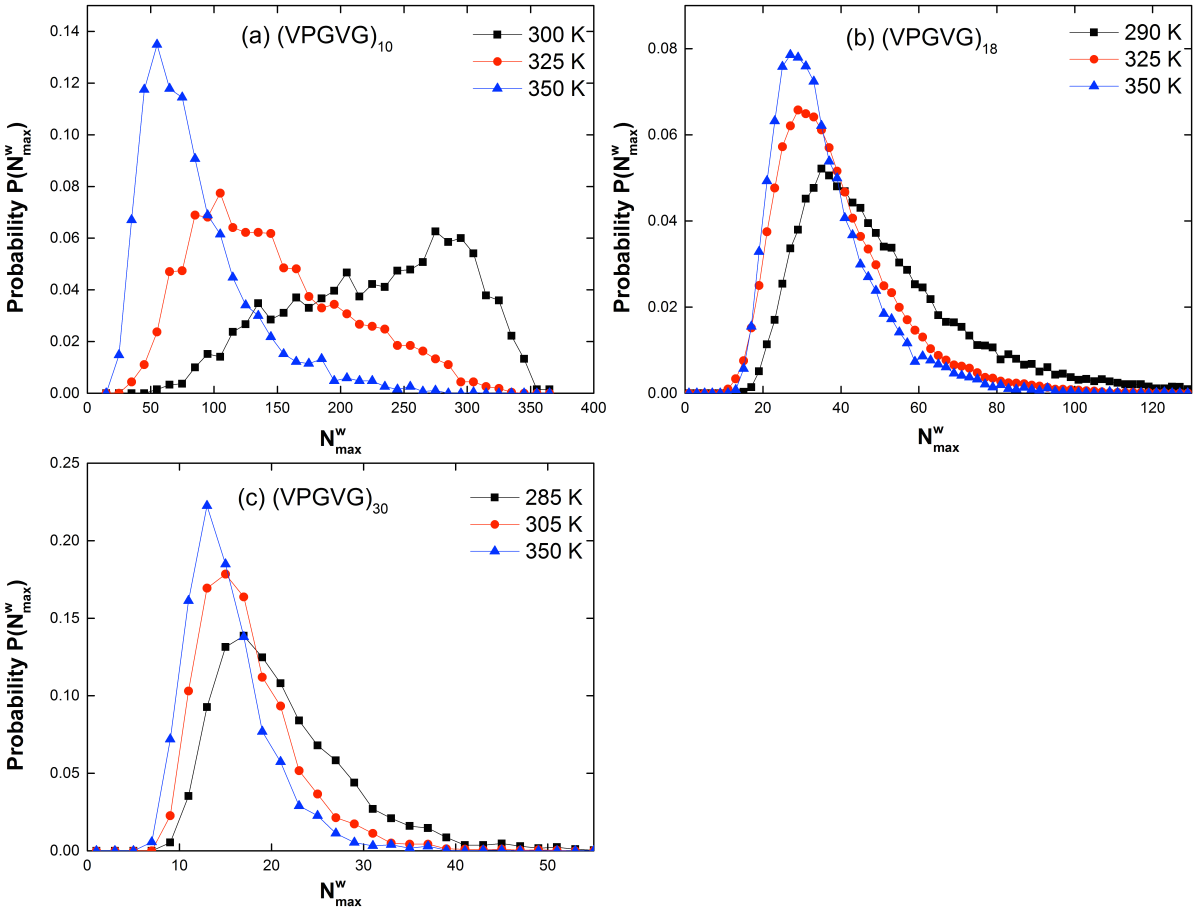
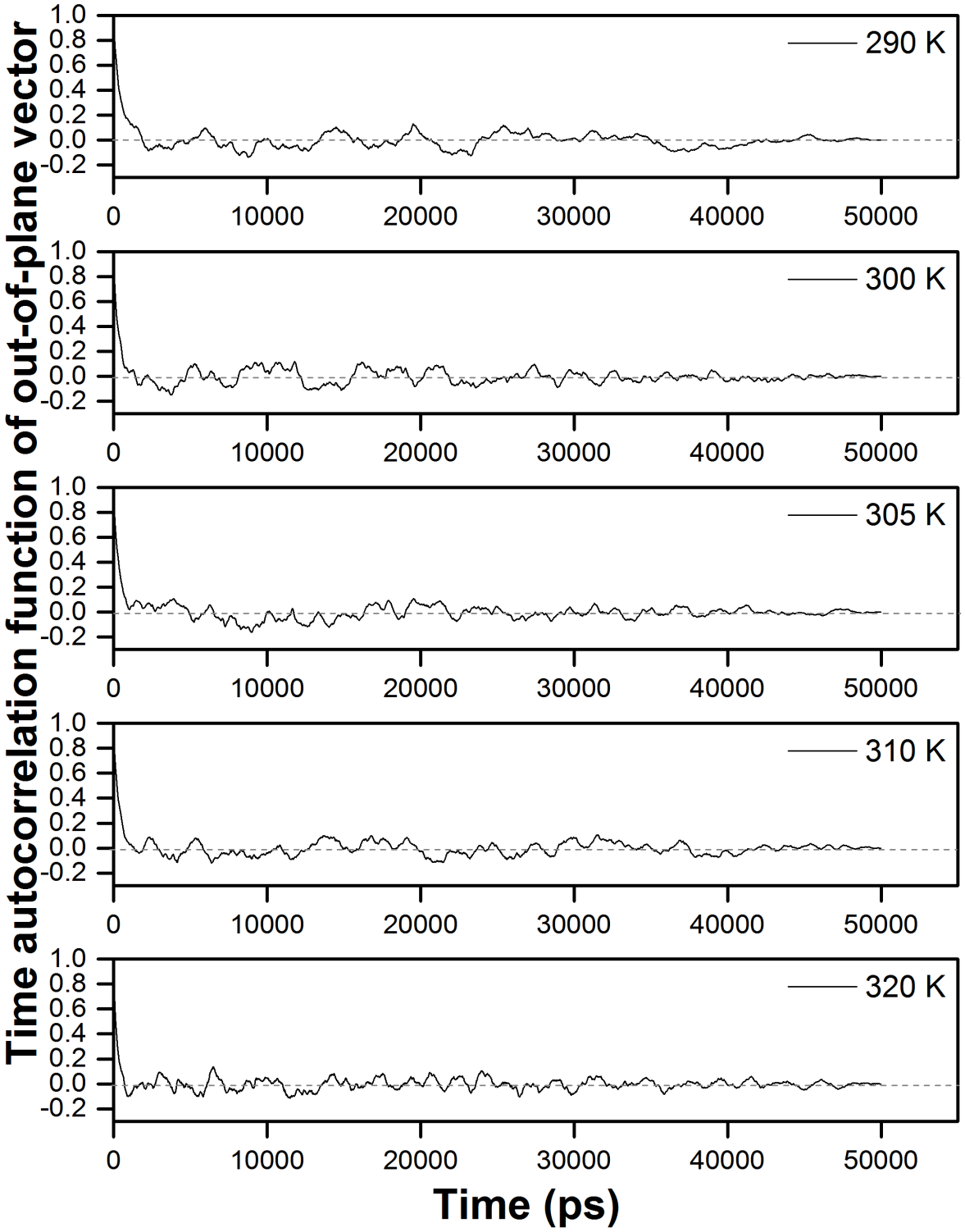


Figure. S2. Probability distribution of the size N_{max} of the largest water network around ELP (VPGVG) of three lengths L=(a) 10, (b) 18 and (c) 30. In each figure, three representative temperatures are included, a low temperature, an intermediate temperature and a high temperature.

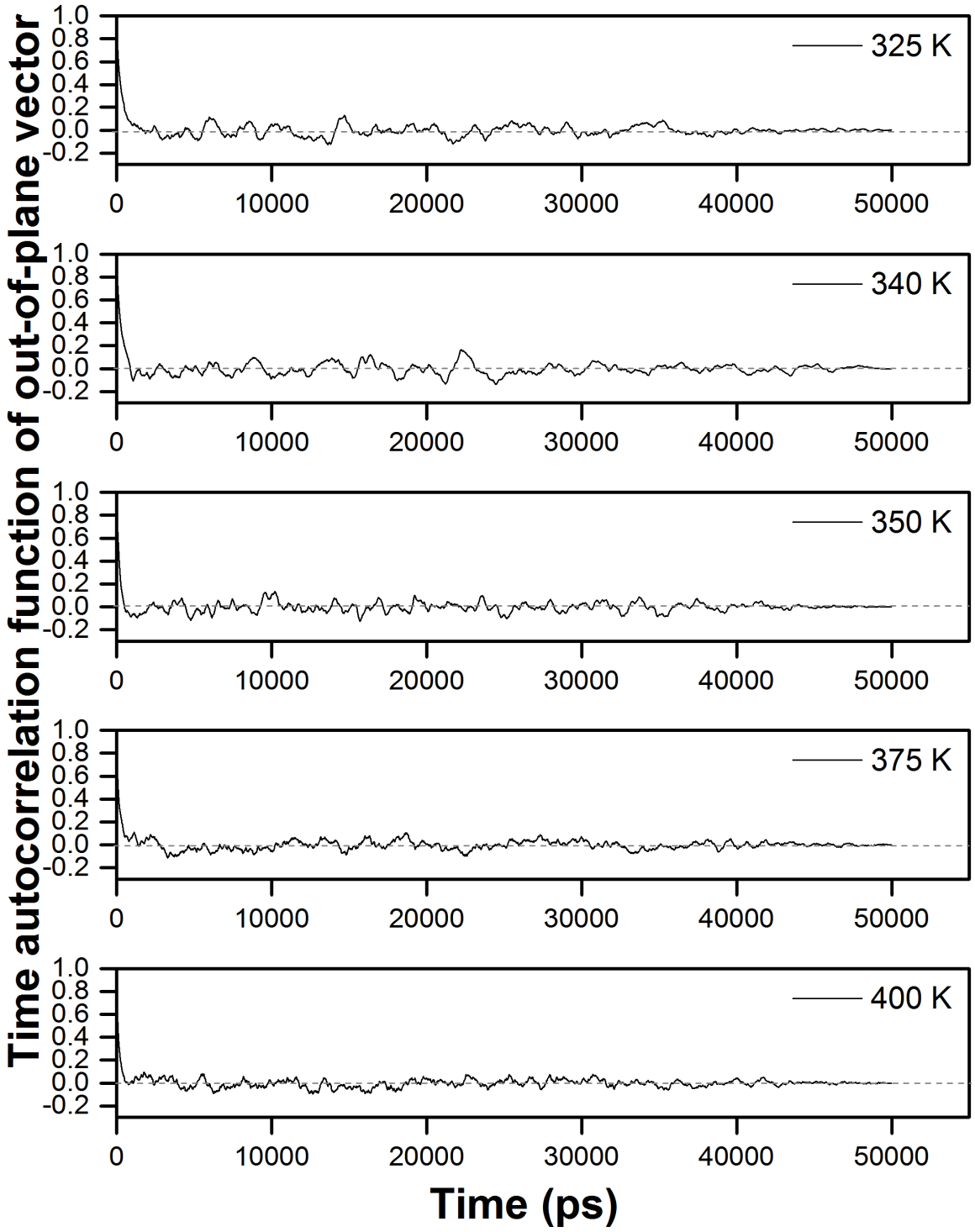
Time autocorrelation function of peptide backbone Cα-Cα bond unit vectors out of plane

A

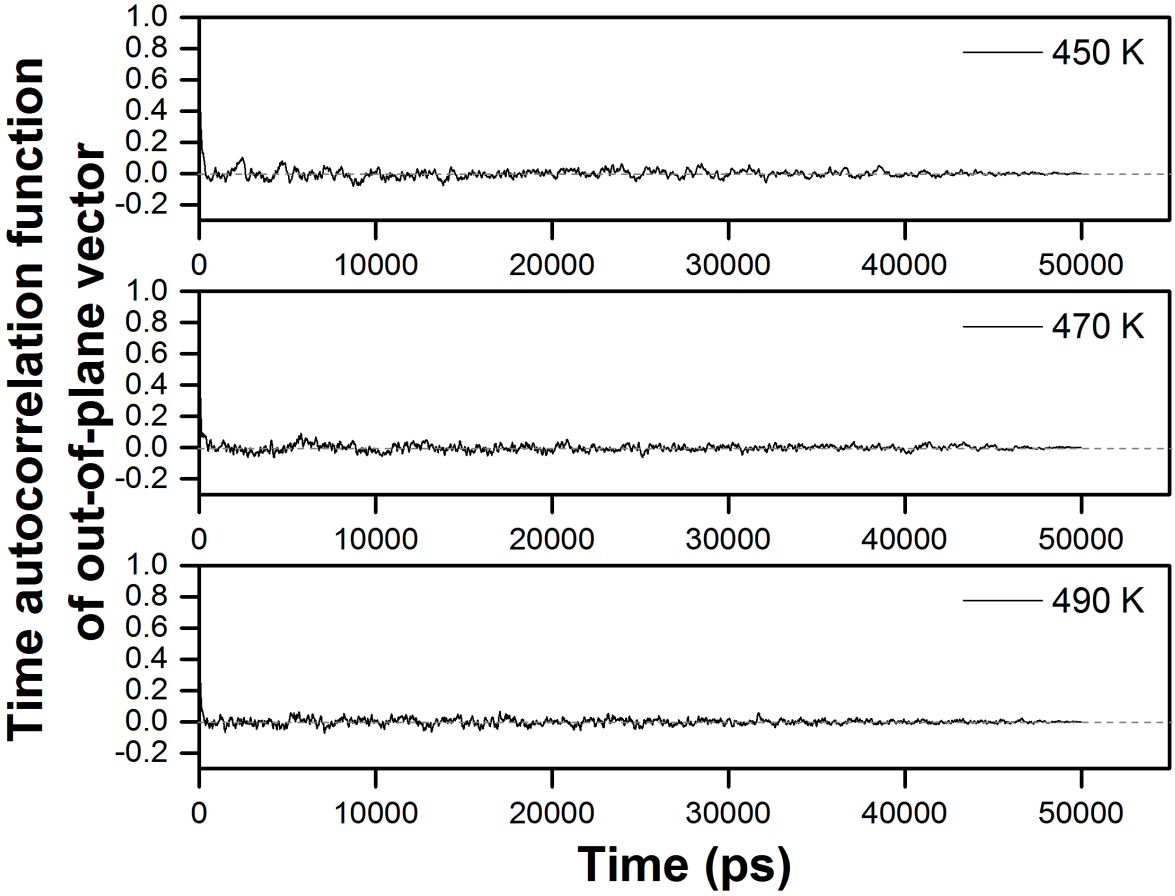
$(VPGVG)_3$: 290 K, 300 K, 305 K, 310 K, 320 K.



$(VPGVG)_3$: 325 K, 340 K, 350 K, 375 K, 400 K.

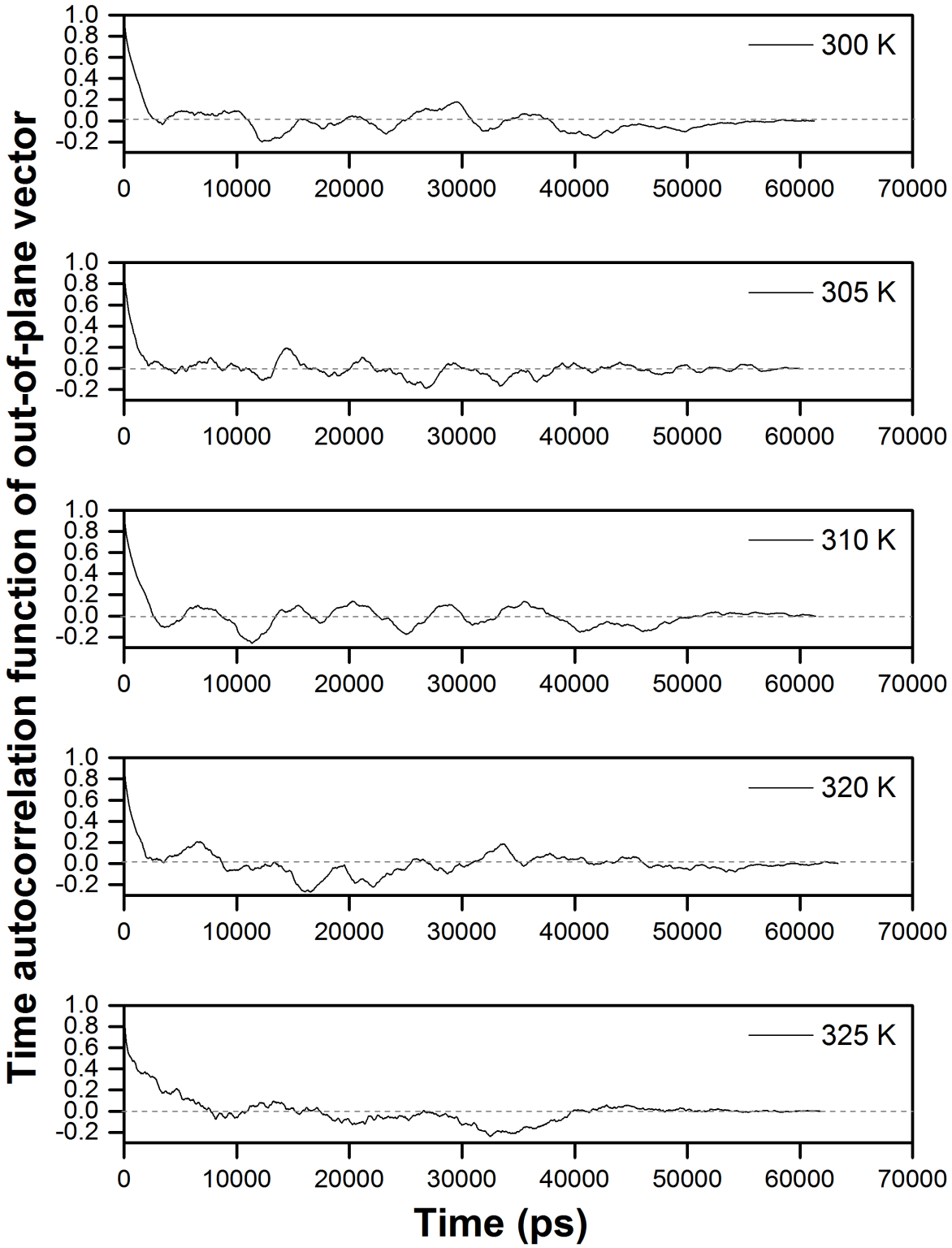


$(VPGVG)_3$: 450 K, 470 K, 490 K.

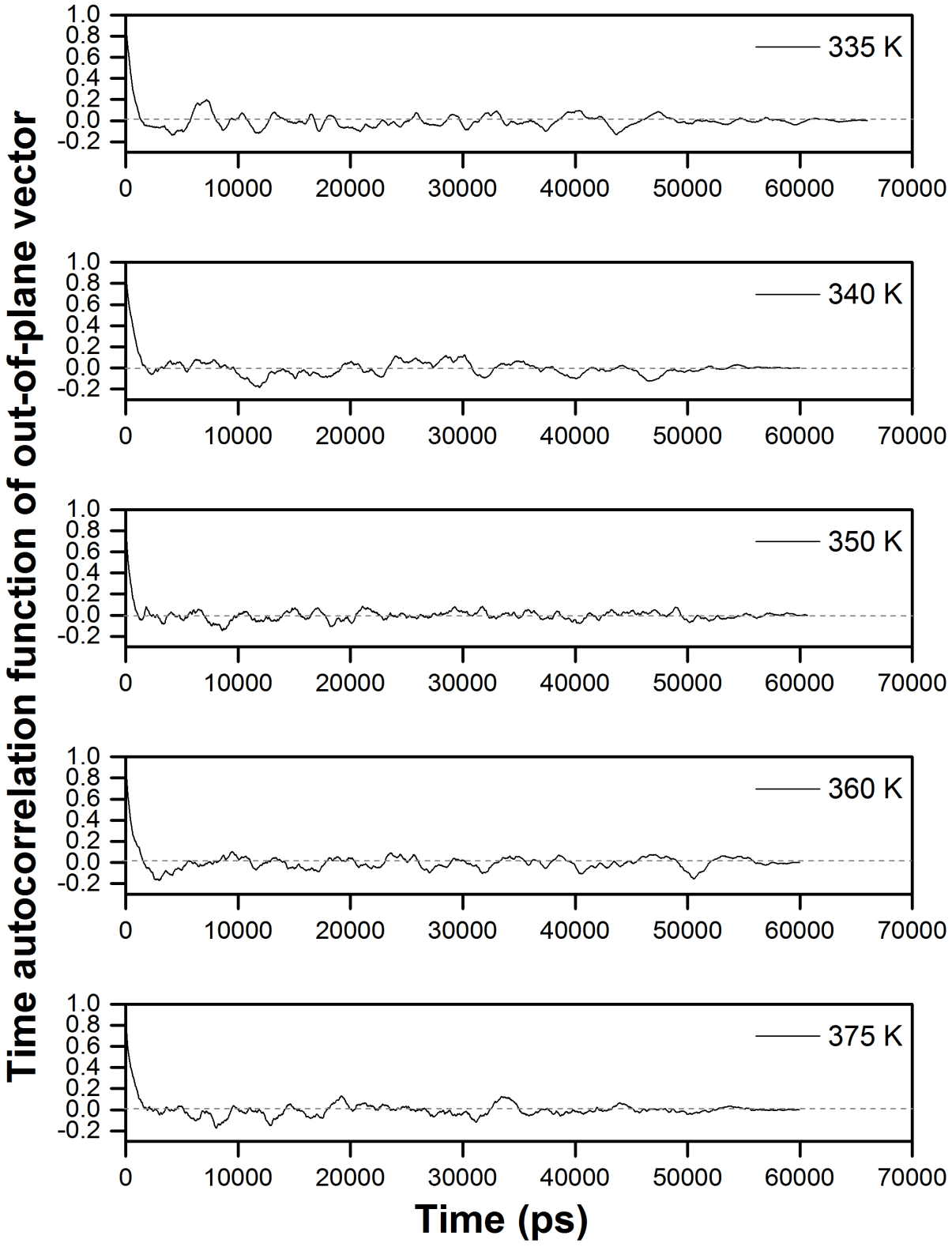


B

$(VPGVG)_{10}$: 300 K, 305 K, 310 K, 320 K, 325 K.

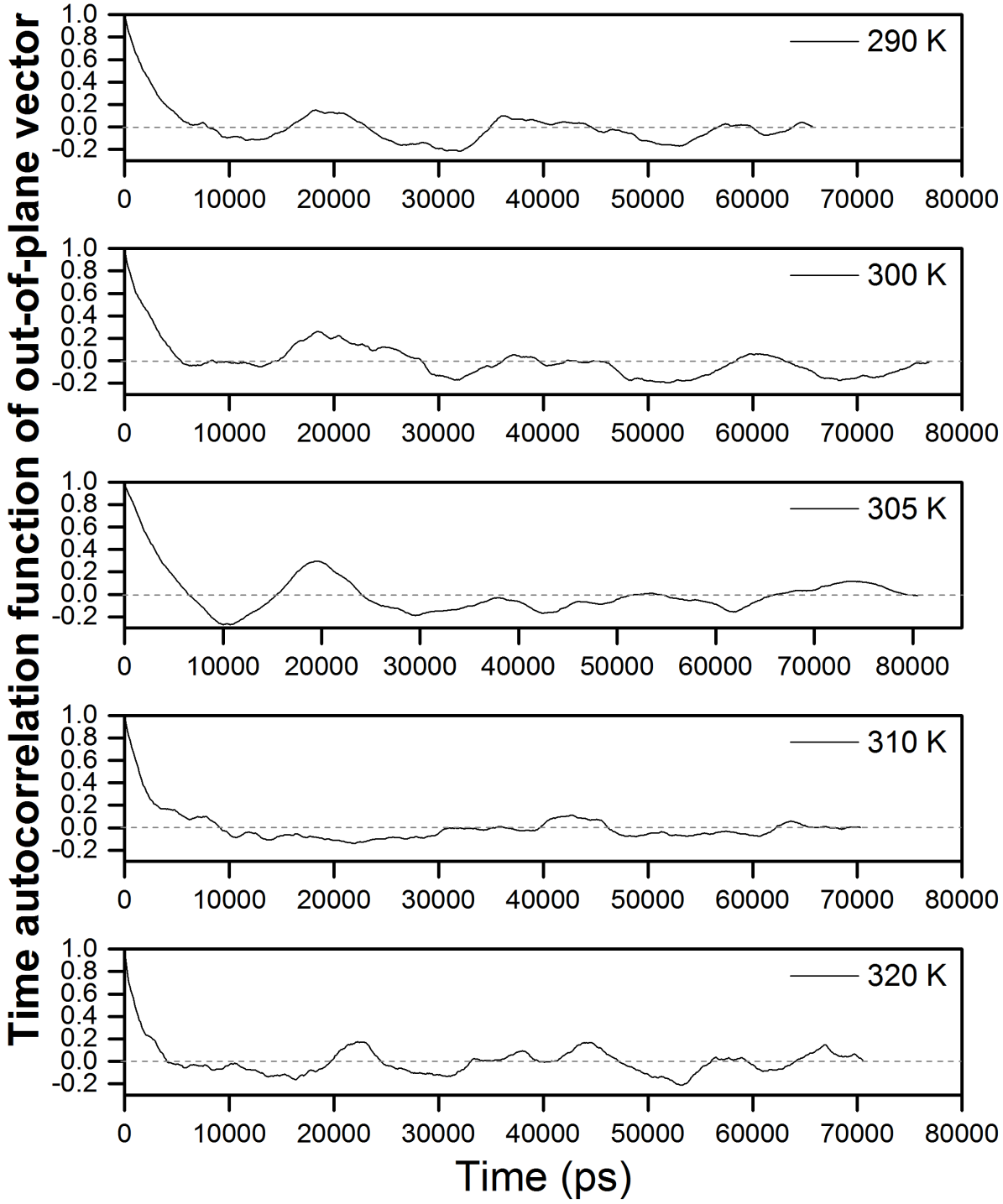


$(VPGVG)_{10}$: 335 K, 340 K, 350 K, 360 K, 375 K.

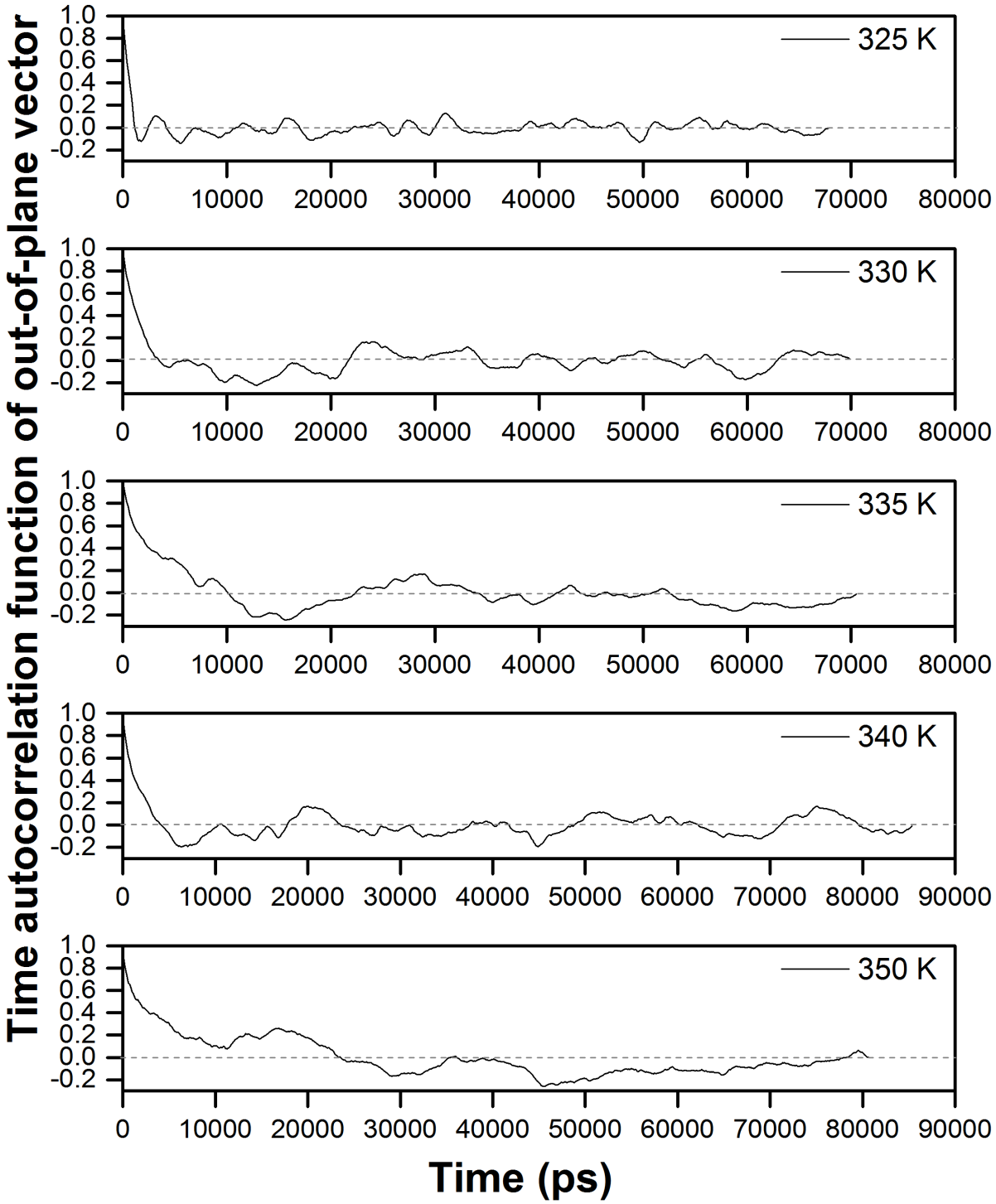


C

$(VPGVG)_{18}$: 290 K, 300 K, 305 K, 310 K, 320 K.

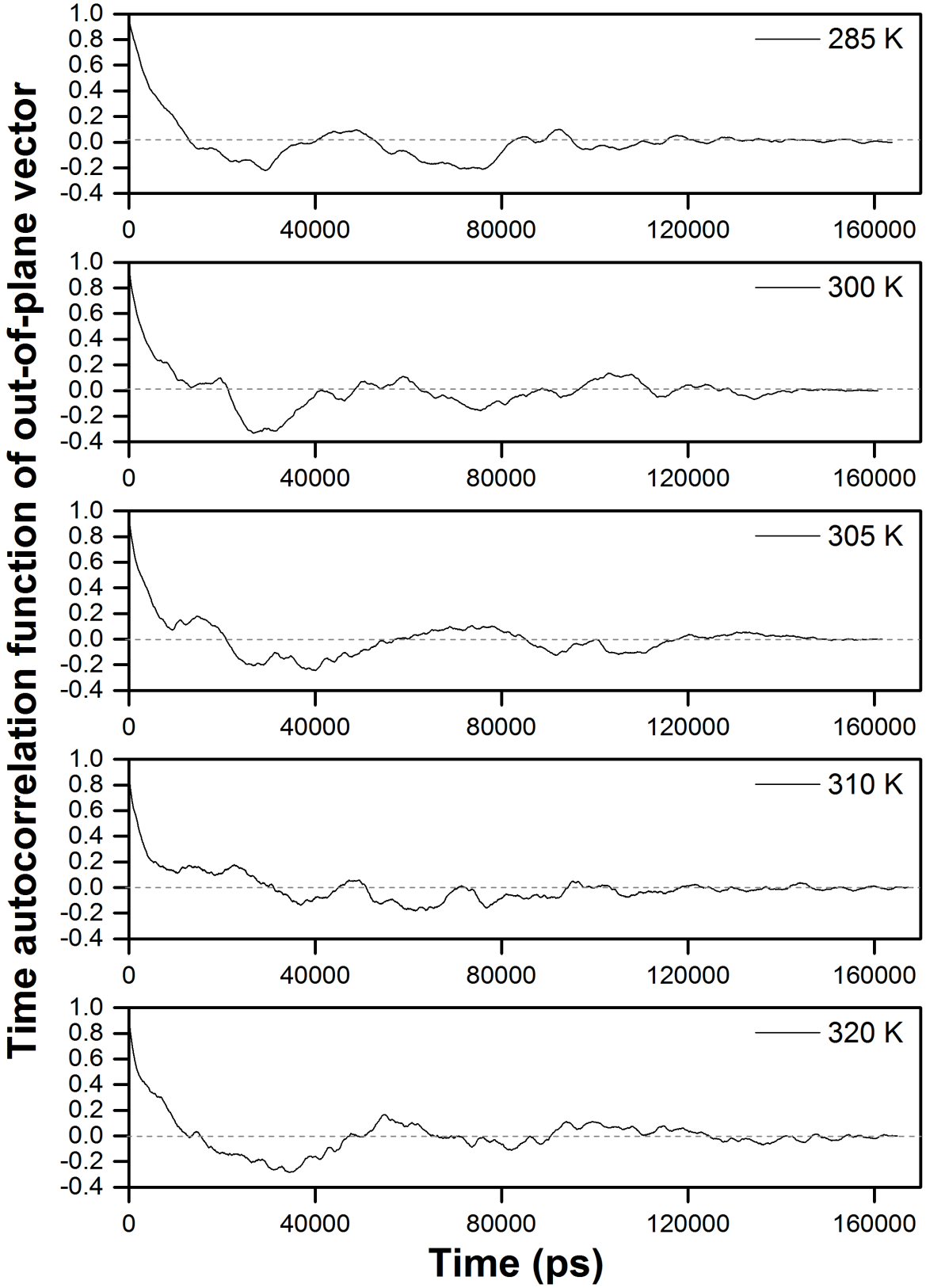


$(VPGVG)_{18}$: 325 K, 330 K, 335 K, 340 K, 350 K.



D

$(VPGVG)_{30}$: 285 K, 300 K, 305 K, 310 K, 320 K.



$(VPGVG)_{30}$: 325 K, 335 K, 350 K.

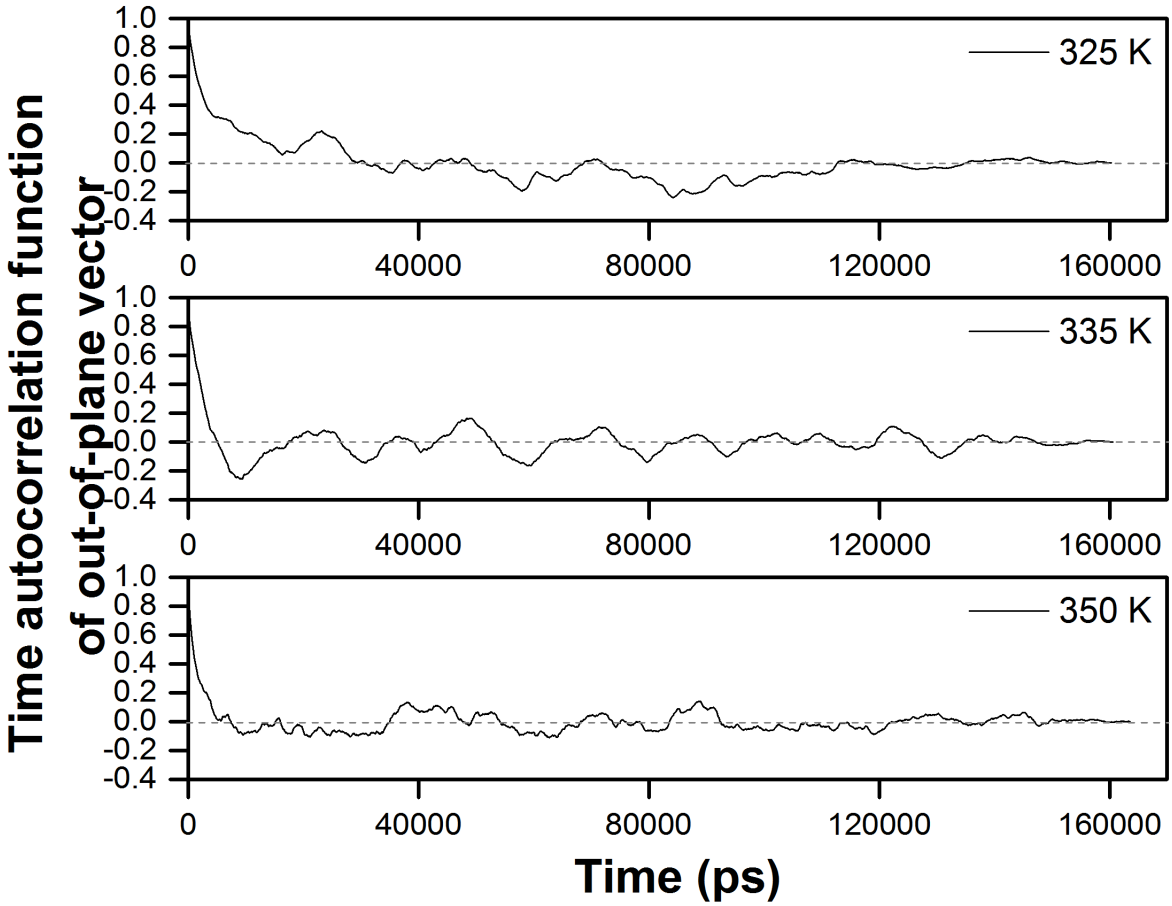


Figure. S3. Time autocorrelation function of peptide backbone Cα-Cα bond unit vectors out of plane. Relaxation time of peptide backbone vectors can be estimated from time autocorrelation profile for (A) (GVG)$(VPGVG)_3$, (B) $(VPGVG)_{10}$, (C) $(VPGVG)_{18}$ and (D) $(VPGVG)_{30}$ when it first reaches zero. The releaxation time is less than 35 ns for ELP $(VPGVG)_n$ of all lengths.

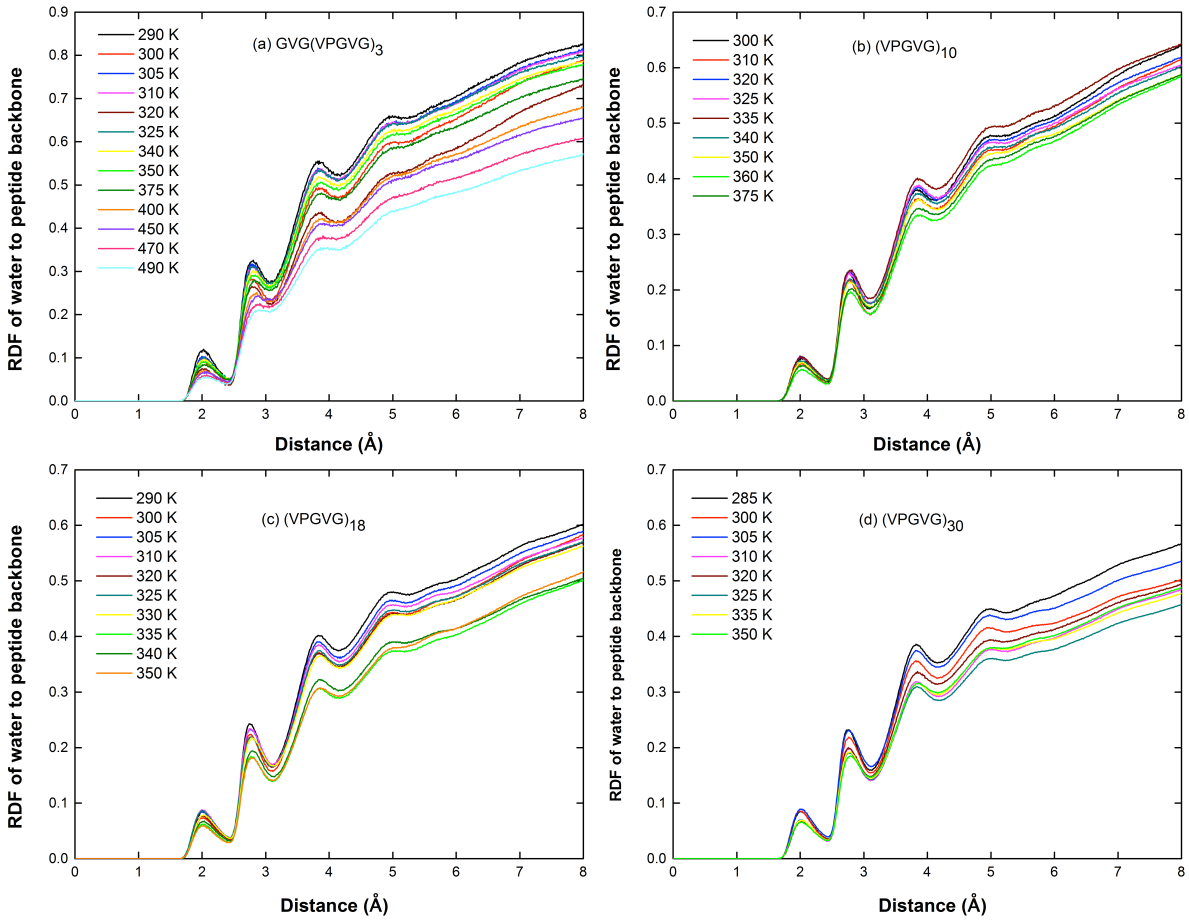
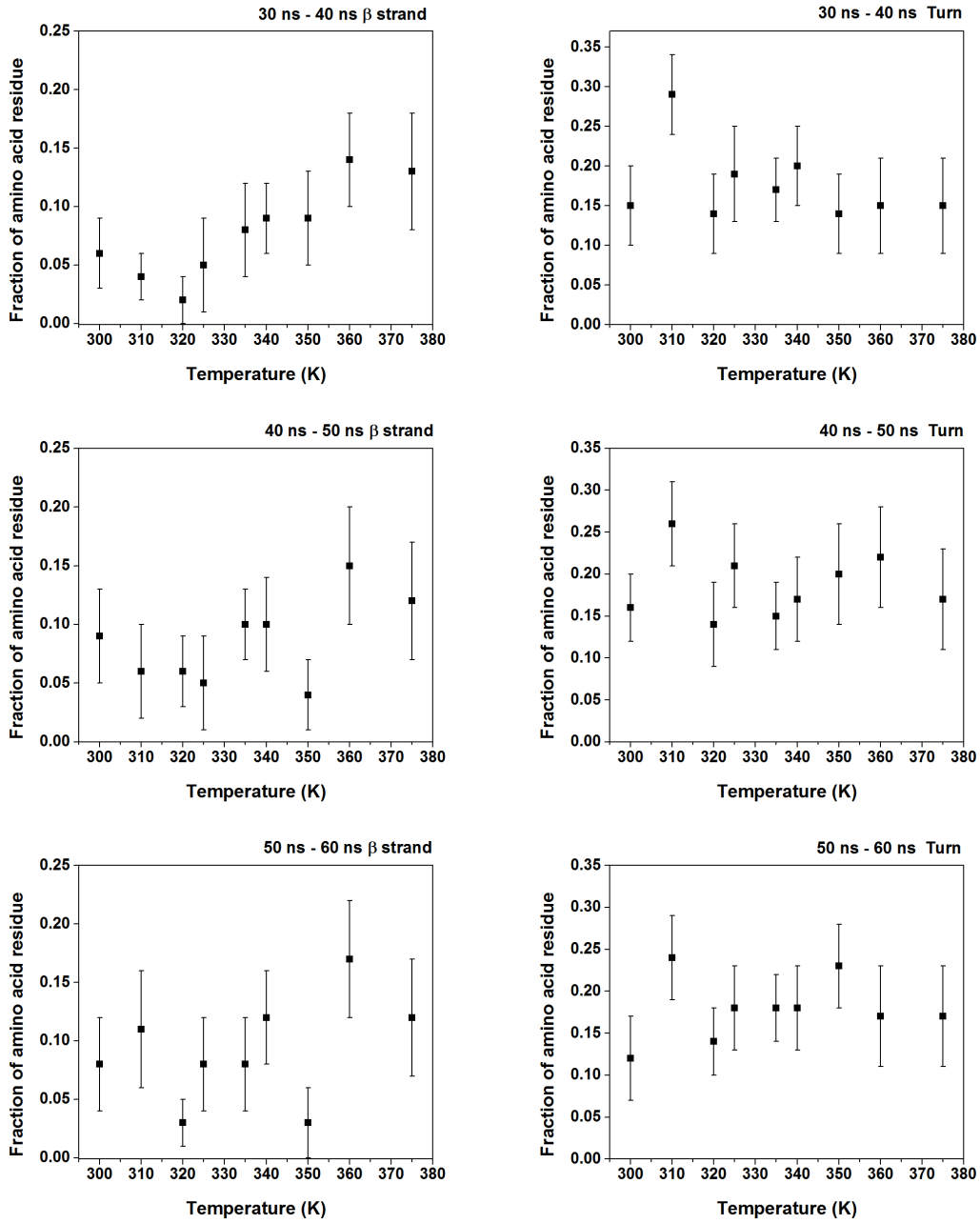


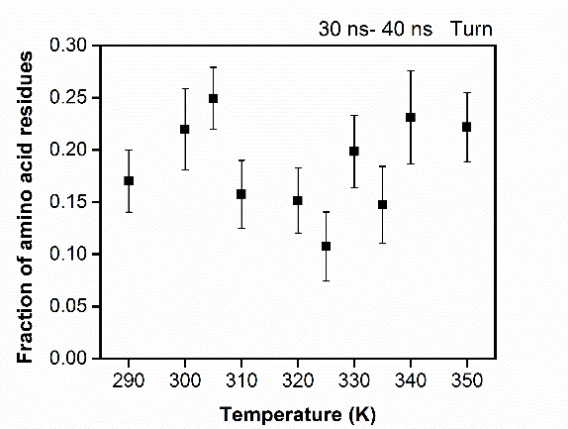
Figure. S4. Radial distribution function of oxygen atoms in water molecules around atoms in peptide of different lengths: (a) (GVG)(VPGVG)$_3$ (b) (VPGVG)$_{10}$ (c) (VPGVG)$_{18}$ (d) (VPGVG)$_{30}$. The position of the first minimum that each curve reaches are approximately the same for all lengths around 2.45 Å, water molecules within this distance to peptide backbone atoms are in the first hydration layer, and are used for hydration analysis.

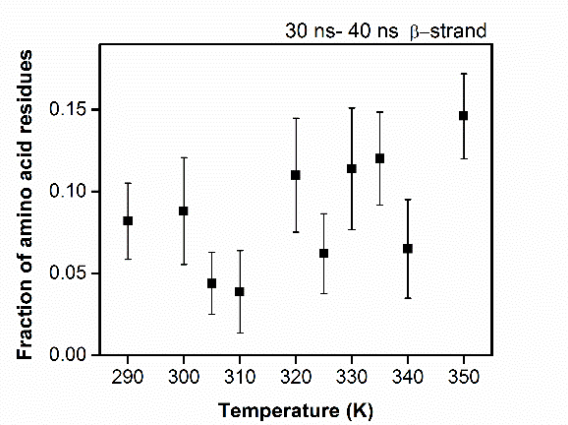
Secondary structure formation as a function of temperature for turn and β-strand structures at different time intervals.

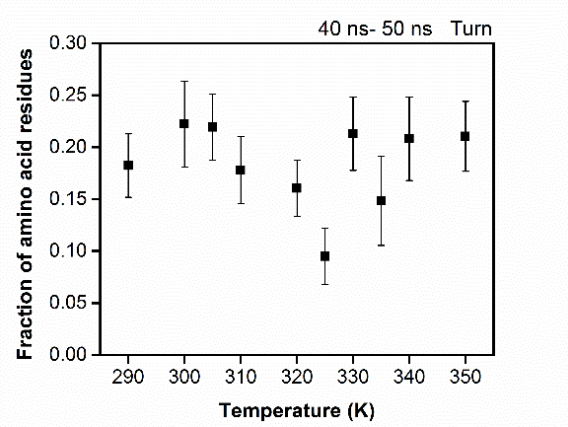
A $(VPGVG)_{10}$

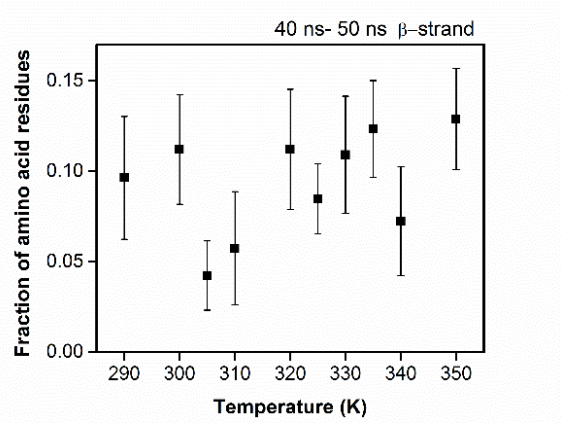


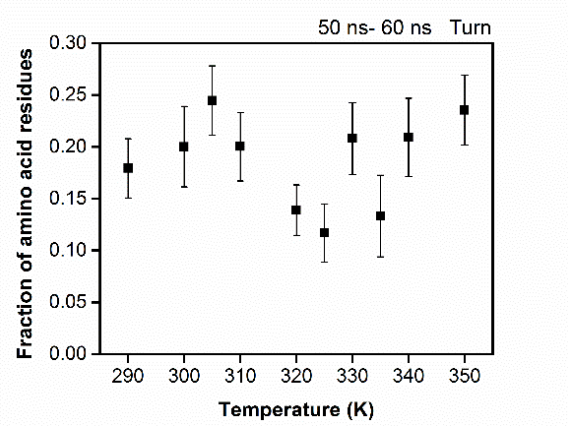
B $(VPGVG)_{18}$:

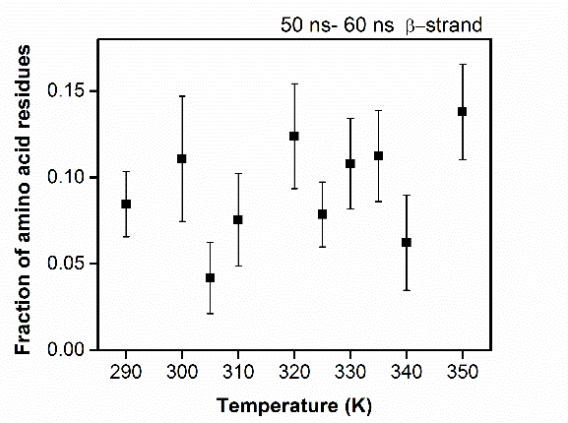

30 ns- 40 ns Turn
Fraction of amino acid residues
Temperature (K)

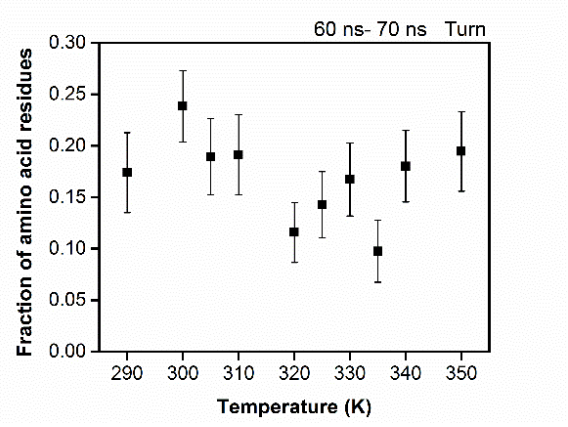

30 ns- 40 ns β–strand
Fraction of amino acid residues
Temperature (K)

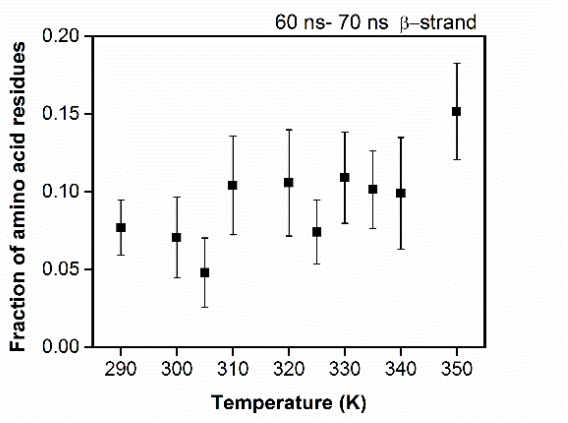

40 ns- 50 ns Turn
Fraction of amino acid residues
Temperature (K)


40 ns- 50 ns β–strand
Fraction of amino acid residues
Temperature (K)


50 ns- 60 ns Turn
Fraction of amino acid residues
Temperature (K)


50 ns- 60 ns β–strand
Fraction of amino acid residues
Temperature (K)


60 ns- 70 ns Turn
Fraction of amino acid residues
Temperature (K)


60 ns- 70 ns β–strand
Fraction of amino acid residues
Temperature (K)

C $(VPGVG)_{30}$

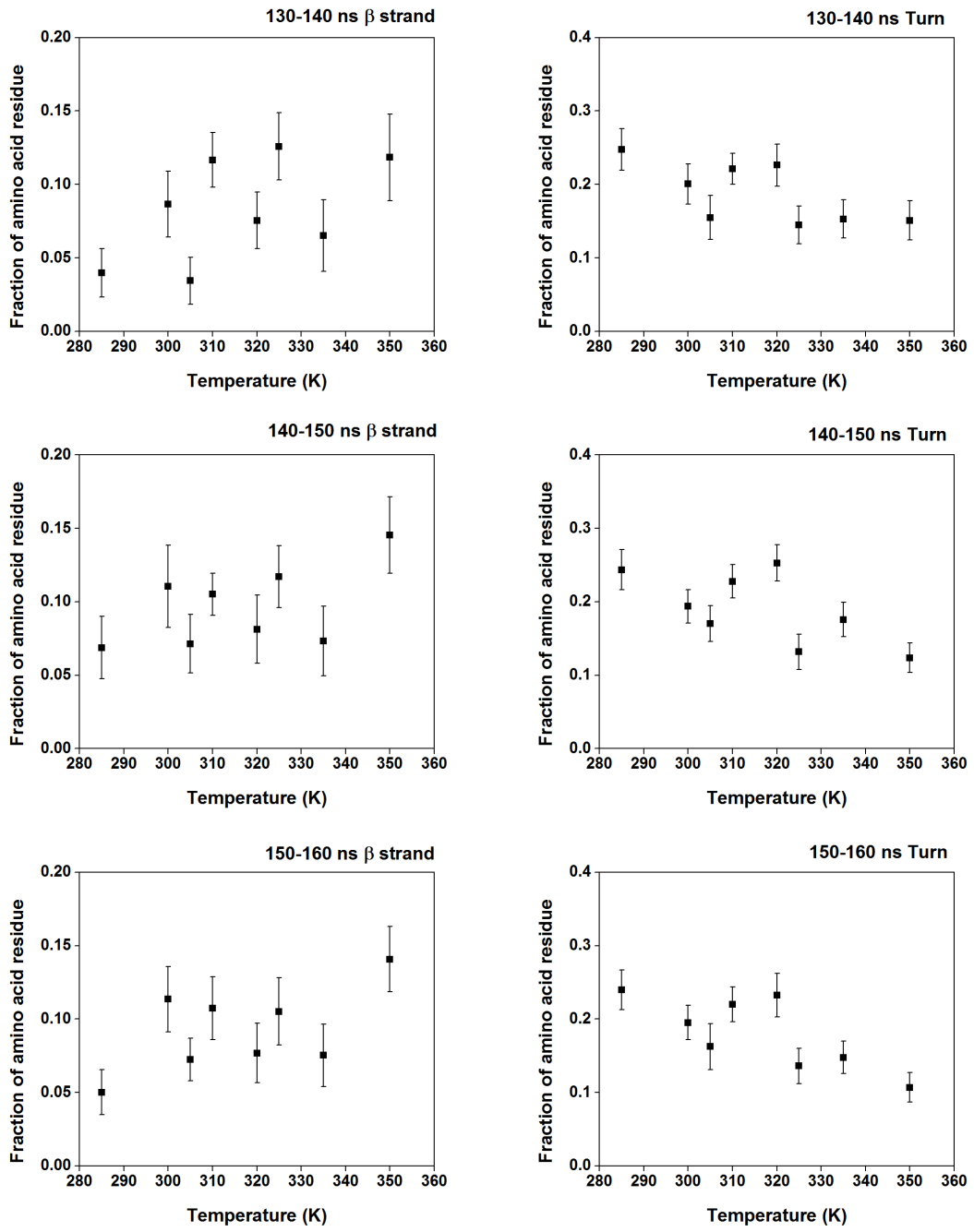


Figure S5. Secondary structure formation as a function of temperature for turn and β-strand structures at different time intervals for (A) $(VPGVG)_{10}$ (B) $(VPGVG)_{18}$ and (C) $(VPGVG)_{30}$.

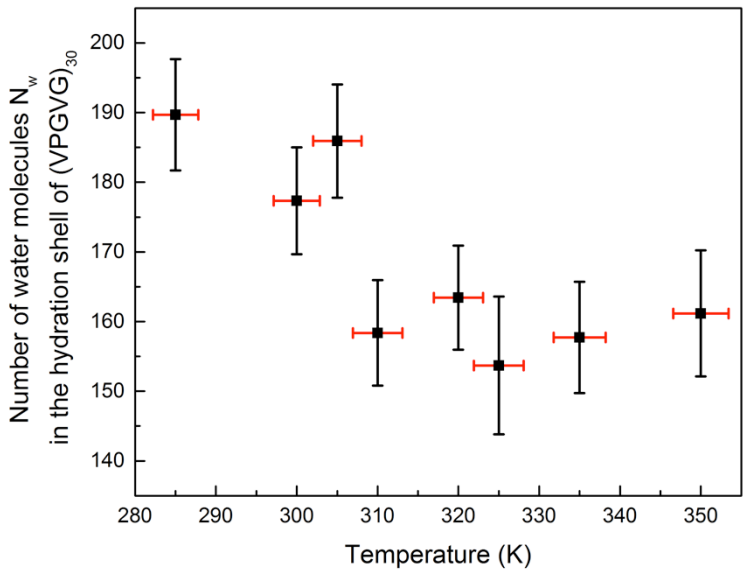


Figure S6. Number of water molecules in the hydration shell of $(VPGVG)_{30}$ versus temperature.

Table S1. Hydrogen-bonding lifetime for $GVG(VPGVG)_3$, $(VPGVG)_{10}$, $(VPGVG)_{18}$ and $(VPGVG)_{30}$ based on two types of hydrogen bonding pairs: N-H group with water and C=O group with water at a low temperature (below T_t) and a high temperature (above T_t)

	$(GVG)(VPGVG)_3$		$(VPGVG)_{10}$		$(VPGVG)_{18}$		$(VPGVG)_{30}$	
	NH-wat	CO-wat	NH-wat	CO-wat	NH-wat	CO-wat	NH-wat	CO-wat
Low T	2.21±0.41	6.50±1.35	2.50±0.65	6.15±1.88	2.41±0.77	5.70±1.51	2.27±0.77	5.88±2.28
High T	1.46±0.08	2.19±0.21	1.87±0.14	3.39±0.49	2.01±0.47	3.57±0.84	2.05±0.42	3.61±0.85