Supporting Information for

The Impact of 4-Thiaproline on Polyproline Conformation

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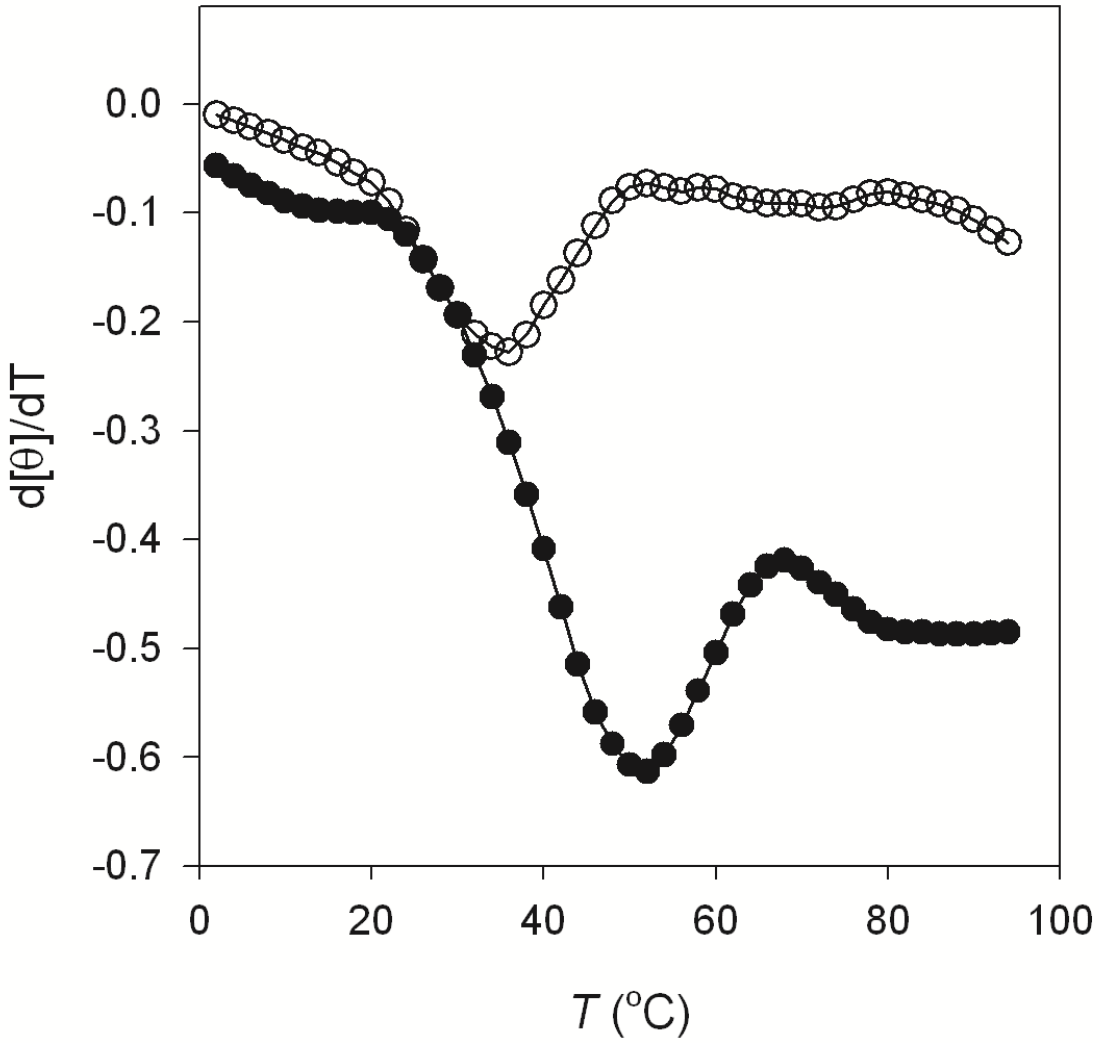

Figure S1. The first derivative of the thermal unfolding curves versus temperature (d[θ]/dT) for P11 (closed circles) and Thp-P11 (open circles) in *n*-propanol.

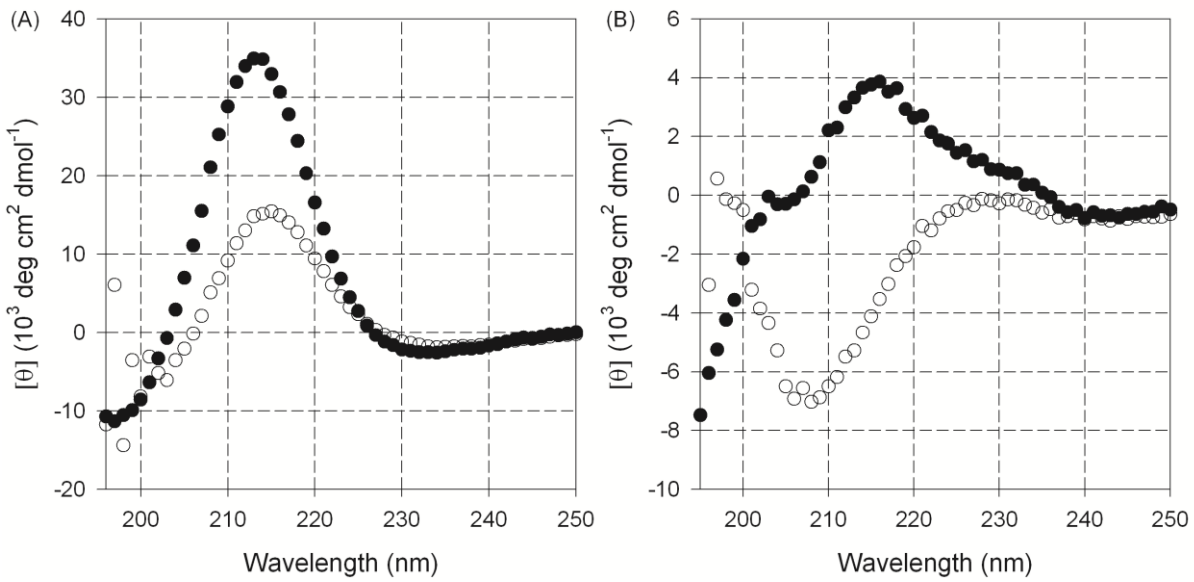

Figure S2. Far-UV CD spectra for (A) P11 and (B) Thp-P11 at 4 °C (closed circles) and 94 °C (open circles) in *n*-propanol.

Table S1. Dihedral Angles Calculated from the Energy-Optimized PPII Structures in Gas Phase[a]

peptide	ring pucker	N → C dihedral angles[b] (deg)														
		ϕ_1	ψ_1	χ_1	ϕ_2	ψ_2	χ_2	ϕ_3	ψ_3	χ_3	ϕ_4	ψ_4	χ_4	ϕ_5	ψ_5	χ_5
P5	All-*exo*	-64	128	-20	-66	128	-27	-66	130	-26	-66	128	-26	-63	147	-28
Thp-P5	All-*exo*	-63	129	-20	-67	130	-27	-64	131	-34	-66	128	-26	-63	148	-28

[a]Calculated at B3LYP/6-31+G(d) level of theory. P5 is Ac-$(Pro)_5$-OMe, and Thp-P5 is Ac-$(Pro)_2$-Thp-$(Pro)_2$-OMe.
[b]An ideal PPII helix has the dihedral angles of (ϕ, ψ) = (-75°, 145°).

Table S2. Dihedral Angles and Energy Differences Calculated from the Energy-Optimized PPII Structures in Water[a]

peptide	ring pucker	$\Delta(E_{exo} - E_{endo})$[b] (kcal/mol)	N → C dihedral angles[c] (deg)													
			ϕ_1	ψ_1	χ_1	ϕ_2	ψ_2	χ_2	ϕ_3	ψ_3	χ_3	ϕ_4	ψ_4	χ_4	ϕ_5	ψ_5	χ_5
P5	All-*exo*	--[d]	-63	145	-24	-60	143	-26	-61	141	-27	-62	144	-26	-58	145	-28
P5	Pro3 *endo*[d]		-63	145	-24	-60	143	-26	-61	141	-27	-62	144	-26	-58	145	-28
Thp-P5	All-*exo*	-0.47	-62	143	-24	-60	135	-27	-64	143	-32	-61	144	-26	-58	145	-28
Thp-P5	Thp *endo*		-62	141	-25	-62	144	-26	-78	163	37	-63	146	-24	-58	145	-27

[a]Calculated at B3LYP/6-31+G(d) level of theory. P5 is Ac-$(Pro)_5$-OMe, and Thp-P5 is Ac-$(Pro)_2$-Thp-$(Pro)_2$-OMe.

[b]ΔE is the minimized energy of the PPI conformation with all residues in an *exo* pucker relative to the respective PPII conformation with Pro3 or Thp in an *endo* pucker.

[c]An ideal PPII helix has the dihedral angles of $(\phi, \psi) = (-75°, 145°)$

[d]Pro3 in the energy-minimized structure of P5 adopted an *exo* pucker, and no *endo*-puckered conformation could be observed for it during the calculation. Thus the relative energy between *exo* and *endo* puckers could not be obtained.