Supplemental Information

Solid-state NMR spectroscopy and isotopic labeling target abundant dipeptide sequences in elastin's hydrophobic domains

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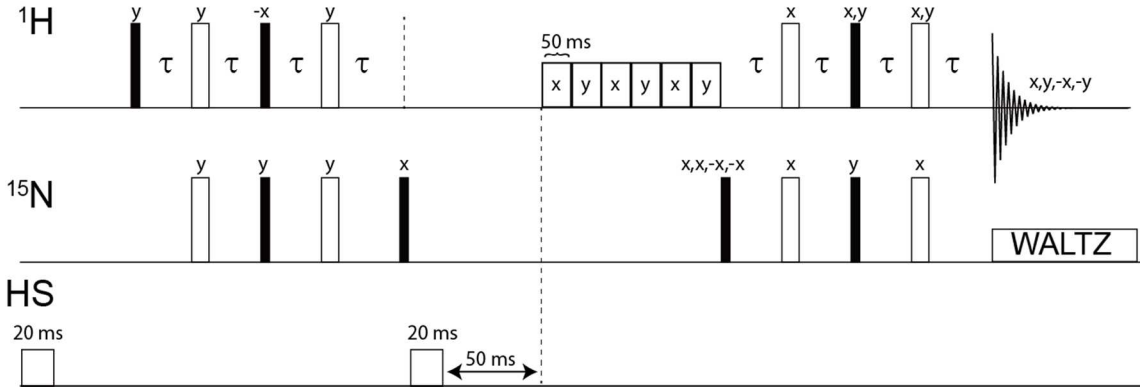

Figure S1. Pulse sequence for ^{15}N-edited ^{1}H MAS NMR experiment. The water suppression was achieved by MISSISSIPPI [S1]. Filled narrow and unfilled wide rectangles represent π/2 and π pulses, respectively. HS indicates homospoil gradients.

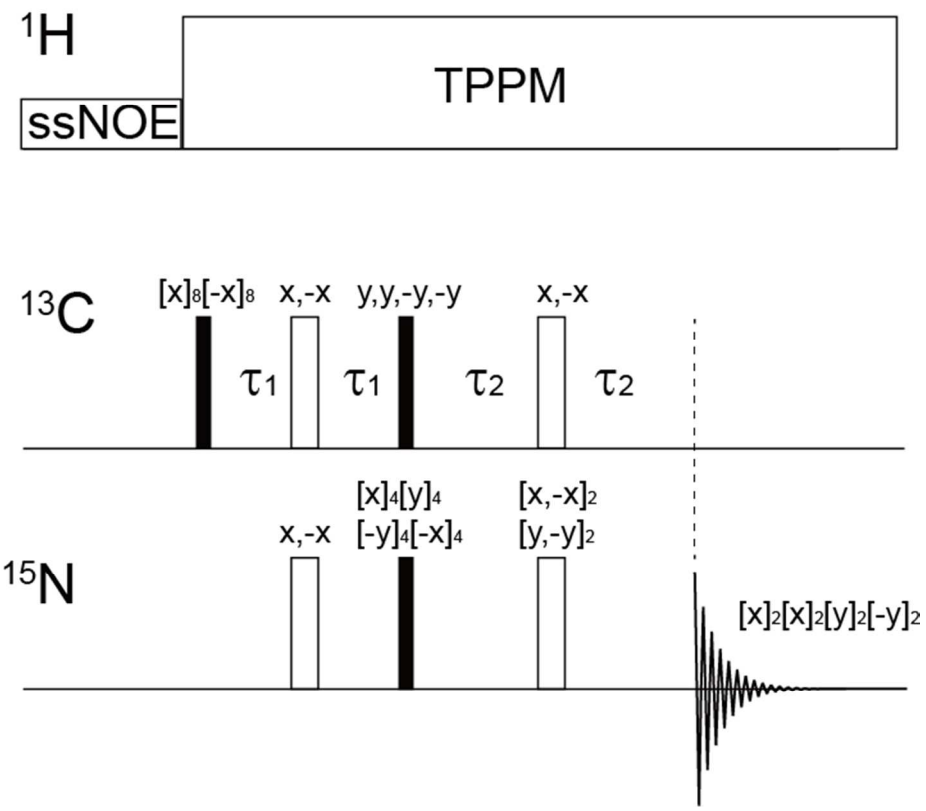

Figure S2. Pulse sequence for ^{13}C-^{15}N refocused INEPT experiment with steady-state NOE for ^{13}C excitation [S2, S3]. Filled narrow and unfilled wide rectangles represent $\pi/2$ and π pulses, respectively.

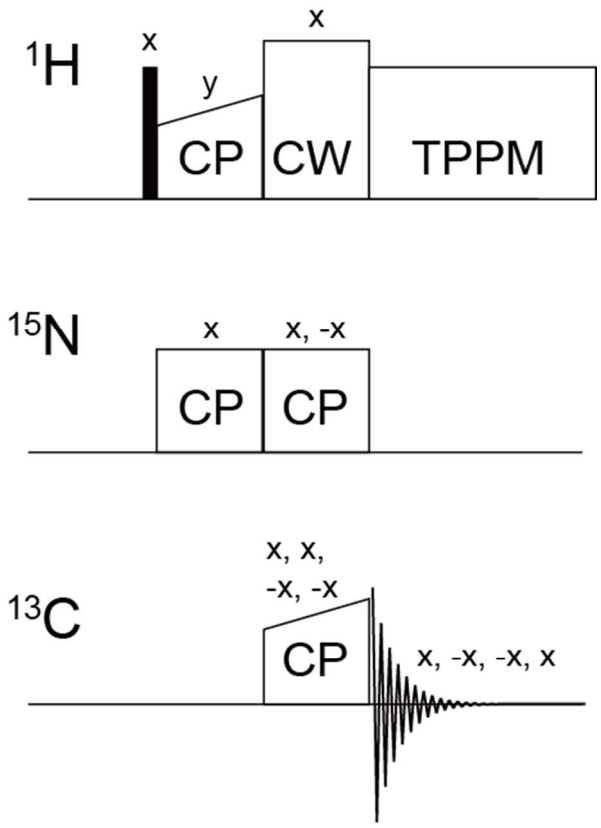

Figure S3. Pulse sequence for ^{1}H-^{15}N-^{13}C DCP experiment [S4].

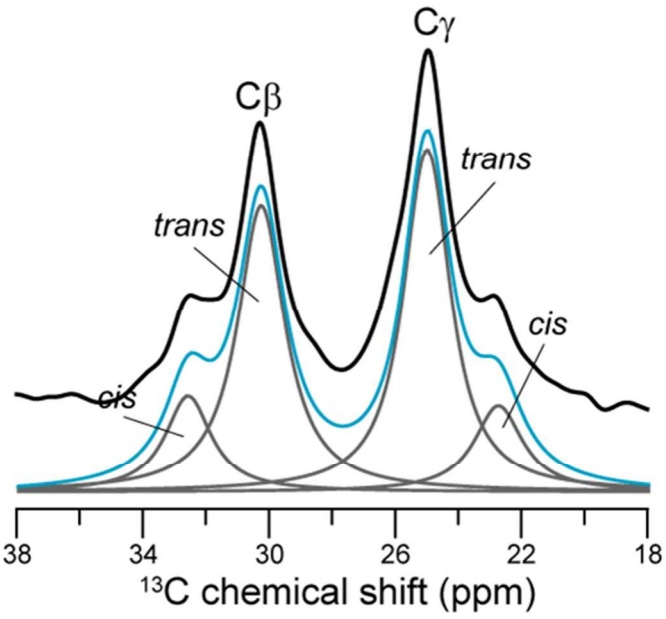

Figure S4. ^{13}C DPMAS NMR spectrum for the Cβ and Cγ region of poly(Gly[^{15}N-Pro]). The spectrum (black) were acquired at 37 °C. The individual contributions from deconvolution are shown in gray. The blue trace is the calculated sum of the individual components.

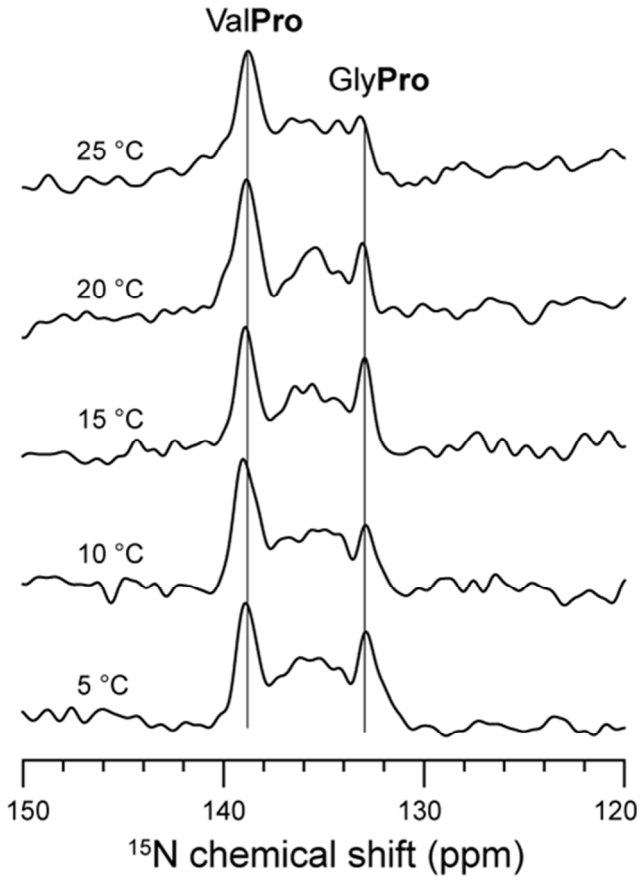

Figure S5. Variable-temperature ^{15}N DPMAS NMR spectra of [^{15}N-Pro] elastin in 8 M urea. Each spectrum was collected with 2048 scans and processed with 20 Hz line broadening. NMR spectra above 30 °C were not collected due to the thermal decomposition of urea.

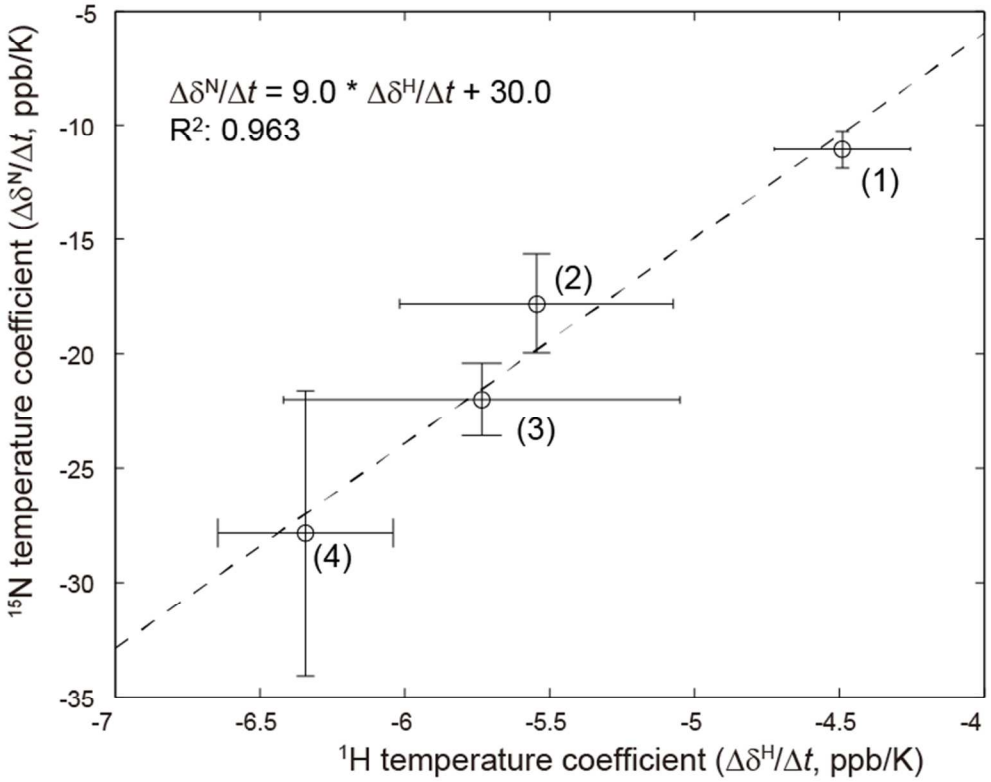

Figure S6. Correlation of $^1H^N$ versus $^{15}N^H$ temperature coefficients shown in Table 1.

Table S1. Deconvolution of selected poly(Gly[^{15}N-Pro]) peaks

	δ (ppm)	assignment	FWHM (Hz)	% area
^{15}N	133.0	*cis*	60	22
	131.7	*trans*	55	78
^{13}Cβ	32.5	*cis*	180	25
	30.2	*trans*	180	75
^{13}Cγ	25.0	*trans*	180	78
	22.7	*cis*	190	22

Table S2. ^{15}N, ^{13}C isotropic chemical shifts (ppm) for proline and valine, respectively, for the ValPro pair.

		random coil	Type II β-turn	α-helix	β-sheet
	elastin in water	elastin in 8 M urea	elastin mimetic	bacteriorhodopsin[c)]	bacteriorhodopsin[c)]
Val**[^{15}N-Pro]**	138.5	138.4	136.9 [a)]	131.8	142.7
[$^{13}C_{C=O}$-Val]Pro	172.5	172.4	172.6 [b)]	170.0	169.0
[$^{13}C_{\alpha}$-Val]Pro	57.6	57.8	57.8 [b)]	62.5	54.3
Δ_{ave}(NCαC=O)		0.13	0.39	3.53	2.94

a) Ref. S5 b) Ref. S6 c) Ref. S7

Table S3. The observed $^{1}H^{N}$ and $^{15}N^{H}$ chemical shifts (ppm) of Gly in [^{15}N-Gly] elastin at different temperatures.

Temperature		Peak (1)	Peak (2)	Peak (3)	Peak (4)
37 ºC	^{1}H	8.16	8.36	8.40	8.46
	^{15}N	107.0	106.5	107.8	110.6
29 ºC	^{1}H	8.18	8.41	8.44	8.49
	^{15}N	107.1	106.6	108.0	110.8
21 ºC	^{1}H	8.22	8.45	8.52	8.55
	^{15}N	107.2	106.8	108.1	111.1
13 ºC	^{1}H	8.27	8.51	8.53	8.61
	^{15}N	107.3	106.8	108.4	111.5
5 ºC	^{1}H	8.29	8.53	8.58	8.66
	^{15}N	107.3	107.1	108.5	111.4

Table S4. Relative volume-intensities of the four peaks found in 2D spectra of [^{15}N-Gly] elastin. The errors are around +/-1%.

Temperature		Peak(1)	Peak(2)	Peak(3)	Peak(4)
37 ºC	%	36	13	44	8
29 ºC	%	32	12	48	8
21 ºC	%	38	8	41	13
13 ºC	%	37	12	43	8
5 ºC	%	33	11	46	11

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