ESI

Chemoenzymatic Synthesis of Polypeptides Consisting of Periodic Di- and Tripeptide Motifs Similar to Elastin

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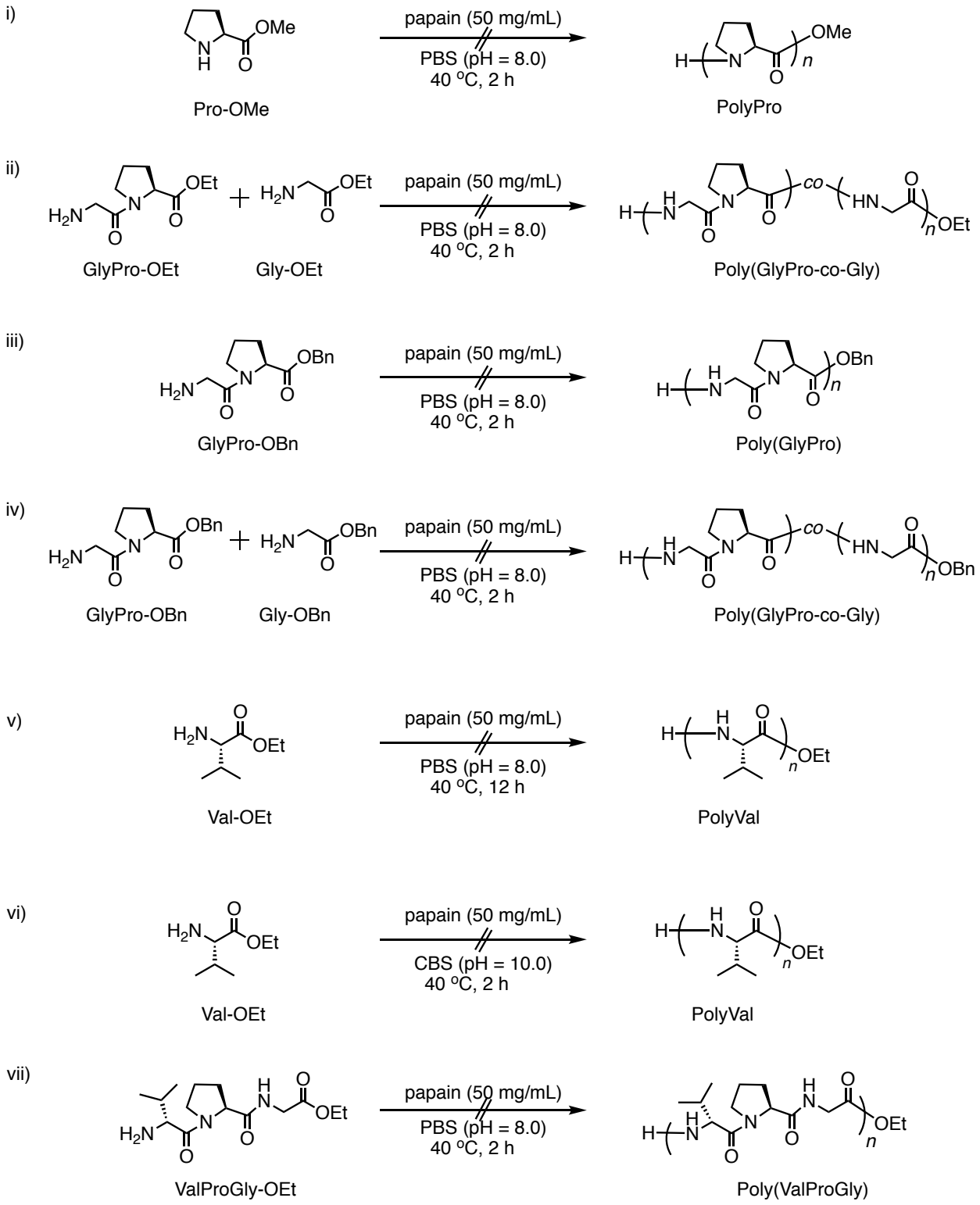

Scheme S1 Chemoenzymatic polymerization of Pro- and Val-containing monomers using papain.

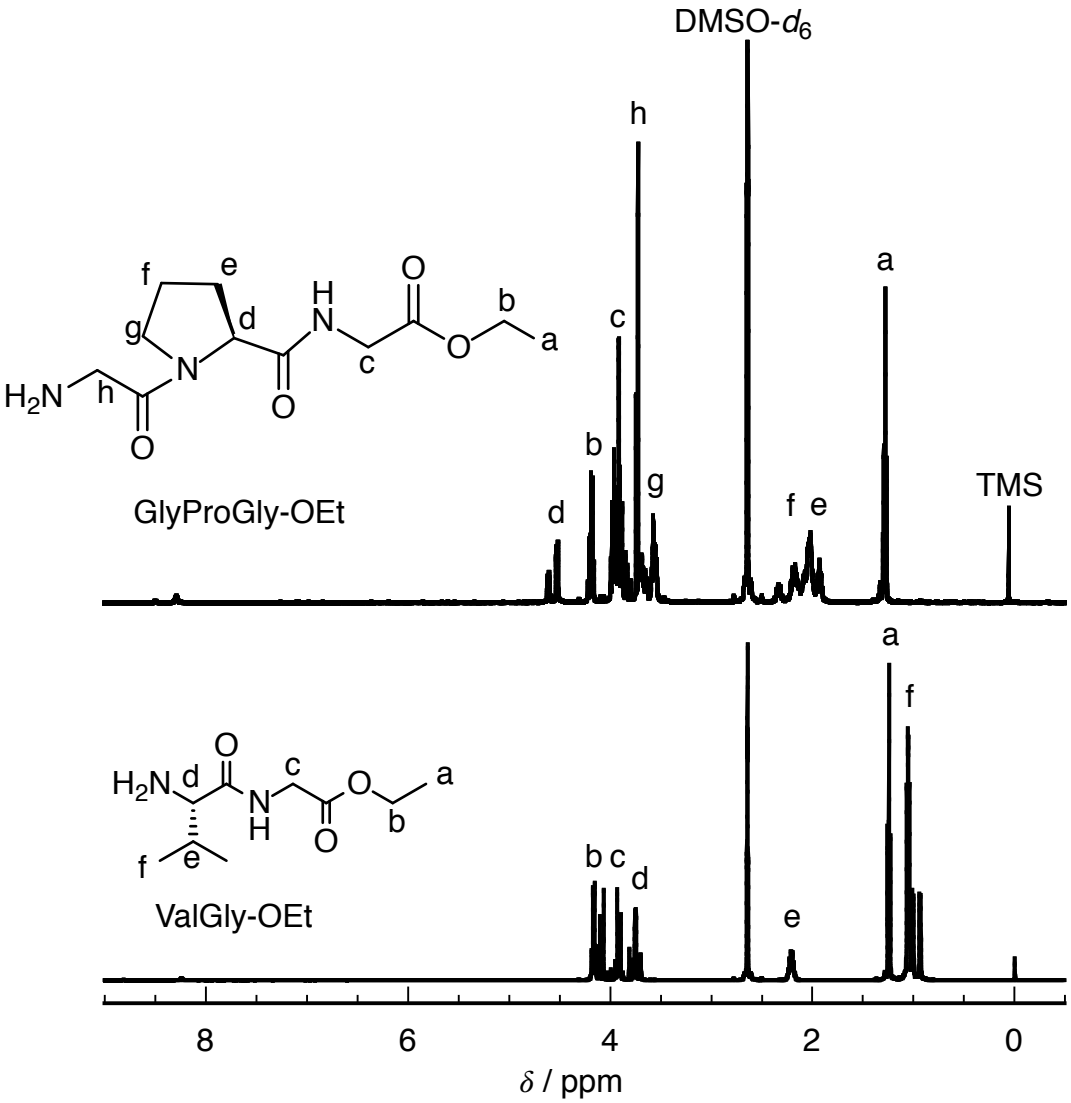

Fig. S1 ^{1}H NMR spectrum of the blank polymerization reactants of GlyProGly-OEt and ValGly-OEt in DMSO-d_6/TFA-d (5/1 volume ratio).

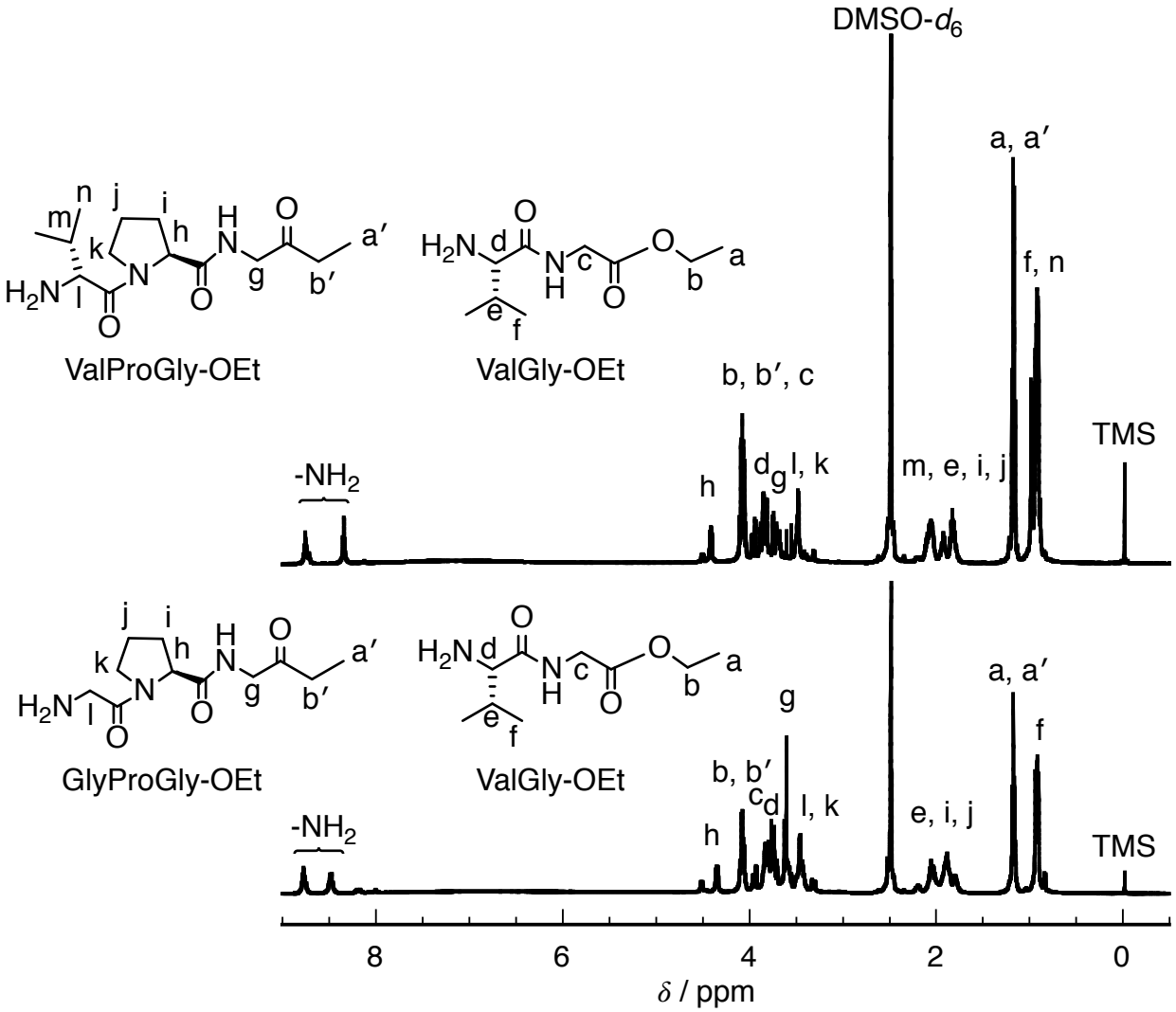

Fig. S2 ^{1}H NMR spectrum of the blank polymerization reactants of ValProGly-OEt/ValGly-OEt and GlyProGly-OEt/ValGly-OEt in DMSO-d_6/TFA-d (5/1 volume ratio).

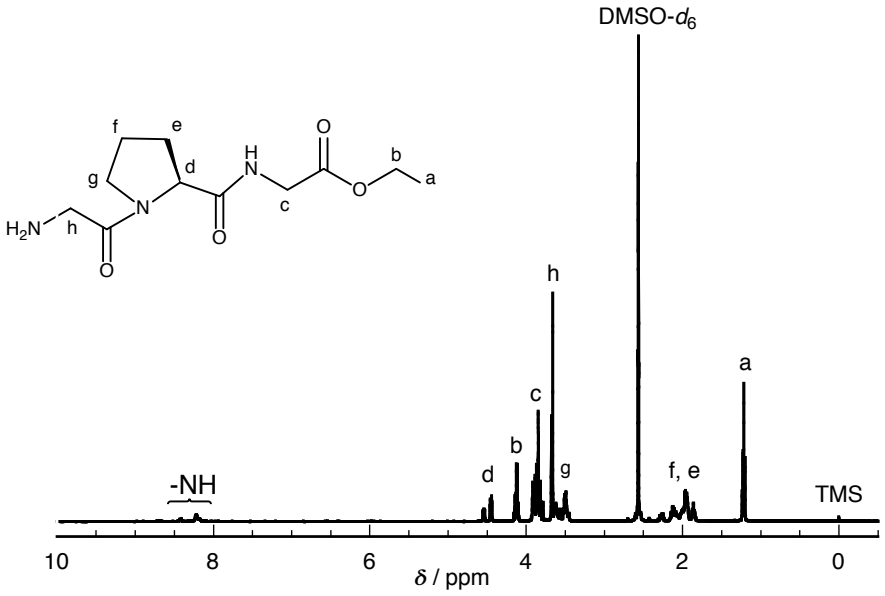

Fig. S3 ^{1}H NMR spectrum of GlyProGly-OEt in DMSO-d_6/TFA-*d* (5/1 volume ratio).

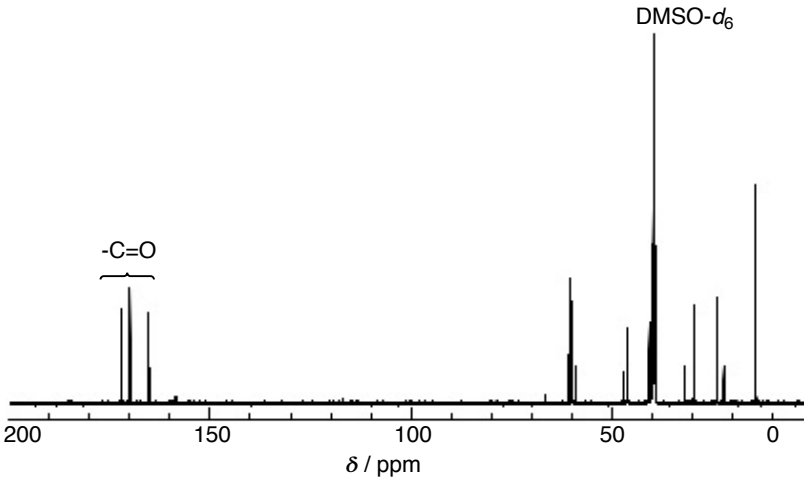

Fig. S4 ^{13}C NMR spectrum of GlyProGly-OEt in DMSO-d_6/TFA-*d* (5/1 volume ratio).

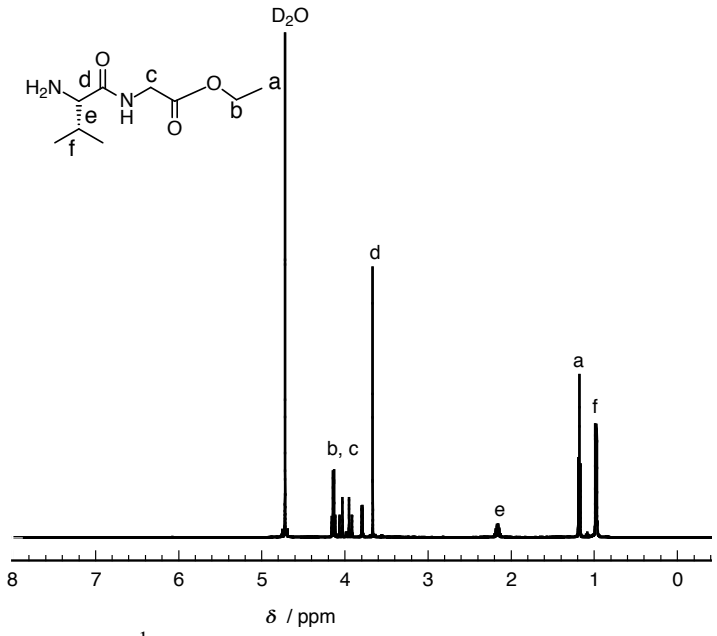

Fig. S5 ^{1}H NMR spectrum of ValGly-OEt in D_2O.

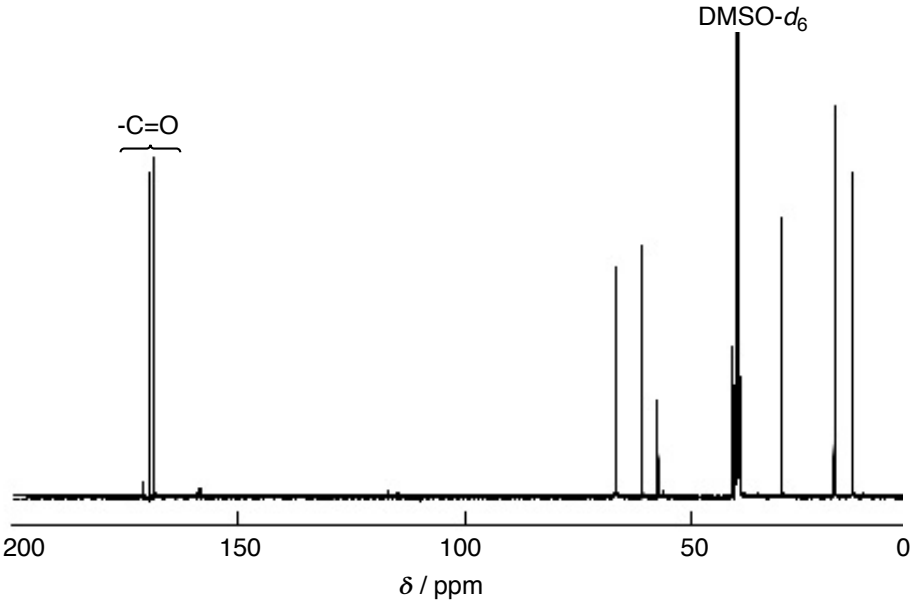

Fig. S6 ^{13}C NMR spectrum of ValGly-OEt in DMSO-d_6/TFA-*d* (5/1 volume ratio).

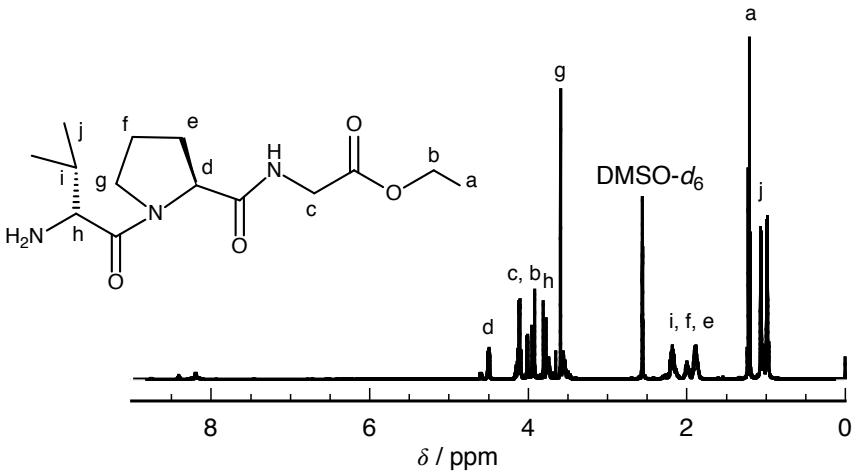

Fig. S7 ^{1}H NMR spectrum of ValProGly-OEt in DMSO-d_6/TFA-*d* (5/1 volume ratio).

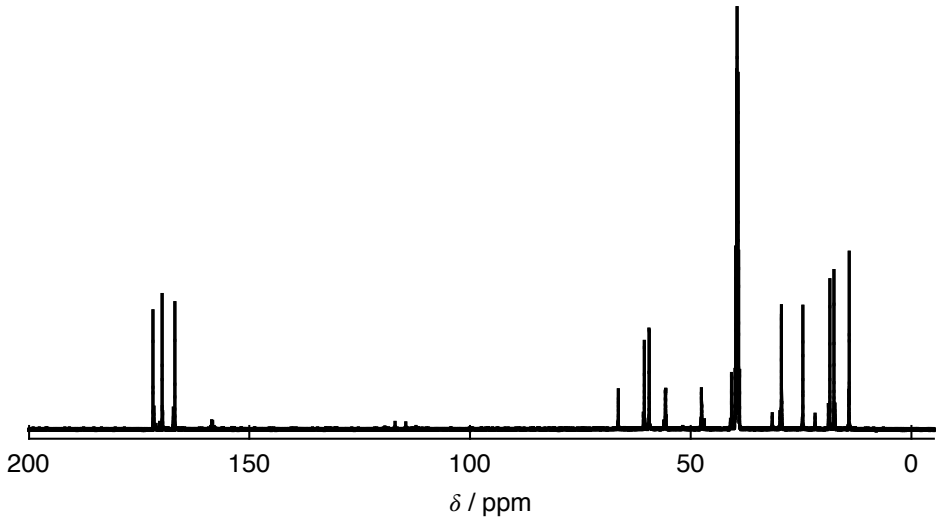

Fig. S8 ^{13}C NMR spectrum of ValProGly-OEt in DMSO-d_6/TFA-*d* (5/1 volume ratio).

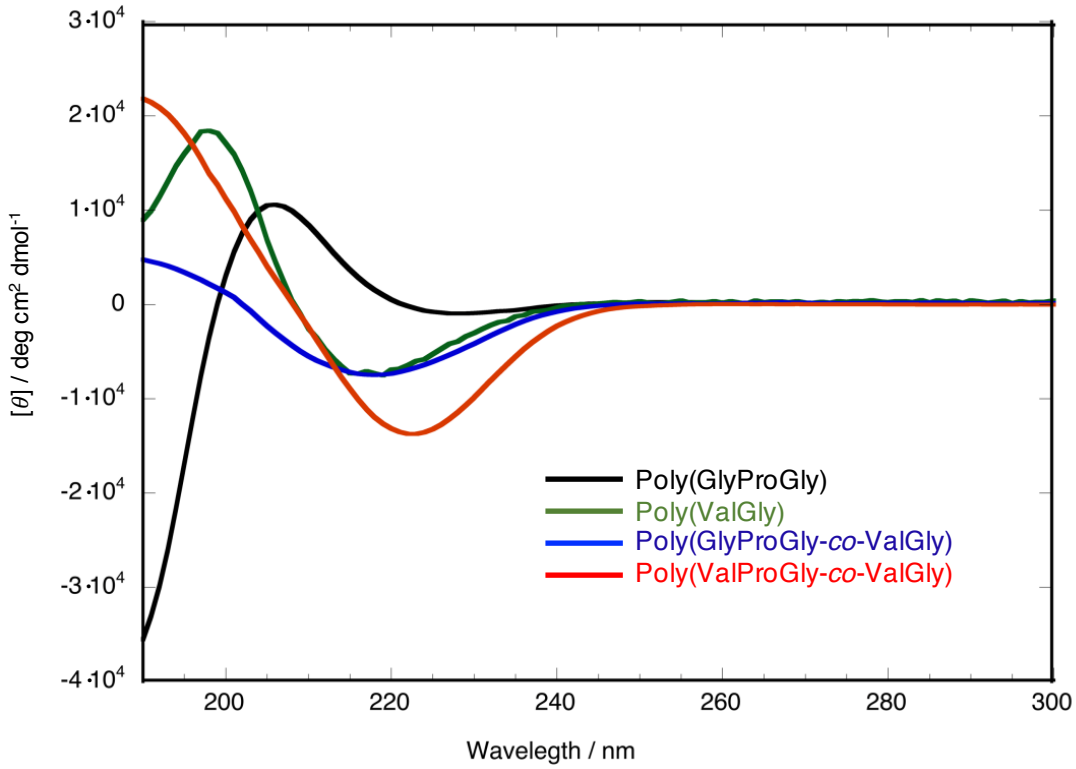

Fig. S9 CD spectra of the polypeptides in 2,2,2-trifluoroethanol (0.1% TFA) solution (1 mM).

CD spectra of all polypeptides were analyzed using in 2,2,2-trifluoroethanol (0.1% TFA) solution (1mM). In the CD spectra of poly(GlyProGly) it has been found that the resulting polypeptide has unordered structure with the ratio of ***unordered***/strand/turns/helix to be ***50.05***/25.72/19.01/5.20. In the CD spectra of poly(ValGly-OEt) the resulting polypeptide has β-strand structure with the ratio of unordered/***strand***/turns/helix to be 29.62/***40.64***/24.42/5.30. The CD spectra of poly(GlyProGly-co-ValGly) has β-strand structure with the ratio of unordrered/***strand***/turns/helix to be 31.06/***37.26***/20.28/11.38. This emphasizes ValGly unit is key for inducing β-strand in the polypeptide chain. The CD spectra of poly(ValProGly-*co*-ValGly) has an unordered structure with the ratio of ***unordered***/strand/turns/helix to be ***32.76***/22.97/29.67/14.58. The values are tabulated in Table S2.

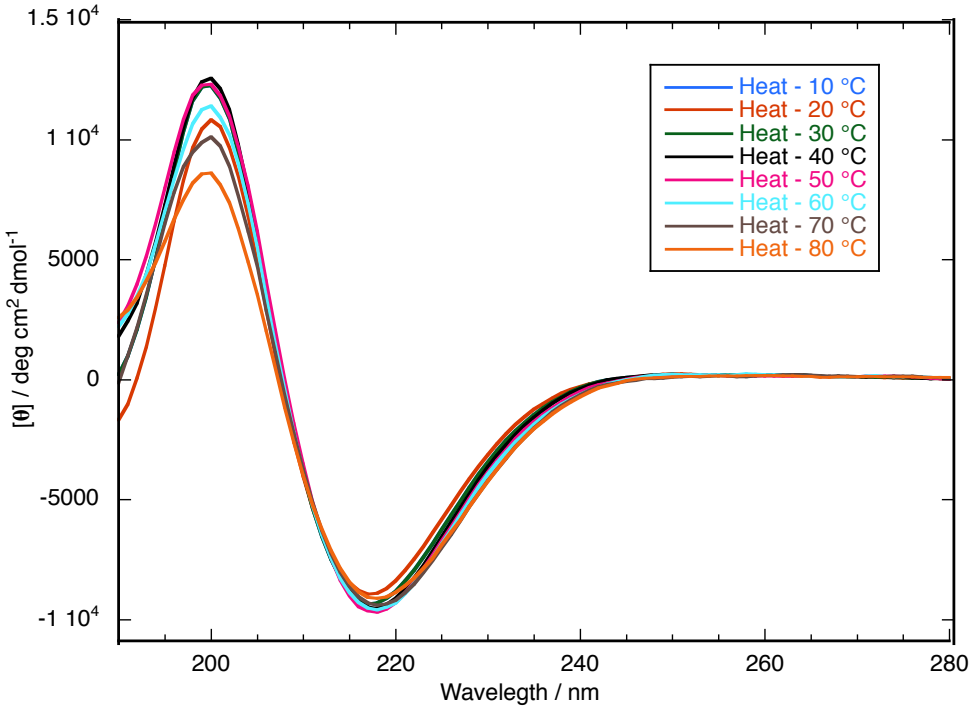

Fig. S10 CD spectra of the poly(GlyProGly-*co*-ValGly) in water at increasing temperatures from 10 to 80 °C (1 mM).

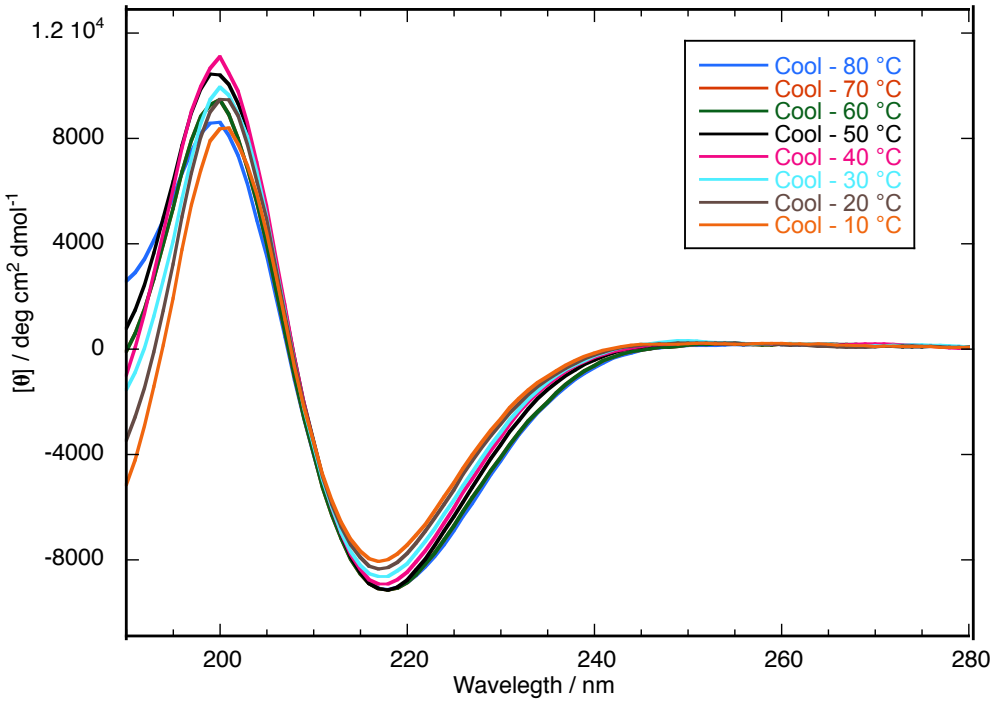

Fig. S11 CD spectra of the poly(GlyProGly-*co*-ValGly) in water at decreasing temperatures from 80 to 10 °C (1 mM).

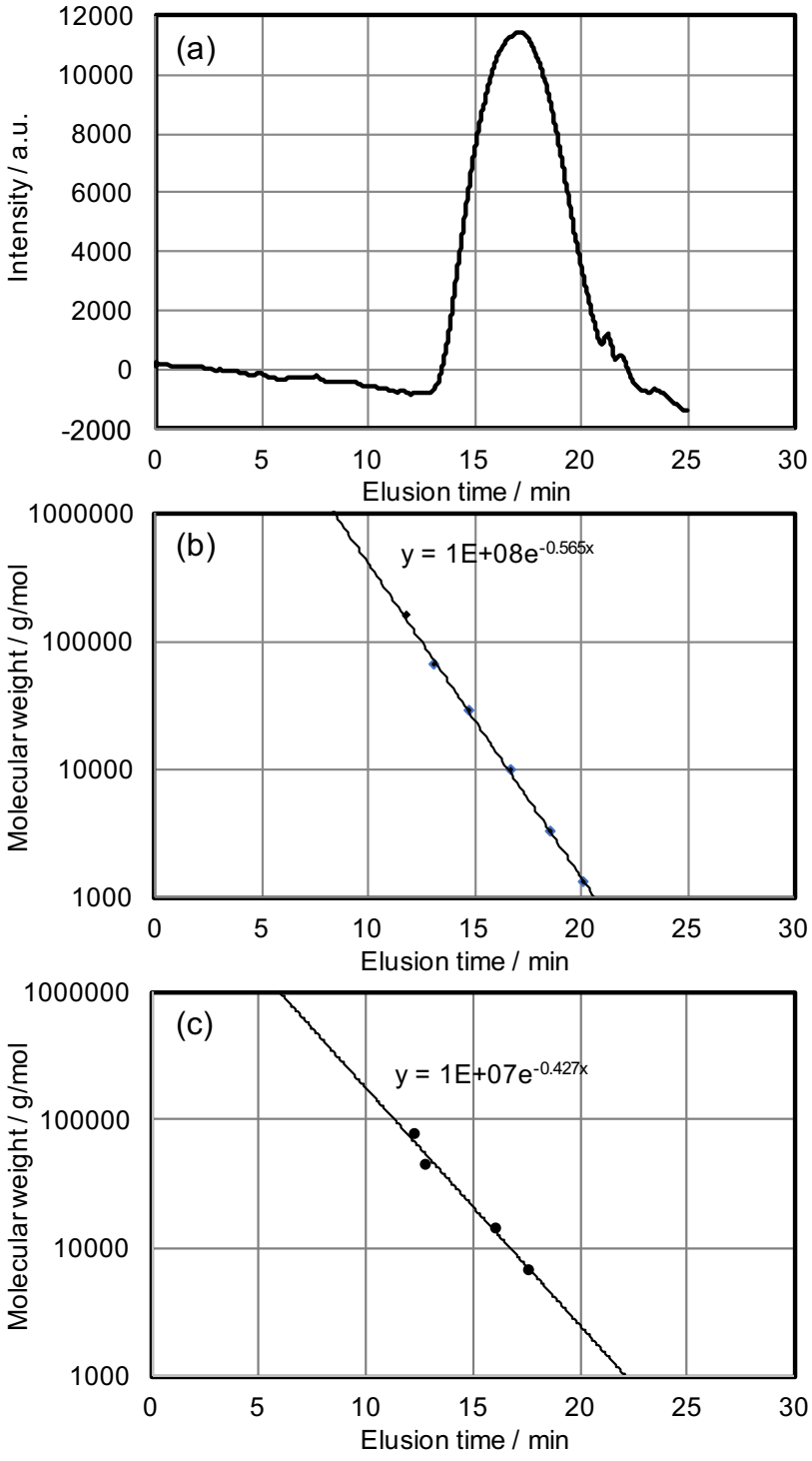

Fig. S12 GPC results of the sample and molecular weight standards. (a) GPC profile of PP-poly(ValProGly-*co*-ValGly) eluted with NMP containing LiBr (10 mM). (b) Calibration curve of polystyrene molecular weight standards. (c) Calibration curve of protein molecular weight standards.

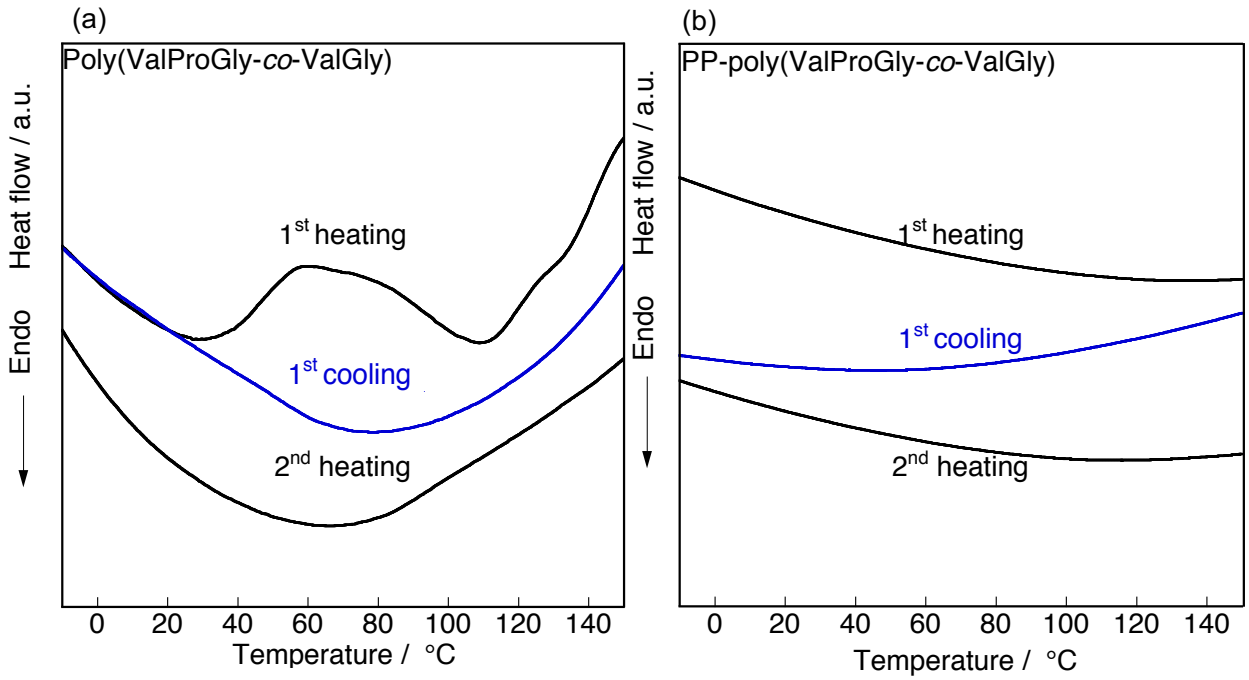

Fig. S13 DSC plot of the poly(ValProGly-*co*-ValGly) (a) and PP-poly(ValProGly-*co*-ValGly) (b). The heating and cooling rates were at 10 °C min^{-1}.

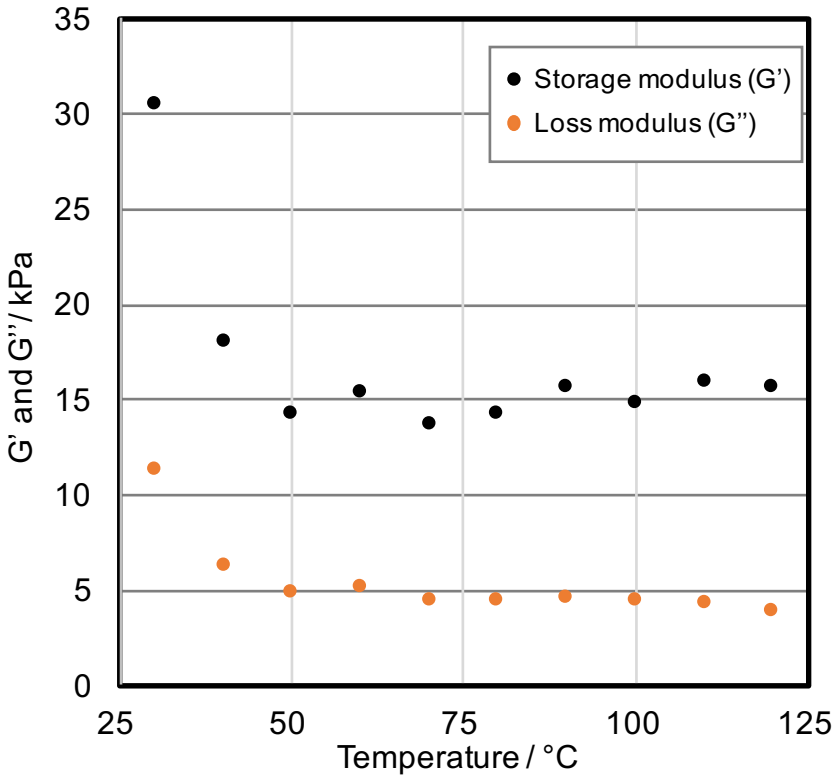

Fig. S14 Storage modulus (G') and loss modulus (G'') of PP-poly(ValProGly-*co*-ValGly) at different temperatures from 30 to 120 °C. The strain and the frequency were 1% and 1 Hz, respectively.

Table S1. Blank tests for chemoenzymatic polymerization of proline and valine containing monomers.[a]

Run	Monomer	Conc. (M)	Time (h)	Yield[b] (%)
1	GlyProGly-OEt	1.0	2	0
2	ValGly-OEt	1.0	2	0
3[c]	GlyProGly-OEt/ValGly-OEt	1.0	2	0
4[c]	ValProGly-OEt/ValGly-OEt	1.0	2	0

[a]Polymerization was carried out using monomer (HCl salt) and papain (50 mg/mL) in phosphate buffer (1 M, pH 8.0) at 40 °C. [b] Precipitation was collected by centrifugation, washed with water, and lyophilized. [c] Molar ratio was 1/1.

Table S2. Percentage of secondary structure calculated by DichroWeb online CD analysis server using using Contin algorithm in combination with reference data set 4.

Polypeptide	**Contin (Set 4)**
Poly(GlyProGly)	**50.05 % unordered** 25.72 % strand 19.01 % turns 5.20 % helix
Poly(ValGly)	29.62 % unordered **40.64 % strand** 24.42 % turns 5.30 % helix
Poly(GlyProGly-*co*-ValGly)	31.06 % unordered **37.26 % strand** 20.28 % turns 11.38 % helix
Poly(ValProGly-*co*-ValGly)	**32.76 % unordered** 22.97 % strand 29.67 % turns 14.58 % helix

Table S3. Percentage of secondary structure calculated by DichroWeb online CD analysis server using Contin algorithm in combination with reference data set 4 for poly(ValProGly-*co*-ValGly) at different temperature.

Contin- Reference set 4

Temp (◦C)	Helix (%)	Strand (%)	Turns (%)	Unordered (%)
Heat-10	5.61	35.50	21.80	37.10
Heat-20	5.90	37.33	21.62	35.13
Heat-30	6.20	37.30	21.20	35.30
Heat-40	6.60	37.40	21.70	34.30
Heat-50	7.50	38.30	21.90	32.30
Heat-60	8.00	38.30	23.20	30.50
Heat-70	8.40	38.80	22.00	30.80
Heat-80	9.31	37.43	22.22	31.03
Cool-70	9.00	37.70	21.70	31.60
Cool-60	8.50	36.60	22.00	32.90
Cool-50	8.00	37.30	21.90	32.80
Cool-40	6.90	37.00	21.60	34.60
Cool-30	6.10	37.60	21.30	35.10
Cool-20	6.00	36.50	21.50	36.00
Cool-10	5.50	35.03	21.92	37.87