**Electronic Supplementary Information**

# A covalently crosslinked silk fibroin hydrogel using enzymatic oxidation and chemoenzymatically synthesized copolypeptide crosslinkers consisting of a GPG tripeptide motif and tyrosine: control of gelation and resilience

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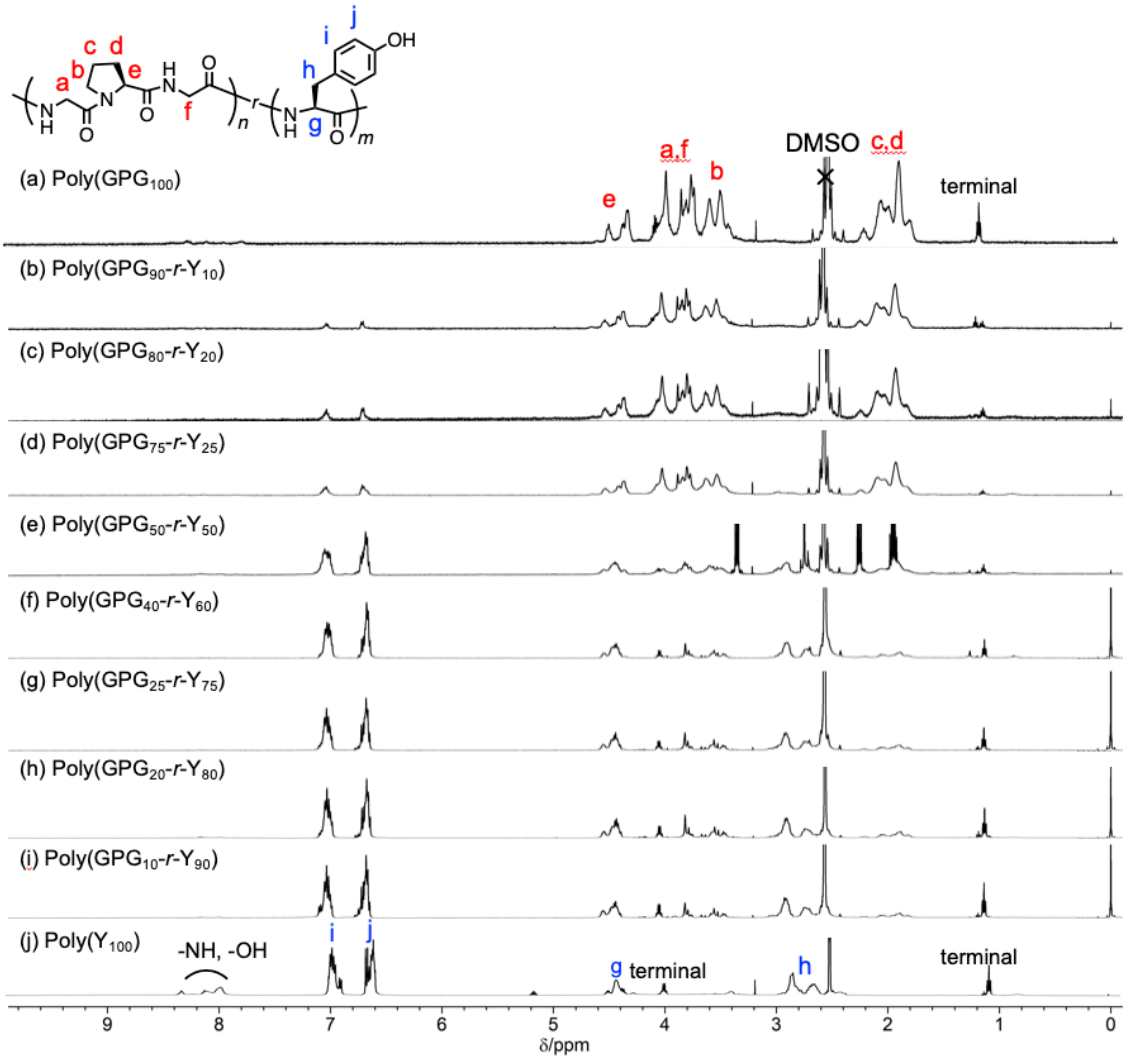
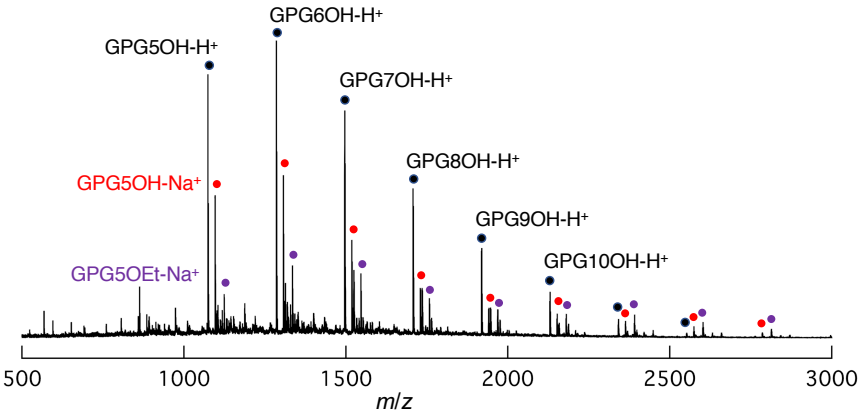
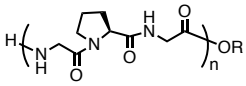



**Figure S1**. $^{1}$H NMR spectra of poly(GPG$_n$-*r*-Y$_m$) (500 MHz, 298 K, DMSO-d$_6$/TFA-d = 5/1 (v/v)).

(a) Poly($GPG_{100}$)



R = H, Additive: $H^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5OH-$H^+$ | GPG6OH-$H^+$ | GPG7OH-$H^+$ | GPG8OH-$H^+$ |
| Theo. | 1074.75 | 1285.66 | 1496.77 | 1707.88 |
| Obsd. | 1074.20 | 1285.24 | 1496.29 | 1709.33 |

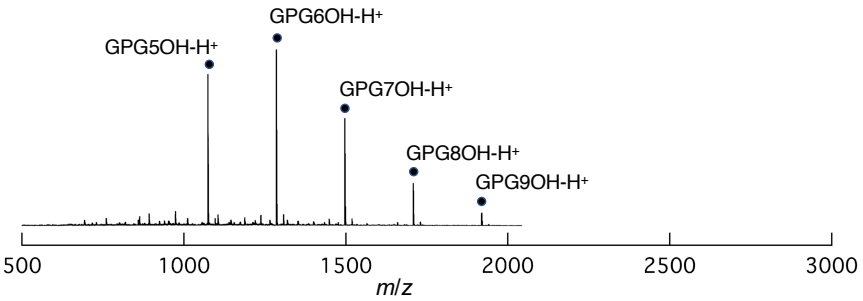
R = H, Additive: $Na^+$ (●)

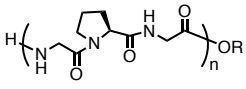
| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5OH-$Na^+$ | GPG6OH-$Na^+$ | GPG7OH-$Na^+$ | GPG8OH-$Na^+$ |
| Theo. | 1096.54 | 1307.65 | 1518.76 | 1729.87 |
| Obsd. | 1096.17 | 1307.21 | 1518.25 | 1729.29 |

R = $C_2H_5$, Additive: $H^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5OEt-$Na^+$ | GPG6OEt-$Na^+$ | GPG7OEt-$Na^+$ | GPG8OEt-$Na^+$ |
| Theo. | 1124.57 | 1335.68 | 1546.79 | 1757.90 |
| Obsd. | 1124.19 | 1335.23 | 1546.27 | 1757.35 |

(b) Poly($GPG_{90}$-*r*-$Y_{10}$)

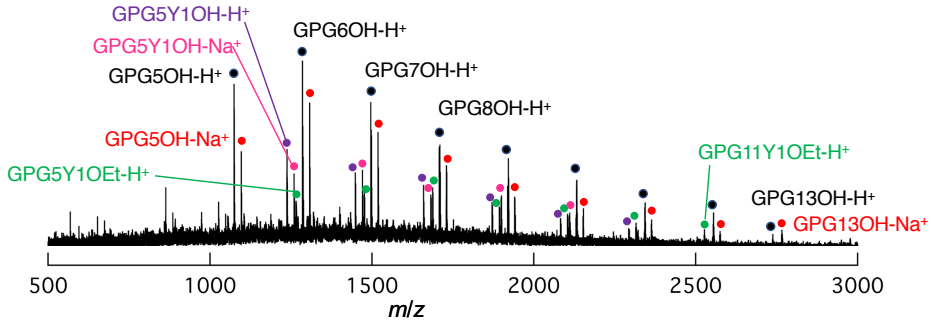


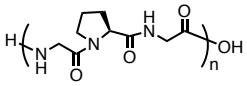



R = H, Additive: $H^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5OH-$H^+$ | GPG6OH-$H^+$ | GPG7OH-$H^+$ | GPG8OH-$H^+$ |
| Theo. | 1074.75 | 1285.66 | 1496.77 | 1707.88 |
| Obsd. | 1074.42 | 1285.51 | 1496.60 | 1707.69 |

(c) Poly(GPG$_{80}$-*r*-Y$_{20}$)



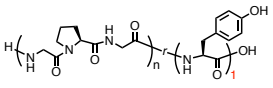



Additive: $H^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5OH-H$^+$ | GPG6OH-H$^+$ | GPG7OH-H$^+$ | GPG8OH-H$^+$ |
| Theo. | 1074.75 | 1285.66 | 1496.77 | 1707.88 |
| Obsd. | 1074.43 | 1285.52 | 1496.61 | 1708.69 |

R = H, Additive: $Na^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5OH-Na$^+$ | GPG6OH-Na$^+$ | GPG7OH-Na$^+$ | GPG8ONa-H$^+$ |
| Theo. | 1096.54 | 1307.65 | 1518.76 | 1729.87 |
| Obsd. | 1096.36 | 1307.51 | 1518.59 | 1729.67 |

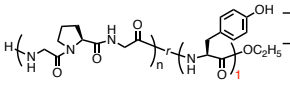


Additive: $H^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5Y1OH-H$^+$ | GPG6Y1OH-H$^+$ | GPG7Y1OH-H$^+$ | GPG8Y1OH-H$^+$ |
| Theo. | 1237.74 | 1448.85 | 1659.96 | 1871.07 |
| Obsd. | 1237.50 | 1448.58 | 1659.66 | 1870.74 |

Additive: $Na^+$ (●)

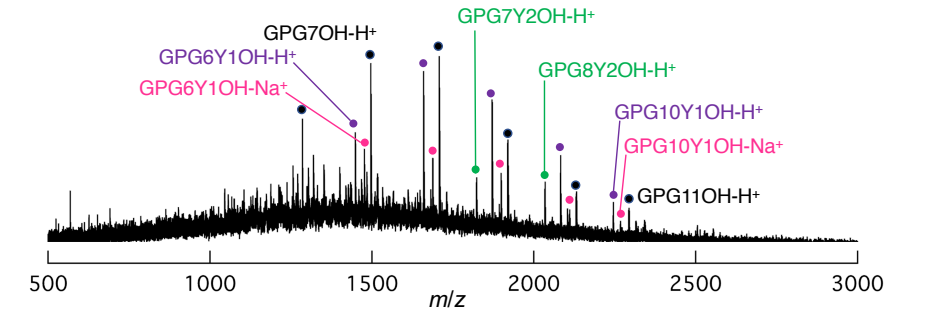
| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5Y1OH-Na$^+$ | GPG6Y1OH-Na$^+$ | GPG7Y1OH-Na$^+$ | GPG8Y1OH-Na$^+$ |
| Theo. | 1259.73 | 1470.84 | 1681.95 | 1893.06 |
| Obsd. | 1259.47 | 1470.56 | 1681.66 | 1892.73 |

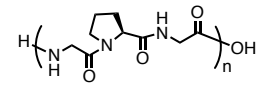


Additive: $H^+$ (●)

| n | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | GPG5Y1OEt-H$^+$ | GPG6Y1OEt-H$^+$ | GPG7Y1OEt-H$^+$ | GPG8Y1OEt-H$^+$ |
| Theo. | 1265.77 | 1476.78 | 1687.99 | 1899.10 |
| Obsd. | 1265.51 | 1476.61 | 1687.69 | 1898.77 |

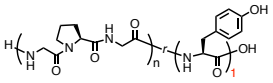
(d) Poly(GPG$_{75}$-*r*-Y$_{25}$)





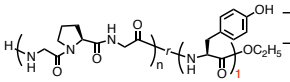
Additive: $H^+$ (●)

| n | 6 | 7 | 8 | 9 |
|---|---|---|---|---|
| code | GPG6OH-$H^+$ | GPG7OH-$H^+$ | GPG8OH-$H^+$ | GPG9OH-$H^+$ |
| Theo. | 1285.66 | 1496.77 | 1707.88 | 1917.99 |
| Obsd. | 1285.51 | 1496.61 | 1707.68 | 1918.75 |



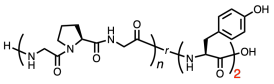
Additive: $H^+$ (●)

| n | 6 | 7 | 8 | 9 |
|---|---|---|---|---|
| code | GPG6Y1OH-$H^+$ | GPG7Y1OH-$H^+$ | GPG8Y1OH-$H^+$ | GPG9Y1OH-$H^+$ |
| Theo. | 1448.85 | 1659.96 | 1871.07 | 2082.18 |
| Obsd. | 1448.58 | 1659.68 | 1870.74 | 2081.80 |



Additive: $H^+$ (●)

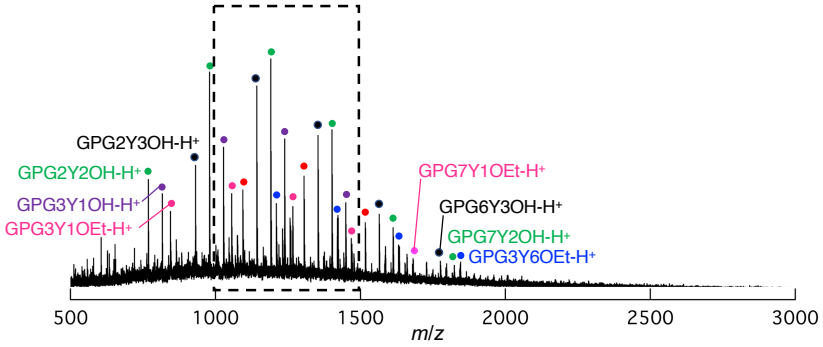
| n | 6 | 7 | 8 | 9 |
|---|---|---|---|---|
| code | GPG6Y1OEt-$H^+$ | GPG7Y1OEt-$H^+$ | GPG8Y1OEt-$H^+$ | GPG9Y1OEt-$H^+$ |
| Theo. | 1476.78 | 1687.99 | 1899.10 | 2110.21 |
| Obsd. | 1476.61 | 1687.70 | 1898.79 | 2110.87 |

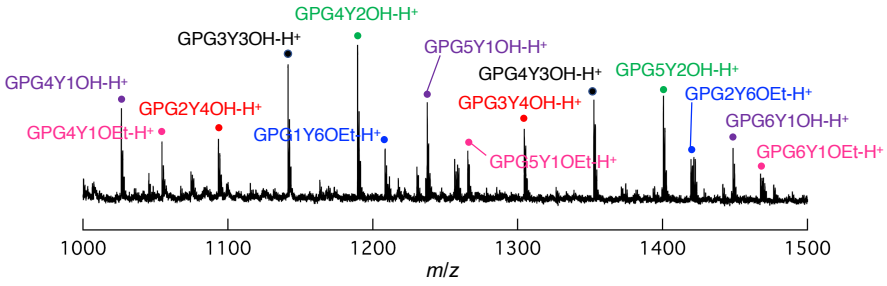


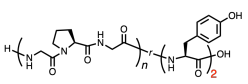
Additive: $H^+$ (●)

| n | 7 | 8 |
|---|---|---|
| code | GPG7Y2OH-$H^+$ | GPG8Y2OH-$H^+$ |
| Theo. | 1823.15 | 2034.26 |
| Obsd. | 1823.69 | 2033.76 |

(e) Poly($GPG_{50}$-*r*-$Y_{50}$)

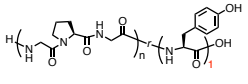


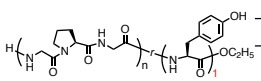
Additive: $H^+$ (●)

| n | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| code | GPG2Y2OH-$H^+$ | GPG3Y2OH-$H^+$ | GPG4Y2OH-$H^+$ | GPG5Y2OH-$H^+$ |
| Theo. | 767.60 | 978.71 | 1189.82 | 1400.93 |
| Obsd. | 767.32 | 978.40 | 1189.50 | 1400.59 |



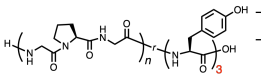
Additive: $H^+$ (●)

| n | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| code | GPG3Y1OH-$H^+$ | GPG4Y1OH-$H^+$ | GPG5Y1OH-$H^+$ | GPG6Y1OH-$H^+$ |
| Theo. | 815.52 | 1026.63 | 1237.74 | 1448.85 |
| Obsd. | 815.34 | 1026.43 | 1237.53 | 1448.62 |



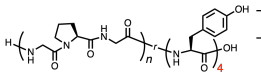
Additive: $H^+$ (●)

| n | 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| code | GPG3Y1OEt-$H^+$ | GPG4Y1OEt-$H^+$ | GPG5Y1OEt-$H^+$ | GPG6Y1OEt-$H^+$ |
| Theo. | 843.55 | 1054.66 | 1265.77 | 1476.88 |
| Obsd. | 843.37 | 1054.46 | 1265.56 | 1476.67 |



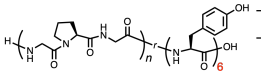
Additive: $H^+$ (●)

| n | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| code | GPG2Y3OH-$H^+$ | GPG3Y3OH-$H^+$ | GPG4Y3OH-$H^+$ | GPG5Y3OH-$H^+$ |
| Theo. | 930.79 | 1141.90 | 1353.01 | 1564.12 |
| Obsd. | 930.37 | 1141.47 | 1352.56 | 1563.65 |



Additive: $H^+$ (●)

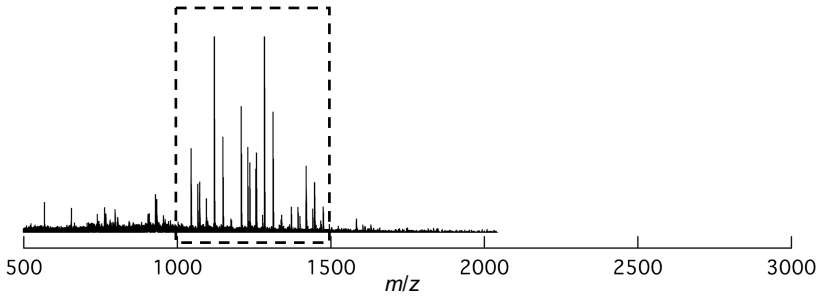
| n | 2 | 3 | 4 |
|---|---|---|---|
| code | GPG2Y4OH-$H^+$ | GPG3Y4OH-$H^+$ | GPG4Y4OH-$H^+$ |
| Theo. | 1093.98 | 1305.09 | 1516.20 |
| Obsd. | 1093.43 | 1304.53 | 1515.62 |

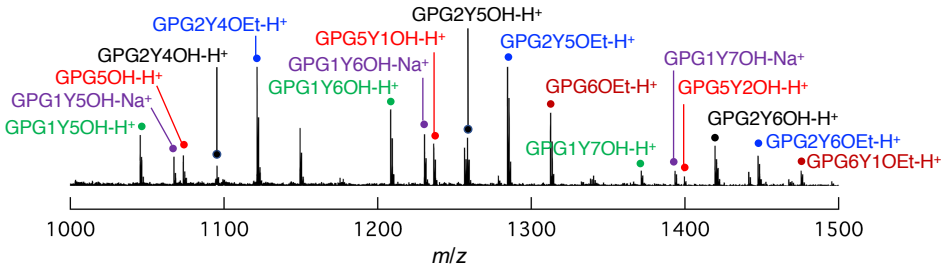


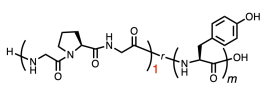
Additive: $H^+$ (●)

| m | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| code | GPG1Y6OH-$H^+$ | GPG2Y6OH-$H^+$ | GPG2Y6OH-$H^+$ | GPG3Y6OH-$H^+$ |
| Theo. | 1209.25 | 1420.36 | 1631.47 | 1842.58 |
| Obsd. | 1208.47 | 1419.56 | 1630.65 | 1842.76 |

## (f) Poly($GPG_{40}$-*r*-$Y_{60}$)



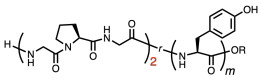



Additive: $H^+$ (●)

| m | 5 | 6 | 7 |
|---|---|---|---|
| code | GPG1Y5OH-$H^+$ | GPG1Y6OH-$H^+$ | GPG1Y7OH-$H^+$ |
| Theo. | 1046.06 | 1209.25 | 1372.44 |
| Obsd. | 1045.39 | 1208.46 | 1371.52 |

Additive: $Na^+$ (●)

| n | 5 | 6 | 7 |
|---|---|---|---|
| code | GPG1Y5OH-$Na^+$ | GPG1Y6OH-$Na^+$ | GPG1Y7OH-$Na^+$ |
| Theo. | 1068.05 | 1231.24 | 1394.43 |
| Obsd. | 1067.37 | 1230.43 | 1393.49 |

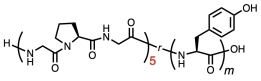


R = H, Additive: $H^+$ (●)

| m | 4 | 5 | 6 |
|---|---|---|---|
| code | GPG2Y4OH-$H^+$ | GPG2Y5OH-$H^+$ | GPG2Y6OH-$H^+$ |
| Theo. | 1093.98 | 1257.17 | 1420.36 |
| Obsd. | 1095.42 | 1256.49 | 1419.55 |

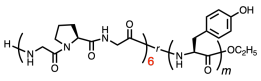
R = $C_2H_5$, Additive: $H^+$ (●)

| n | 4 | 5 | 6 |
|---|---|---|---|
| code | GPG2Y4OEt-$H^+$ | GPG2Y5OEt-$H^+$ | GPG2Y5OEt-$H^+$ |
| Theo. | 1122.01 | 1285.20 | 1448.39 |
| Obsd. | 1121.42 | 1284.48 | 1447.56 |



Additive: $H^+$ (●)

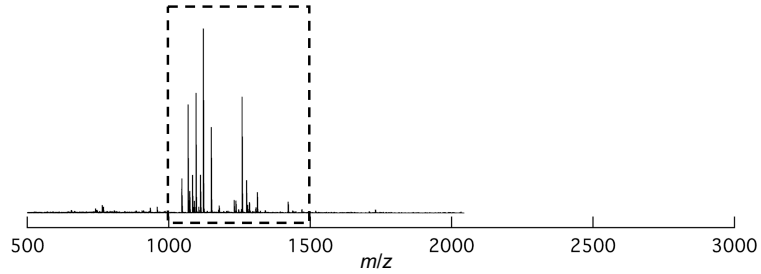
| m | 0 | 1 | 2 |
|---|---|---|---|
| code | GPG5OH-$H^+$ | GPG5Y1OH-$H^+$ | GPG5Y2OH-$H^+$ |
| Theo. | 1074.55 | 1237.74 | 1400.93 |
| Obsd. | 1073.43 | 1236.48 | 1399.23 |

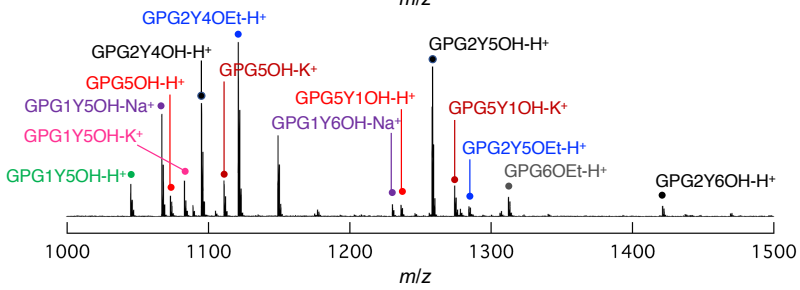


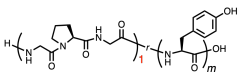
Additive: $H^+$ (●)

| m | 0 | 1 |
|---|---|---|
| code | GPG6OEt-$H^+$ | GPG6Y1OEt-$H^+$ |
| Theo. | 1313.69 | 1476.88 |
| Obsd. | 1312.51 | 1475.57 |

(g) Poly($GPG_{25}$-*r*-$Y_{75}$)



Additive: $H^+$ (●)

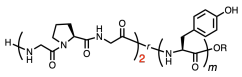
| m | 5 |
|---|---|
| code | GPG1Y5OH-$H^+$ |
| Theo. | 1046.06 |
| Obsd. | 1045.39 |

Additive: $H^+$ (●)

| m | 5 |
|---|---|
| code | GPG1Y5OH-$K^+$ |
| Theo. | 1275.84 |
| Obsd. | 1274.44 |

Additive: $Na^+$ (●)

| n | 5 | 6 |
|---|---|---|
| code | GPG1Y5OH-$Na^+$ | GPG1Y6OH-$Na^+$ |
| Theo. | 1068.05 | 1231.24 |
| Obsd. | 1067.37 | 1230.43 |

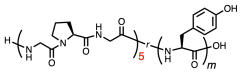


R = H, Additive: $H^+$ (●)

| m | 4 | 5 | 6 |
|---|---|---|---|
| code | GPG2Y4OH-$H^+$ | GPG2Y5OH-$H^+$ | GPG2Y6OH-$H^+$ |
| Theo. | 1093.98 | 1257.17 | 1420.36 |
| Obsd. | 1095.41 | 1258.46 | 1421.53 |

R = $C_2H_5$, Additive: $H^+$ (●)

| n | 4 | 5 |
|---|---|---|
| code | GPG2Y4OEt-$H^+$ | GPG2Y5OEt-$H^+$ |
| Theo. | 1122.01 | 1285.20 |
| Obsd. | 1121.42 | 1284.50 |

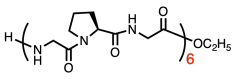


Additive: $H^+$ (●)

| m | 0 | 1 |
|---|---|---|
| code | GPG5OH-$H^+$ | GPG5Y1OH-$H^+$ |
| Theo. | 1074.55 | 1237.74 |
| Obsd. | 1073.43 | 1236.48 |

Additive: $K^+$ (●)

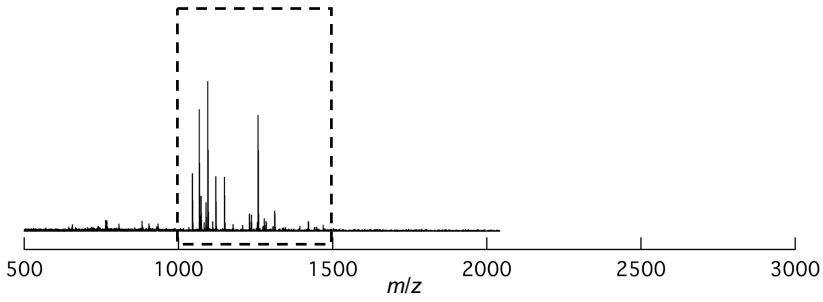
| m | 0 | 1 |
|---|---|---|
| code | GPG5OH-$H^+$ | GPG5Y1OH-$H^+$ |
| Theo. | 1112.65 | 1275.84 |
| Obsd. | 1111.37 | 1274.44 |

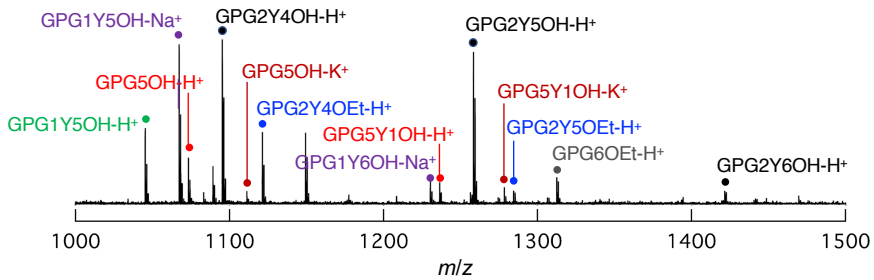


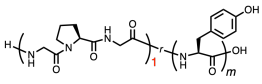
Additive: $H^+$ (●)

| m | 0 |
|---|---|
| code | GPG6OEt-$H^+$ |
| Theo. | 1313.69 |
| Obsd. | 1312.51 |

(h) Poly($GPG_{20}$-*r*-$Y_{80}$)



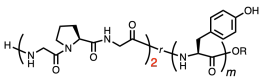



Additive: $H^+$ (●)

| m | 5 |
|---|---|
| code | GPG1Y5OH-$H^+$ |
| Theo. | 1046.06 |
| Obsd. | 1045.38 |

Additive: $Na^+$ (●)

| n | 5 | 6 |
|---|---|---|
| code | GPG1Y5OH-$Na^+$ | GPG1Y6OH-$Na^+$ |
| Theo. | 1068.05 | 1231.24 |
| Obsd. | 1067.35 | 1230.41 |

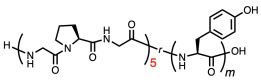


R = H, Additive: $H^+$ (●)

| m | 4 | 5 | 6 |
|---|---|---|---|
| code | GPG2Y4OH-$H^+$ | GPG2Y5OH-$H^+$ | GPG2Y6OH-$H^+$ |
| Theo. | 1093.98 | 1257.17 | 1420.36 |
| Obsd. | 1095.39 | 1258.44 | 1421.50 |

R = $C_2H_5$, Additive: $H^+$ (●)

| n | 4 | 5 |
|---|---|---|
| code | GPG2Y4OEt-$H^+$ | GPG2Y5OEt-$H^+$ |
| Theo. | 1122.01 | 1285.20 |
| Obsd. | 1121.40 | 1284.46 |

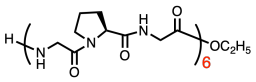


Additive: $H^+$ (●)

| m | 0 | 1 |
|---|---|---|
| code | GPG5OH-$H^+$ | GPG5Y1OH-$H^+$ |
| Theo. | 1074.55 | 1237.74 |
| Obsd. | 1073.40 | 1236.47 |

Additive: $K^+$ (●)

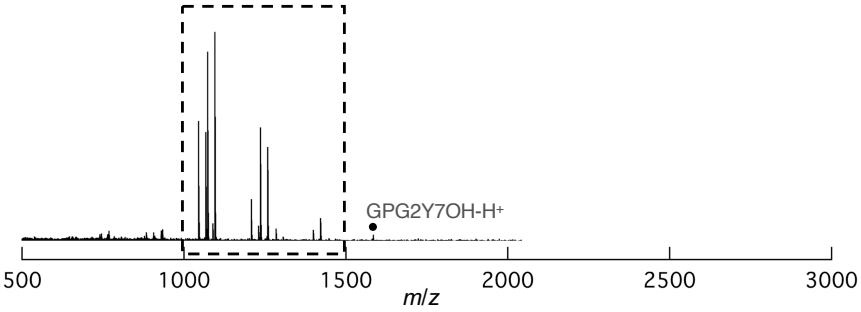
| m | 0 | 1 |
|---|---|---|
| code | GPG5OH-$H^+$ | GPG5Y1OH-$H^+$ |
| Theo. | 1112.65 | 1275.84 |
| Obsd. | 1111.37 | 1278.43 |

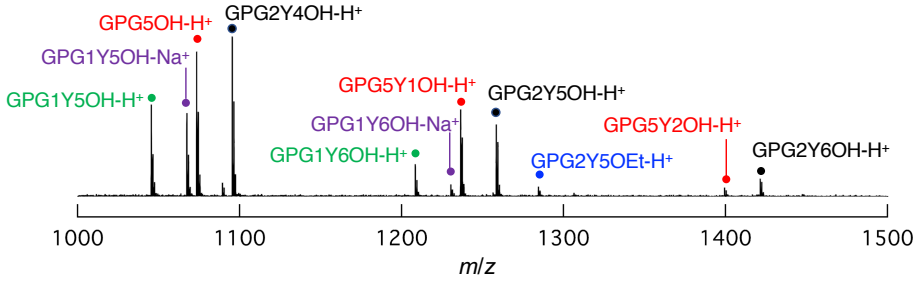


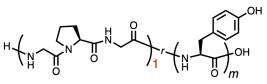
Additive: $H^+$ (●)

| m | 0 |
|---|---|
| code | GPG6OEt-$H^+$ |
| Theo. | 1313.69 |
| Obsd. | 1312.51 |

(i) Poly($GPG_{10}$-*r*-$Y_{90}$)



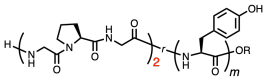


Additive: $H^+$ (●)

| m | 5 | 6 |
|---|---|---|
| code | GPG1Y5OH-$H^+$ | GPG1Y6OH-$H^+$ |
| Theo. | 1046.06 | 1209.25 |
| Obsd. | 1045.21 | 1208.23 |

Additive: $Na^+$ (●)

| n | 5 | 6 |
|---|---|---|
| code | GPG1Y5OH-$Na^+$ | GPG1Y6OH-$Na^+$ |
| Theo. | 1068.05 | 1231.24 |
| Obsd. | 1067.19 | 1230.23 |

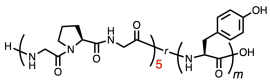


R = H, Additive: $H^+$ (●)

| m | 4 | 5 | 6 |
|---|---|---|---|
| code | GPG2Y4OH-$H^+$ | GPG2Y5OH-$H^+$ | GPG2Y6OH-$H^+$ |
| Theo. | 1093.98 | 1257.17 | 1420.36 |
| Obsd. | 1095.21 | 1258.25 | 1421.29 |

R = $C_2H_5$, Additive: $H^+$ (●)

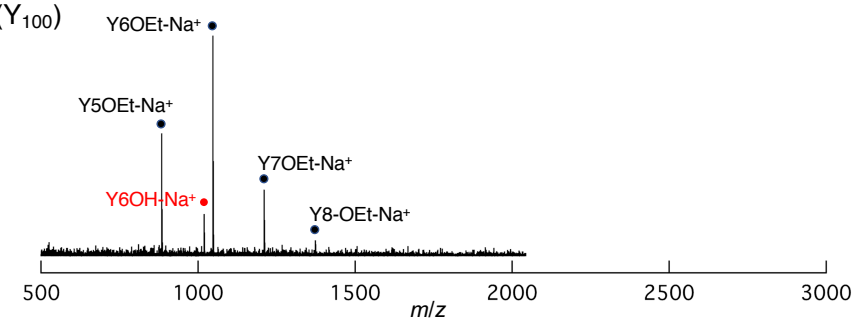
| n | 5 |
|---|---|
| code | GPG2Y5OEt-$H^+$ |
| Theo. | 1285.20 |
| Obsd. | 1284.27 |

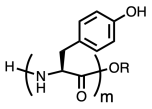


Additive: $H^+$ (●)

| m | 0 | 1 | 2 |
|---|---|---|---|
| code | GPG5OH-$H^+$ | GPG5Y1OH-$H^+$ | GPG5Y2OH-$H^+$ |
| Theo. | 1074.55 | 1237.74 | 1400.93 |
| Obsd. | 1073.24 | 1236.26 | 1399.28 |

(j) Poly($Y_{100}$)



R = $C_2H_5$, Additive: $Na^+$ (●)

| m | 5 | 6 | 7 | 8 |
|---|---|---|---|---|
| code | Y5OEt-$Na^+$ | Y6OEt-$Na^+$ | Y7OEt-$Na^+$ | Y8OEt-$Na^+$ |
| Theo. | 885.00 | 1048.19 | 1211.38 | 1374.57 |
| Obsd. | 884.10 | 1047.12 | 1210.14 | 1373.16 |

R = H, Additive: $Na^+$ (●)

| m | 6 |
|---|---|
| code | Y6OH-$Na^+$ |
| Theo. | 1020.13 |
| Obsd. | 1019.10 |

**Figure S2.** MALIDI-TOF MS of poly($GPG_n$-*r*-$Y_m$) (matrix: dithranol, mode: positive reflectron). The peaks were assigned with the label "GPGnYmOR-Additive", where n, m, R, and Additive represent the repeating number of GPG unit, that of Y unit, C-terminal structure (H or Et), and adducted cation (H+ or Na+ or K+), respectively.

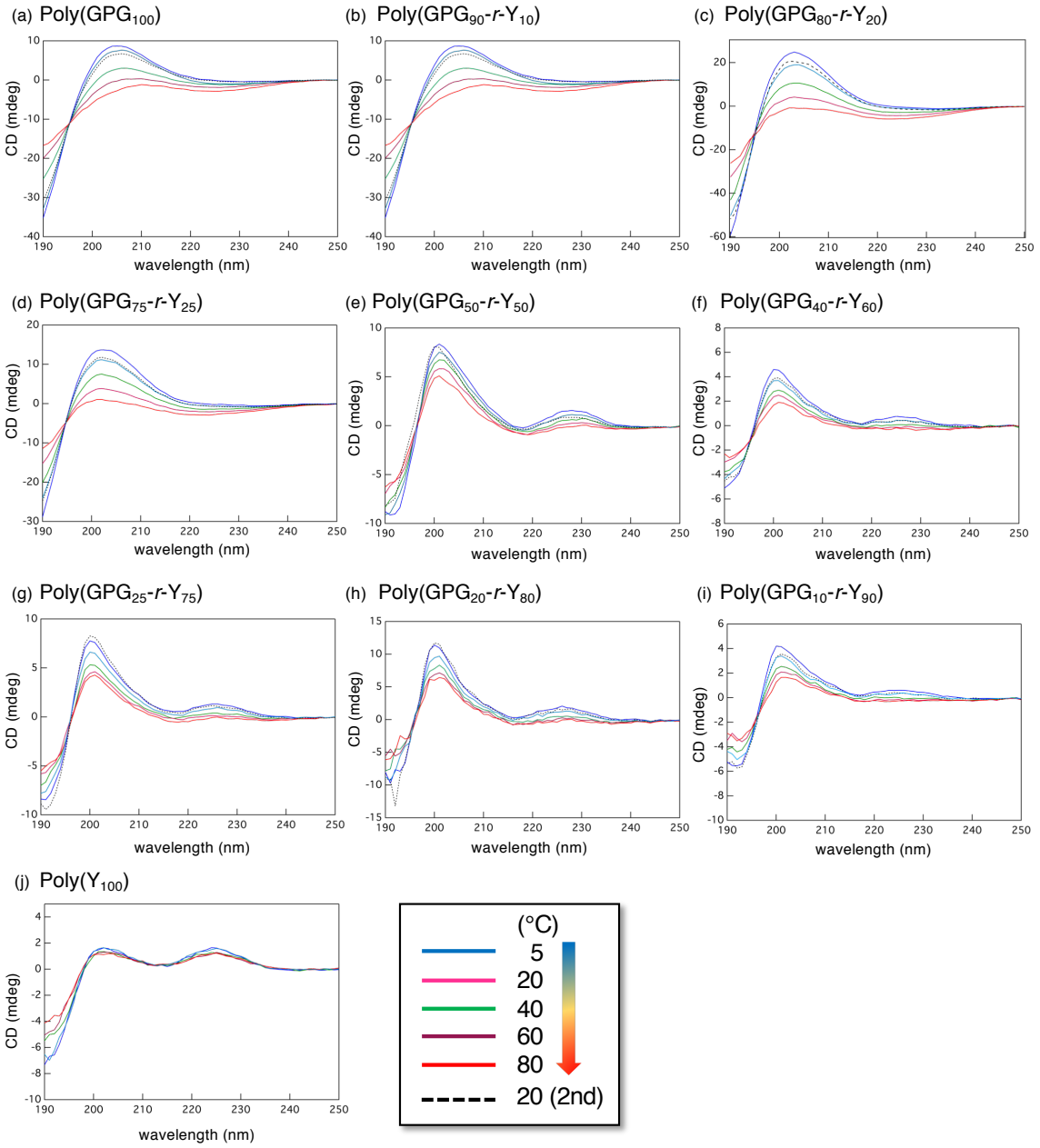



**Figure S3.** CD spectra of poly(GPG$_n$-*r*-Y$_m$) at various temperatures in 2,2,2-trifuluoroethanol (TFE).

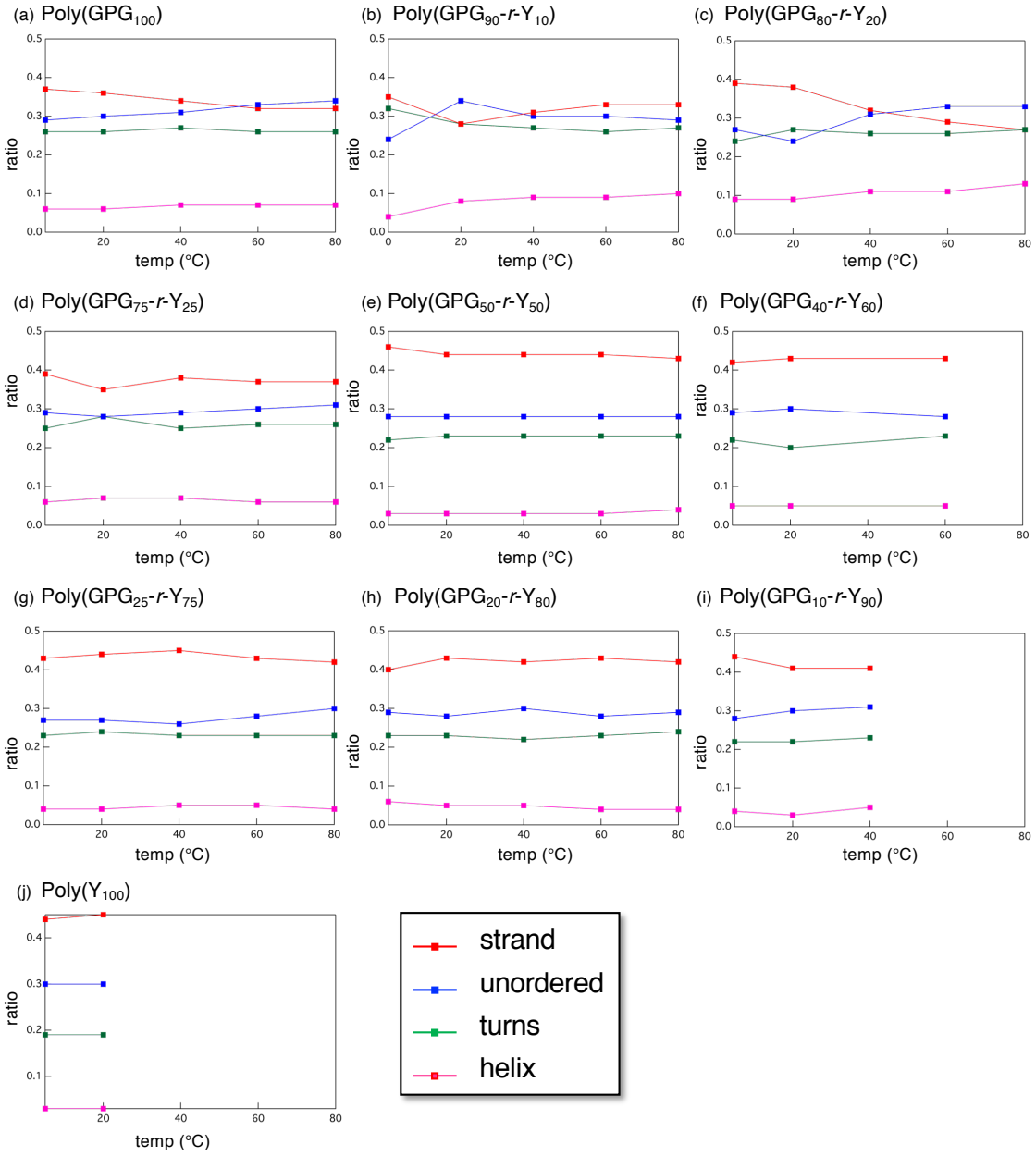



**Figure S4.** The contents of secondary structures of poly(GPG$_n$-*r*-Y$_m$) at various temperatures. They were calculated by DichroWeb online CD analysis server using CDSSTR algorithm in combination with reference data set 4.

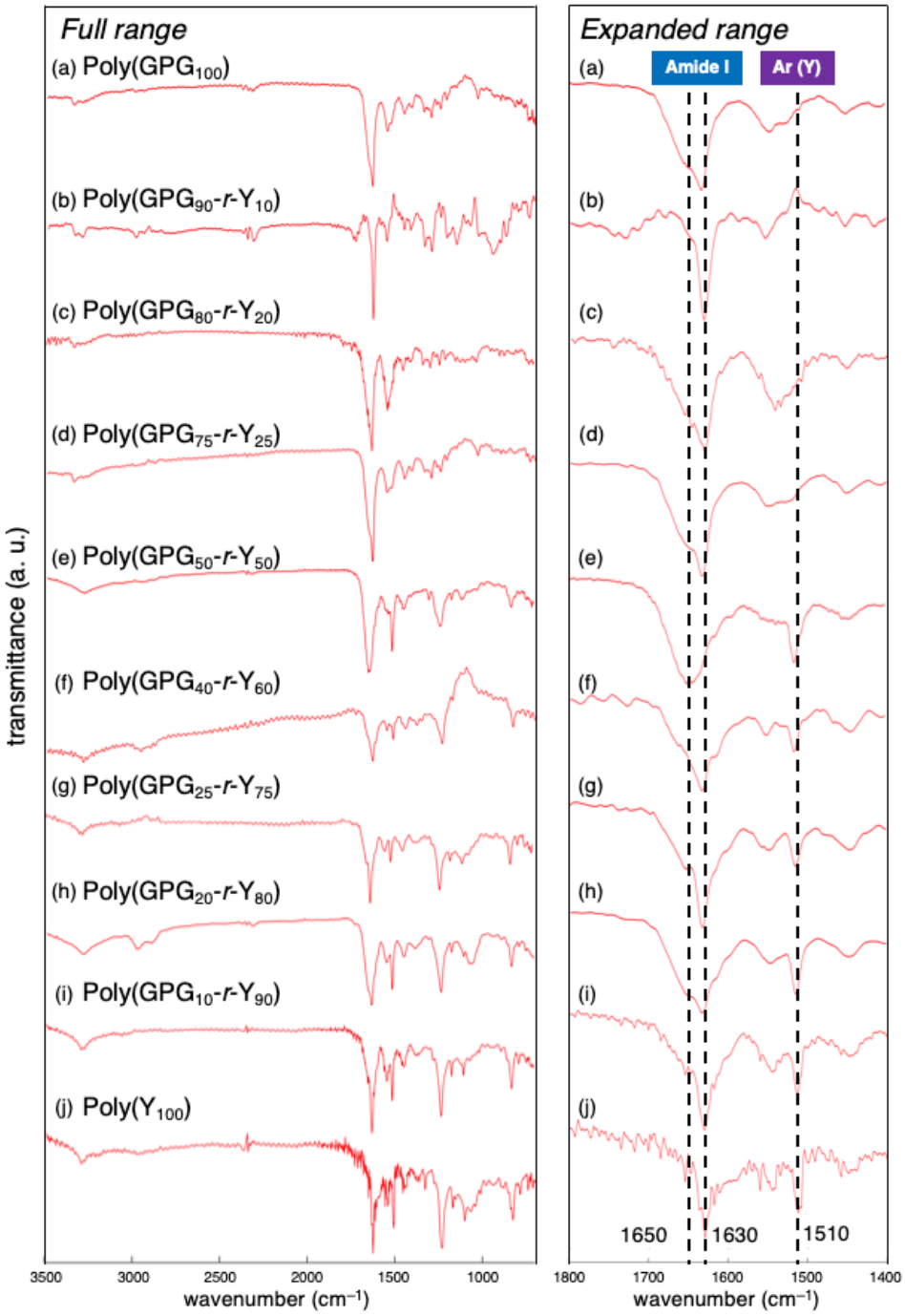



**Figure S5.** ATR-FT-IR spectra of poly(GPG$_n$-*r*-Y$_m$). Amide I absorptions of 1650 and 1630 cm$^{-1}$ are corresponded to the peaks of random and $\beta$-sheet structures, respectively.

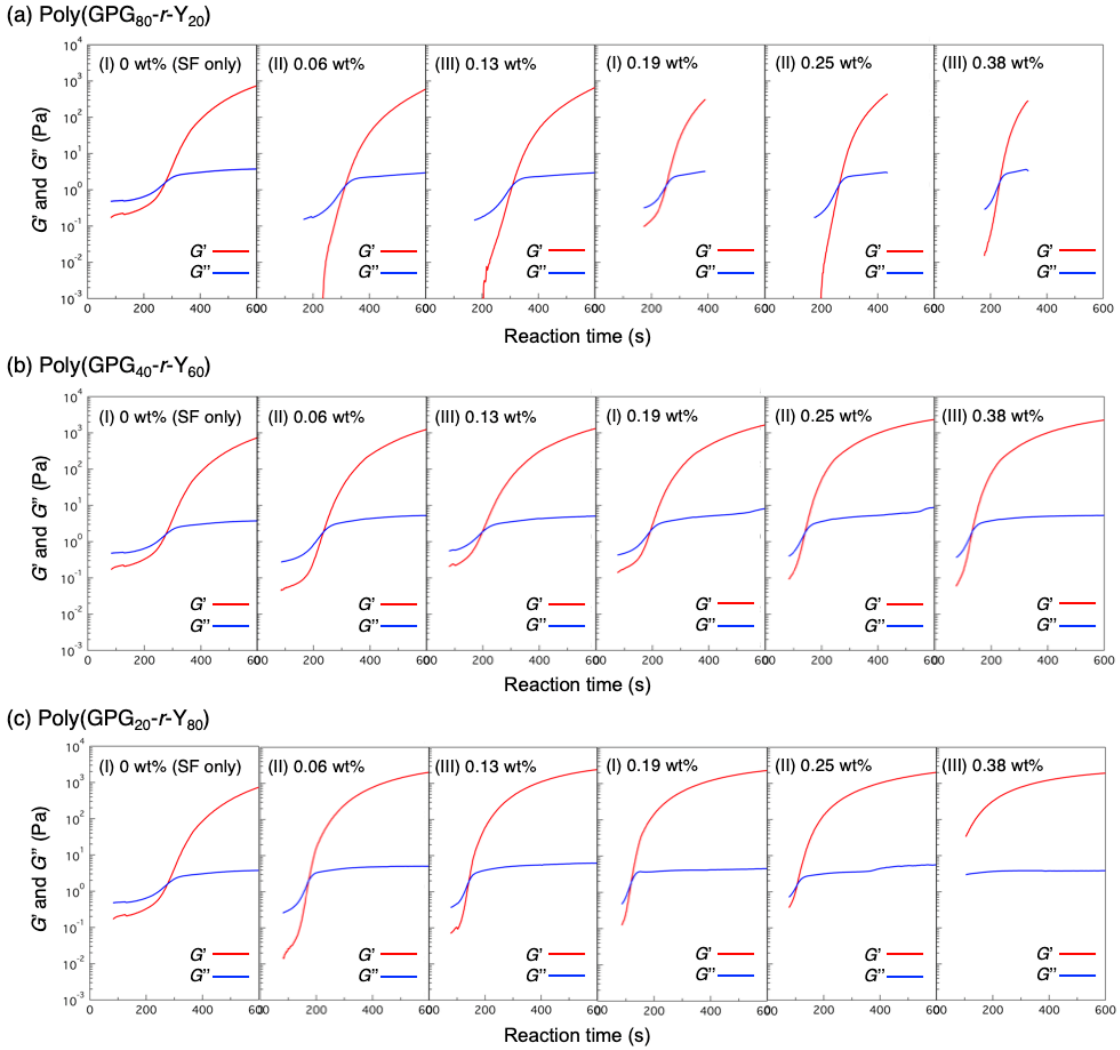



**Figure S6.** Time-dependent $G'$ and $G''$ during the gelation of SF solution using poly($GPG_n$-*r*-$Y_m$) crosslinker.

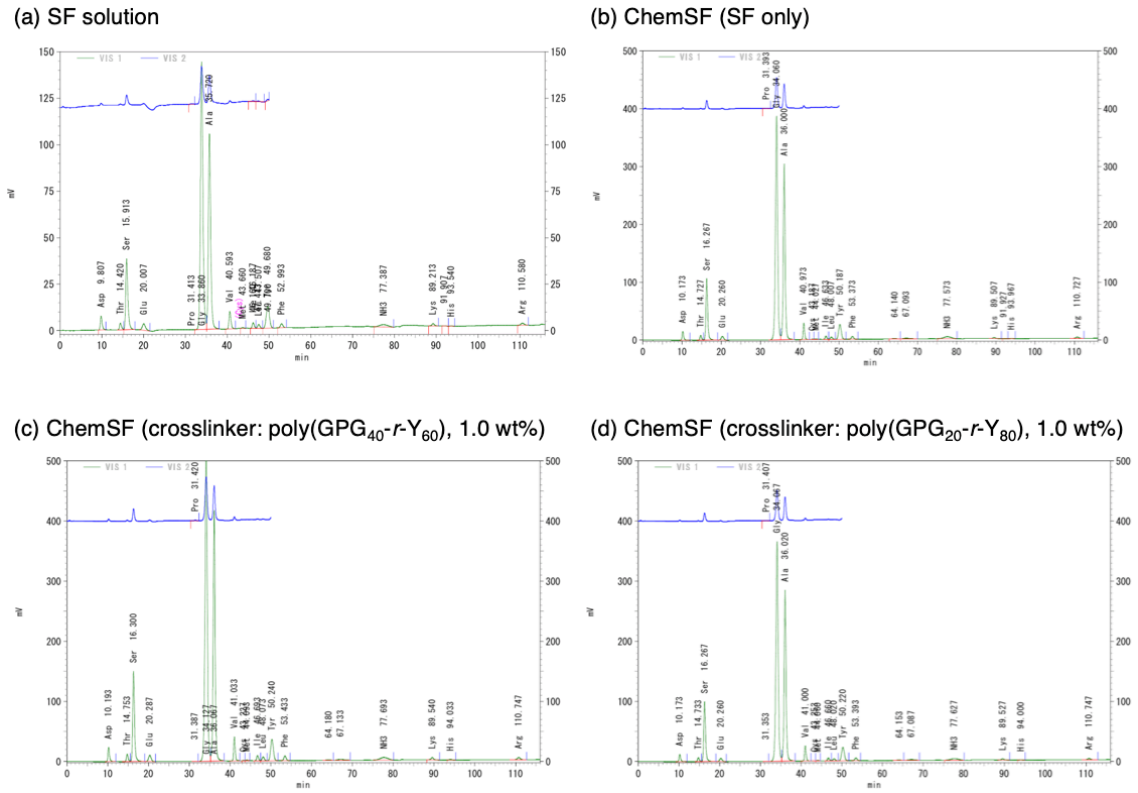



**Figure S7**. Amino acid analysis data by HPLC. The calculated ratio of each amino acid was shown in Table S3.

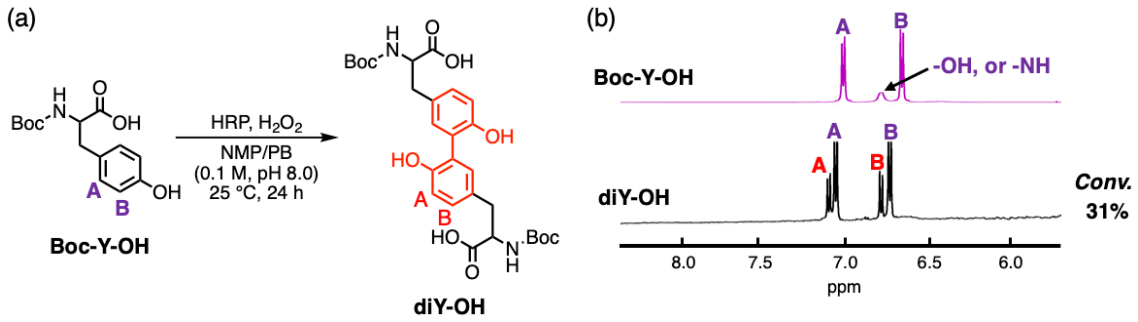



**Figure S8**. (a) Model enzymatic reaction using Boc-Y-OH. (b) partial $^{1}$H NMR of Boc-Y-OH and diY-OH. (500 MHz, DMSO-$d_6$).

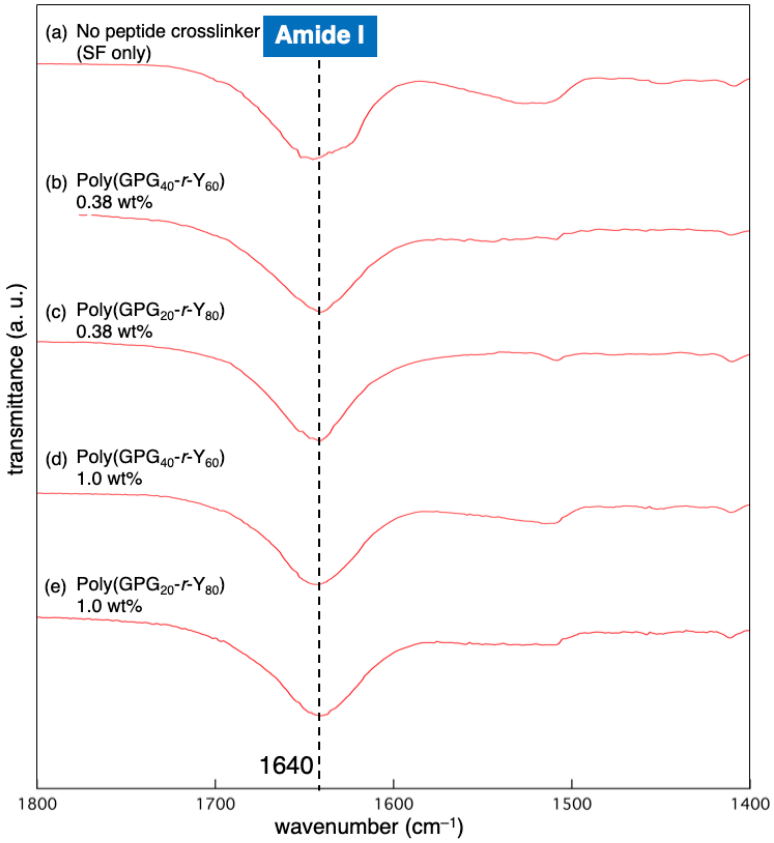



**Figure S9.** ATR-FT-IR spectra of ChemSF prepared with poly($GPG_n$-*r*-$Y_m$) crosslinker.

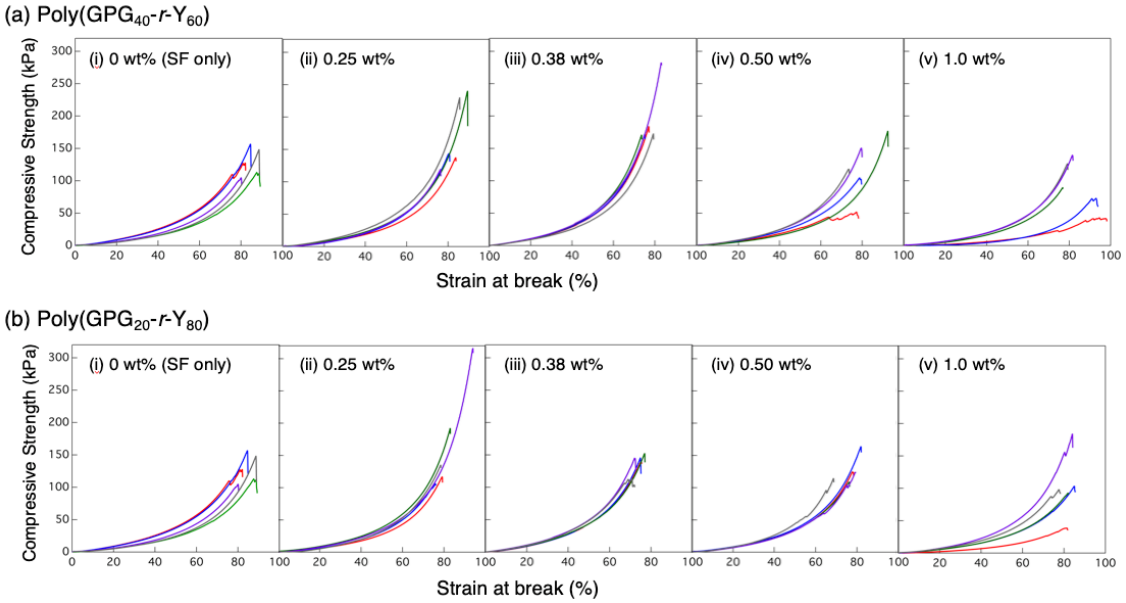



**Figure S10.** Stress-strain curves of ChemSF samples obtained by using poly($GPG_n$-*r*-$Y_m$) crosslinker. The compression rate: 10 mm/min.

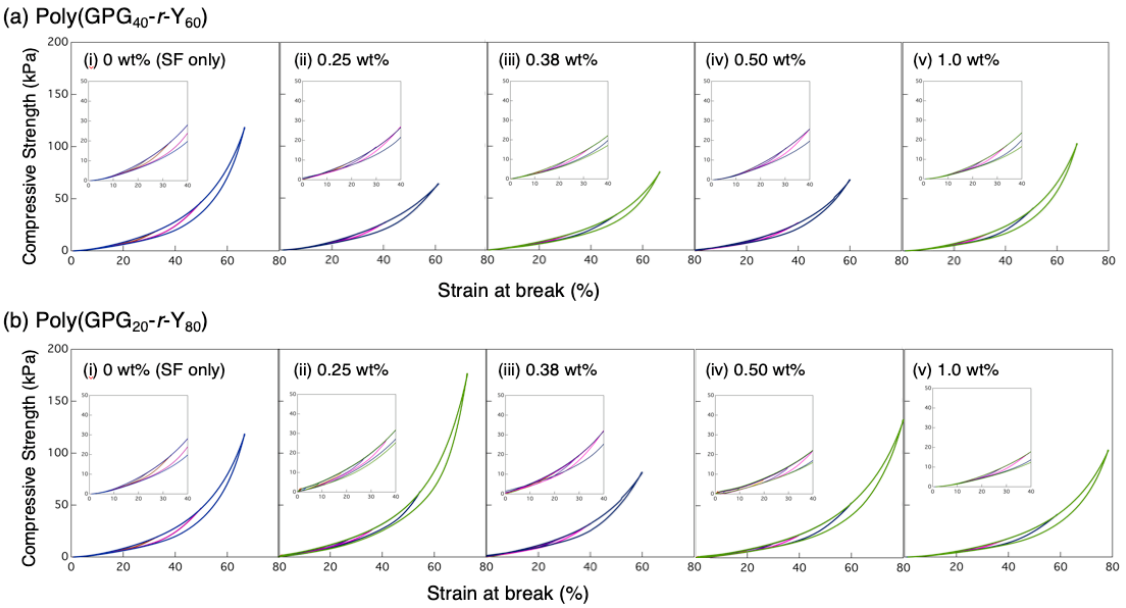
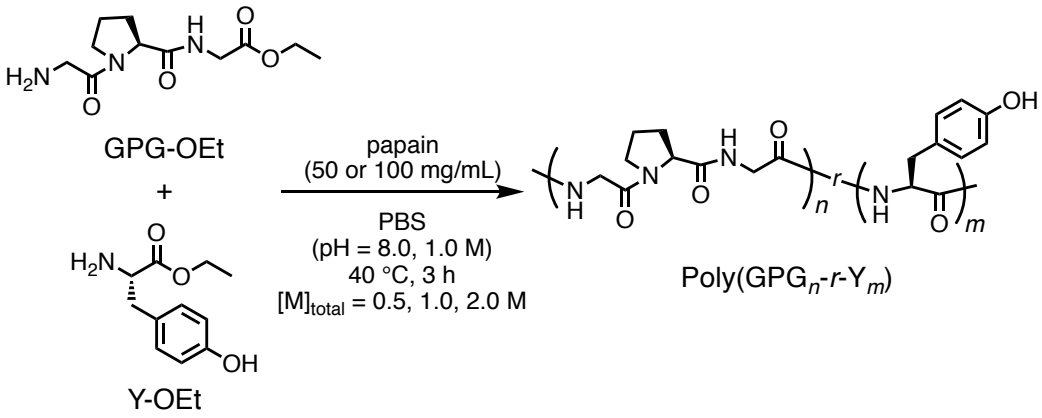



**Figure S11.** Stress-strain curves of cyclic tests on ChemSF samples obtained by using Poly($GPG_n$-*r*-$Y_m$) crosslinker (inset: magnified range). The loading and unloading rate: 10 mm/min.

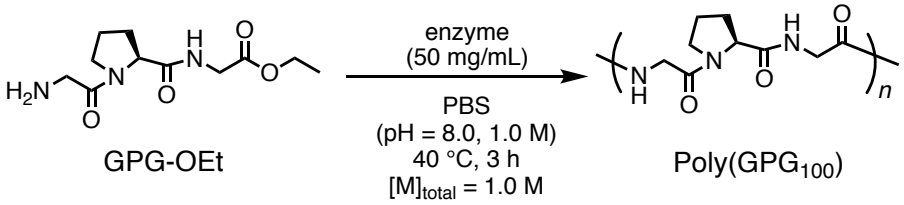
**Table S1**. Total monomer concentration and papain concentration effects for the chemoenzymatic copolymerization of GPG and Y




| run | monomer (%) | | $[M]_{total}$ (M) | papain conc. (mg/mL) | yield (%)[a] | $M_p$[b] | composition (%)[c] | |
|---|---|---|---|---|---|---|---|---|
| | GPG | Y | | | | | GPG | Y |
| 1 | | | 2.0 | 100 | 10 | 1100 | 89 | 11 |
| 2 | | | 2.0 | 50 | 6 | 1100 | 88 | 12 |
| 3 | 80 | 20 | 1.0 | 100 | 16 | 1300 | 90 | 10 |
| 4 | | | 1.0 | 50 | 11 | 1100 | 90 | 10 |
| 5 | | | 0.5 | 50 | 5 | 1100 | 87 | 13 |
| 6 | | | 2.0 | 100 | –[d] | –[e] | –[e] | –[e] |
| 7 | | | 2.0 | 50 | –[d] | –[e] | –[e] | –[e] |
| 8 | 60 | 40 | 1.0 | 100 | 4 | 1300 | 41 | 59 |
| 9 | | | 1.0 | 50 | –[d] | –[e] | –[e] | –[e] |
| 10 | | | 0.5 | 50 | –[d] | –[e] | –[e] | –[e] |
| 11 | | | 2.0 | 100 | 3 | –[e] | 21 | 77 |
| 12 | | | 2.0 | 50 | –[d] | –[e] | –[e] | –[e] |
| 13 | 40 | 60 | 1.0 | 100 | 12 | 1100 | 36 | 64 |
| 14 | | | 1.0 | 50 | 15 | 1100 | 29 | 71 |
| 15 | | | 0.5 | 50 | 23 | 1100 | 2 | 98 |

[a]$H_2O$-insoluble part. [b]Detected by MALDI-TOF MS. [c]Measured by $^1H$ NMR. [d]No precipitate was formed. [e]Not determined.

**Table S2**. Chemoenzymatic homopolymerization of GPG using several enzymes




GPG-OEt — Poly($GPG_{100}$)

| run | enzyme | conc. (mg/mL) | Yield (%) | $M_p$[c] |
|---|---|---|---|---|
| 1 | papain | 50 | 39[a] | 1300 |
| 2 | bromelain | 10 | 17[a] | 1300 |
| 3 | bromelain | 50 | 22[a] | 1100 |
| 12 | proteinase K | 10 | 33[b] | 800 |
| 13 | proteinase K | 5 | 28[b] | 800 |
| 15 | proteinase K | 2 | 30[b] | 800 |

[a]$H_2O$-insoluble part. [b]Obtained from $H_2O$-soluble part by dialysis. [c]Detected by MALDI-TOF MS.

**Table S3**. Calculated secondary structures of poly($GPG_n$-*r*-$Y_m$)

| code | Structure (%)[a] | | | |
|---|---|---|---|---|
| | $\alpha$-helix | $\beta$-strand | $\beta$-turn | unordered |
| Poly($GPG_{100}$) | 6 | 37 | 26 | 29 |
| Poly($GPG_{90}$-*r*-$Y_{10}$) | 8 | 34 | 28 | 28 |
| Poly($GPG_{80}$-*r*-$Y_{20}$) | 9 | 38 | 27 | 24 |
| Poly($GPG_{75}$-*r*-$Y_{25}$) | 7 | 35 | 28 | 28 |
| Poly($GPG_{50}$-*r*-$Y_{50}$) | 3 | 44 | 23 | 28 |
| Poly($GPG_{40}$-*r*-$Y_{60}$) | 5 | 46 | 20 | 30 |
| Poly($GPG_{25}$-*r*-$Y_{75}$) | 6 | 44 | 24 | 26 |
| Poly($GPG_{20}$-*r*-$Y_{80}$) | 5 | 43 | 23 | 28 |
| Poly($GPG_{10}$-*r*-$Y_{90}$) | 3 | 41 | 22 | 30 |
| Poly($Y_{100}$) | 3 | 45 | 19 | 30 |

[a]The content was calculated by using CDSSTR algorithm in combination with reference data set 4.

**Table S4**. Amino acid analysis of ChemSF

| A. A. | Content (%) | | | |
|---|---|---|---|---|
| | entry 1 | entry 2 | entry 3 | entry 4 |
| Asp | 1.84 | 1.34 | 1.51 | 1.14 |
| Thr | 0.96 | 0.78 | 0.86 | 0.69 |
| **Ser** | **10.47** | **10.27** | **10.42** | **10.39** |
| Glu | 1.39 | 0.95 | 1.09 | 0.82 |
| **Gly** | **43.33** | **45.10** | **44.61** | **46.02** |
| Ala | 28.69 | 29.84 | 29.62 | 30.17 |
| Val | 2.30 | 2.19 | 2.20 | 2.10 |
| Cys | 0.00 | 0.03 | 0.02 | 0.01 |
| Met | 0.09 | 0.06 | 0.07 | 0.05 |
| Ile | 0.74 | 0.51 | 0.59 | 0.48 |
| Leu | 0.58 | 0.46 | 0.53 | 0.44 |
| **Tyr** | **5.07** | **3.78** | **3.74** | **3.56** |
| Phe | 0.68 | 0.61 | 0.68 | 0.58 |
| $NH_3$ | 2.64 | 2.96 | 2.63 | 2.41 |
| Lys | 0.35 | 0.24 | 0.37 | 0.28 |
| His | 0.07 | 0.09 | 0.13 | 0.09 |
| Arg | 0.49 | 0.41 | 0.46 | 0.40 |
| **Pro** | **0.32** | **0.39** | **0.44** | **0.37** |

Entry 1: SF solution, entry 2: ChemSF without poly($GPG_n$-*r*-$Y_m$) (SF only), entry 3: ChemSF with 1 wt% of poly($GPG_{40}$-*r*-$Y_{60}$), entry 4: ChemSF with 1 wt% of poly($GPG_{20}$-*r*-$Y_{80}$).