Supporting Information:

Monitoring the stabilities of a mixture of peptides by mass spectrometry based techniques

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Table S1. Calculated rate constants for the dissociation of the Xaa-Pro-Gly-Gly peptides obtained from fits of the kinetics data.

Sequence	70 °C	80 °C	90 °C
APGG[a]	$1.4 \pm 0.1 \times 10^{-2}$	$3.5 \pm 0.5 \times 10^{-2}$	$6.6 \pm 0.5 \times 10^{-2}$
DPGG	$1.3 \pm 0.0 \times 10^{-2}$	$2.7 \pm 0.2 \times 10^{-2}$	$5.1 \pm 0.5 \times 10^{-2}$
EPGG	$1.0 \pm 0.1 \times 10^{-2}$	$2.3 \pm 0.1 \times 10^{-2}$	$3.6 \pm 0.4 \times 10^{-2}$
FPGG[a]	$1.2 \pm 0.1 \times 10^{-2}$	$3.3 \pm 0.3 \times 10^{-2}$	$6.5 \pm 0.4 \times 10^{-2}$
GPGG[a]	$4.1 \pm 0.2 \times 10^{-3}$	$1.1 \pm 0.2 \times 10^{-2}$	$1.9 \pm 0.2 \times 10^{-2}$
HPGG	$1.2 \pm 0.1 \times 10^{-2}$	$2.9 \pm 0.3 \times 10^{-2}$	$6.3 \pm 0.6 \times 10^{-2}$
IPGG[a]	$9.9 \pm 0.5 \times 10^{-3}$	$2.3 \pm 0.1 \times 10^{-2}$	$4.3 \pm 0.3 \times 10^{-2}$
KPGG	$9.5 \pm 0.3 \times 10^{-3}$	$2.1 \pm 0.2 \times 10^{-2}$	$1.2 \pm 0.2 \times 10^{-1}$
LPGG[a]	$1.3 \pm 0.0 \times 10^{-2}$	$4.0 \pm 0.3 \times 10^{-2}$	$9.0 \pm 1.0 \times 10^{-2}$
MPGG	$8.7 \pm 0.3 \times 10^{-3}$	$2.7 \pm 0.3 \times 10^{-2}$	$4.6 \pm 0.6 \times 10^{-2}$
NPGG	$1.3 \pm 0.1 \times 10^{-2}$	$2.9 \pm 0.5 \times 10^{-2}$	$5.6 \pm 1.0 \times 10^{-2}$
PPGG[a]	$7.4 \pm 0.5 \times 10^{-3}$	$1.6 \pm 0.2 \times 10^{-2}$	$3.3 \pm 0.6 \times 10^{-2}$
QPGG	$3.4 \pm 0.7 \times 10^{-2}$	$9.1 \pm 0.8 \times 10^{-2}$	$1.8 \pm 0.3 \times 10^{-1}$
RPGG	$1.5 \pm 0.2 \times 10^{-2}$	$3.8 \pm 0.7 \times 10^{-2}$	$15.4 \pm 5.6 \times 10^{-2}$
SPGG[a]	$1.6 \pm 0.1 \times 10^{-2}$	$3.2 \pm 0.3 \times 10^{-2}$	$7.2 \pm 1.2 \times 10^{-2}$
TPGG[a]	$1.5 \pm 0.2 \times 10^{-2}$	$3.4 \pm 0.1 \times 10^{-2}$	$6.2 \pm 0.6 \times 10^{-2}$
VPGG[a]	$9.5 \pm 0.2 \times 10^{-3}$	$2.2 \pm 0.1 \times 10^{-2}$	$4.9 \pm 0.3 \times 10^{-2}$
WPGG	$5.0 \pm 0.5 \times 10^{-3}$	$1.2 \pm 0.1 \times 10^{-2}$	$3.3 \pm 0.1 \times 10^{-2}$
YPGG	$4.6 \pm 0.5 \times 10^{-3}$	$8.7 \pm 0.3 \times 10^{-3}$	$2.2 \pm 0.3 \times 10^{-2}$

[a] Signifies peptides which were fit best by including an intermediate step prior to dissociation.

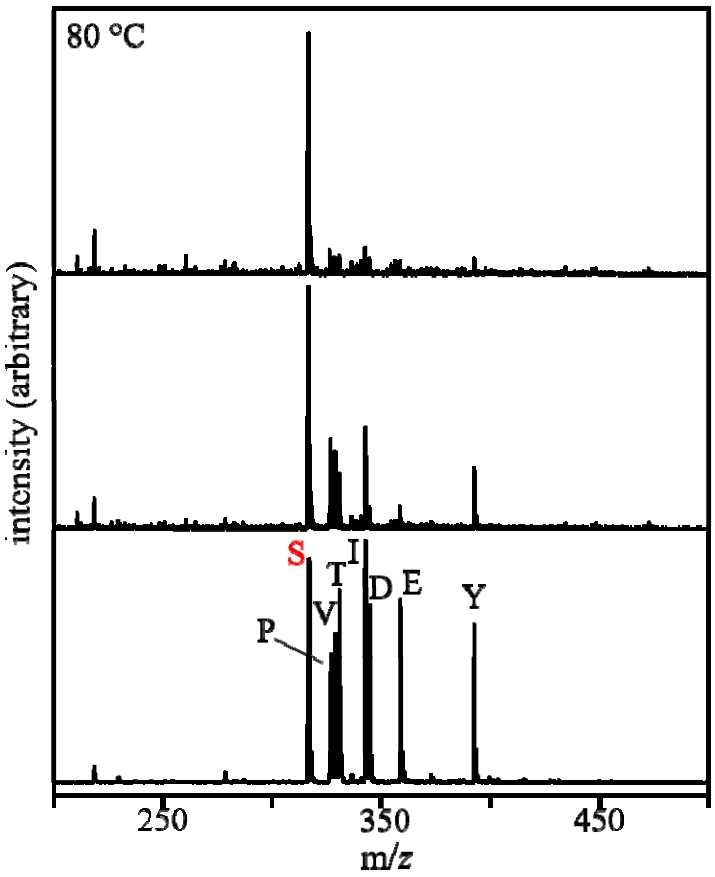

Figure S1. Representative mass spectral distributions for a mixture of XPGG peptides at 80 °C. The peaks in the 0 min distribution are labeled by the first residue in the sequence with the red label indicating the internal standard used in the experiment.

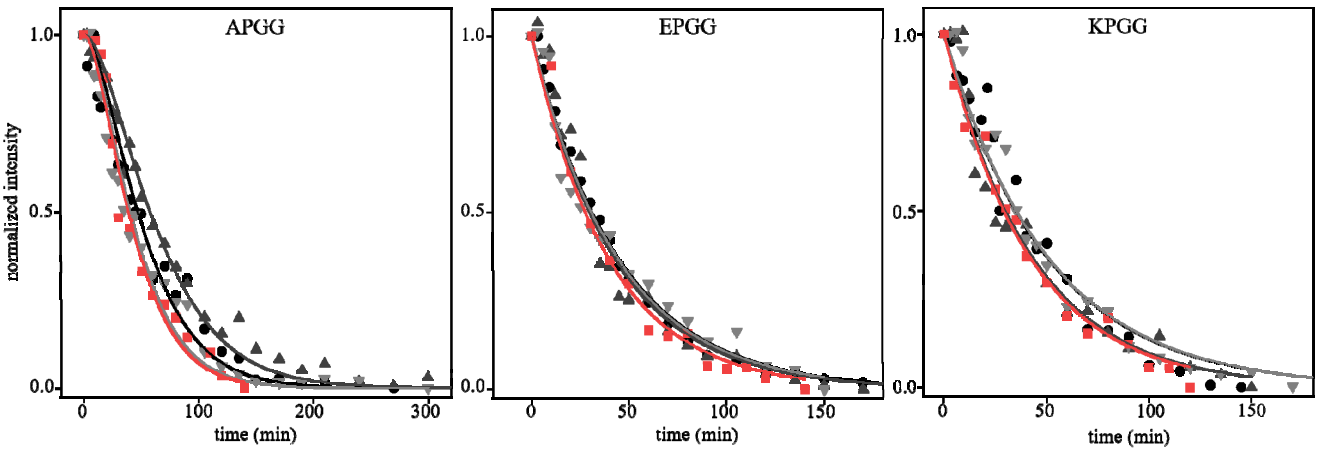

Figure S2. Kinetics plots for APGG, EPGG, and KPGG at 80 °C. Black, dark gray, and gray symbols and lines for each system represent the kinetics plots from the peptides run as part of a mixture, and red symbols and lines represent the peptide run individually to check whether rates were influenced in the mixture.

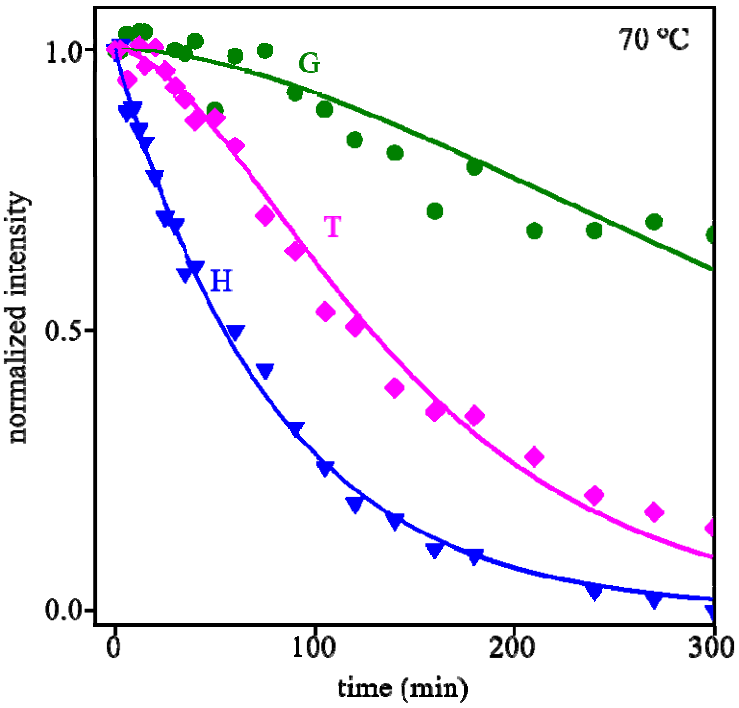

Figure S3. Kinetics plots of the early time points shown for three different peptides (GPGG, TPGG, and HPGG) at 70 °C to better demonstrate the difference between peptides which demonstrate a lag time (GPGG and TPGG) and a peptide which doesn't (HPGG). The relative intensities are plotted as a function of time.

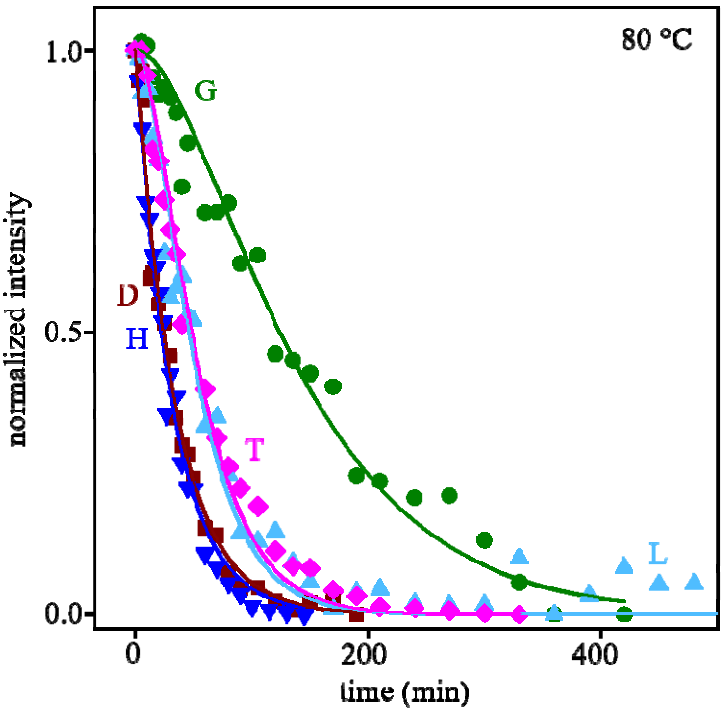

Figure S4. Kinetics plots shown for five different XPGG peptides (DPGG, HPGG, TPGG, LPGG, and GPGG) at 80 °C, incubated in a n-propanol:0.5% acetic acid solution. The relative intensities are plotted as a function of time.

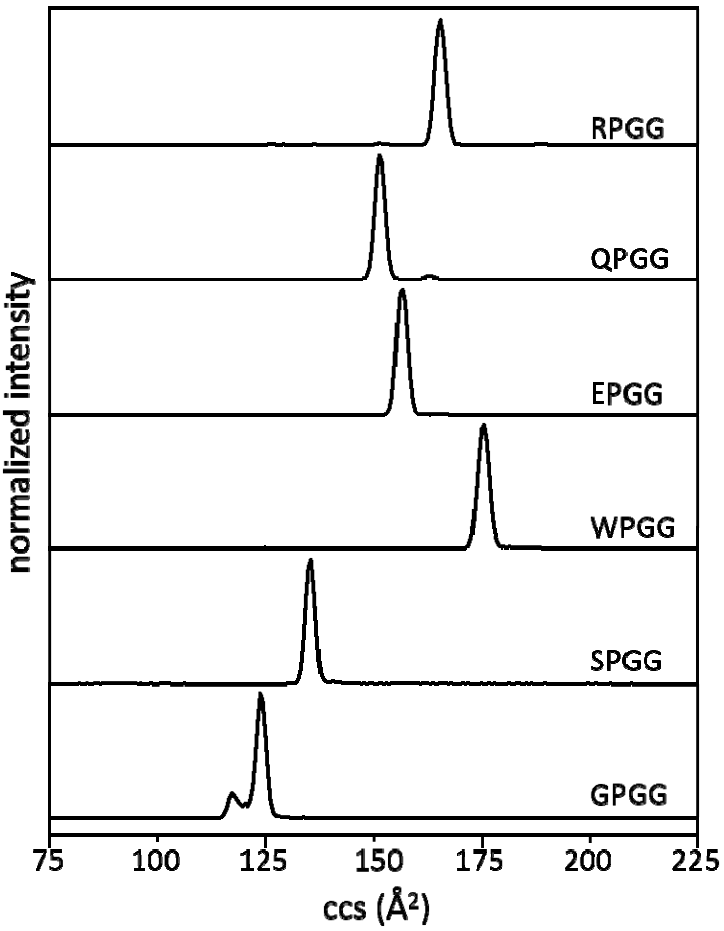

Figure S5. Collision cross sections distributions of a few of the peptides studied. One peptide from each of the groups (Figure 4) is shown. A small second peak is observed for almost all of the peptides studied which we associate with *cis/trans* isomerization of the Xaa-Pro bond.