Origins of life and molecular information: selectivity in mineral surface induced prebiotic amino acids polymerization

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Supporting Information

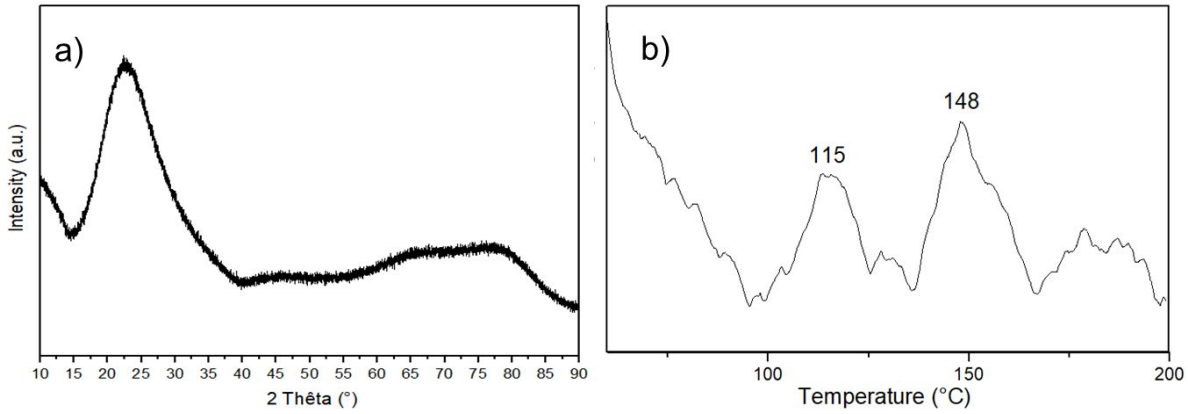

Figure S1. a) XRD and b) TGA spectra of Leu+Glu/SiO_2 system

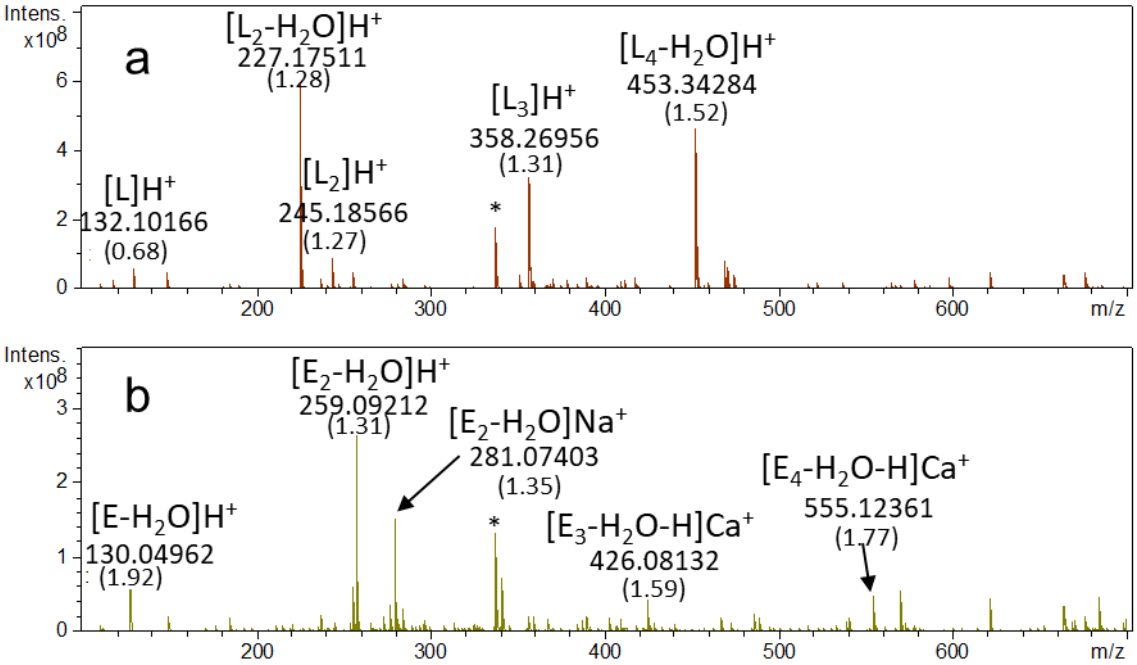

Figure S2. Positive ESI mass spectrum of desorption solution from thermally activated Leu/SiO_2 (a) and Glu/SiO_2 (b) systems using high resolution mass spectrometry (HRMS) detection.

In Figure S2a, the predominant peak at m/z 227.17515 corresponds to stoichiometry $[L_2\text{-}H_2O]H^+$. It can be assigned to a cyclic dimer cyclo(L-L), i.e. a substituted diketopiperazine (DKP), in accordance to previous works on surface catalyzed polymerization. The monomer ion, LH^+, is still detected at low abundance (m/z 132.10182), meaning that polymerization is not quantitative. Other oligomer compounds are also detected. The linear dipeptide $[L_2]H^+$ has an intensity five times smaller than the cyclic $[L_2\text{-}H_2O]H^+$, and its presence is not surprising since it constitutes a likely intermediate in the formation of the latter. Peaks corresponding to the stoechiometries $[L_3]H^+$ and $[L_4\text{-}H_2O]H^+$ could be due, respectively, to a linear trimer and a cyclic tetramer. However, they could also be assigned to non-covalent multimer ions, respectively between the monomer and DKP (L,cyclo(L-L)H^+) and between two DKP species (cyclo(L-L),cyclo(L-L)H^+). Since the constituting elements of these two adducts are indeed present in the solution, this assignment may be more likely than supposing a cyclic tetramer.

In Figure S2b, the desorption solution of activated Glu/SiO_2 does not show any untransformed monomer, but does show $[E\text{-}H_2O]H^+$, corresponding to internal cyclization (PyroGlu formation). The most intense peaks nominally correspond to dimers: $[E_2\text{-}H_2O]H^+$ and the corresponding sodium form, $[E_2\text{-}H_2O]Na^+$. However, an alternative assignment could be the non-covalent complexes (pE,pEH^+) and (pE,pENa^+). This possibility has been specifically addressed by additional experiments (see Figures S3 and S4).

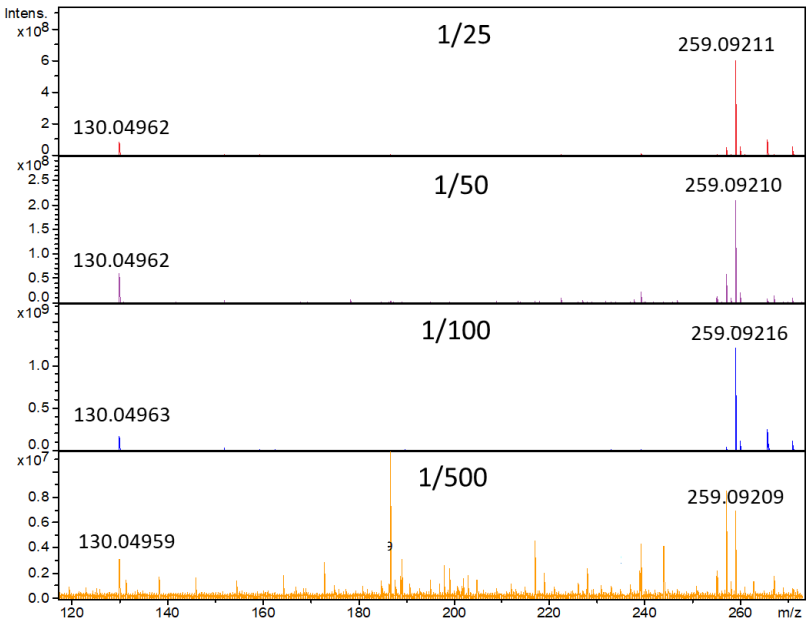

Figure S3. Positive ESI mass spectrum of desorption solution from thermally activated Glu/SiO_2 at different solution dilutions for HRMS analysis.

Evidence indicating that the species detected at m/z 259.0921 in the activated Glu/SiO_2 sample correspond to non-covalent multimer ions. The desorption solution was diluted 25, 50, 100 and 500 times: the 259.0921/130.0496 intensity ratio, where the species at m/z 130.0496 is the pE monomer, decreases upon dilution as expected for non-covalent complex species formed during the ESI processes.

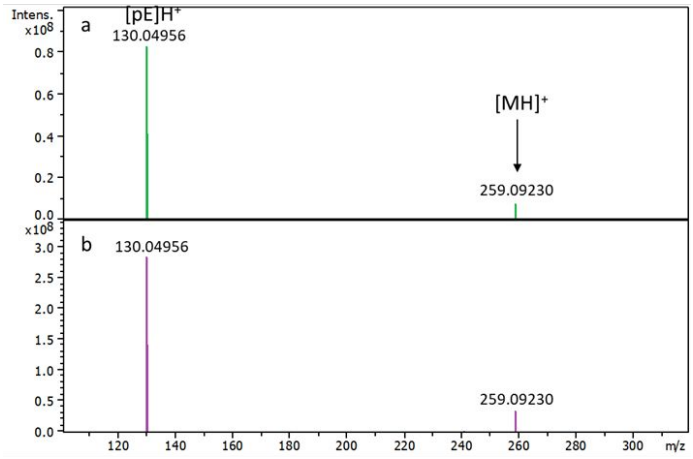

Figure S4. MS/MS spectra of the m/z 259.09230 precursor ion resulting from (a) E+pE mixture and (b) thermally activated Glu/SiO_2 sample

A mixture containing pyroglutamic acid (pE) and glutamic acid was prepared to form non-covalent dimer ions and compare their gas phase stability with supposed non-covalent species in the Glu/SiO_2 sample. Both MS/MS spectra are similar, indicating that m/z 259.09230 ions should correspond to a non-covalent dimer formed by two pyroGlu units.

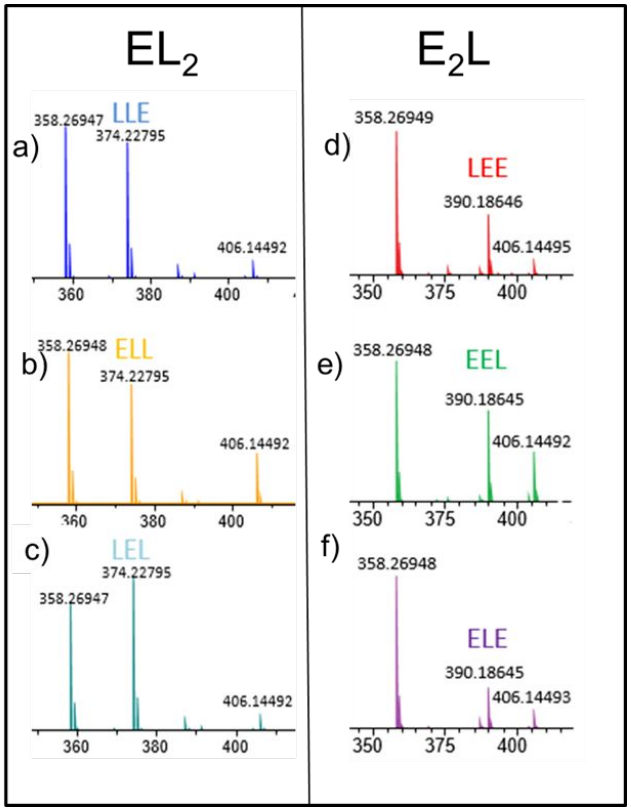

Figure S5. Positive ESI mass spectra from equimolar mixtures of the reference tripeptides. Each solution contains an equal amount of LLL (m/z 358,26945), EEE (m/z 406,14492), and one hetero-trimer a) LLE, b) ELL, c) LEL, d) LEE, e) EEL and f) ELE sequences.

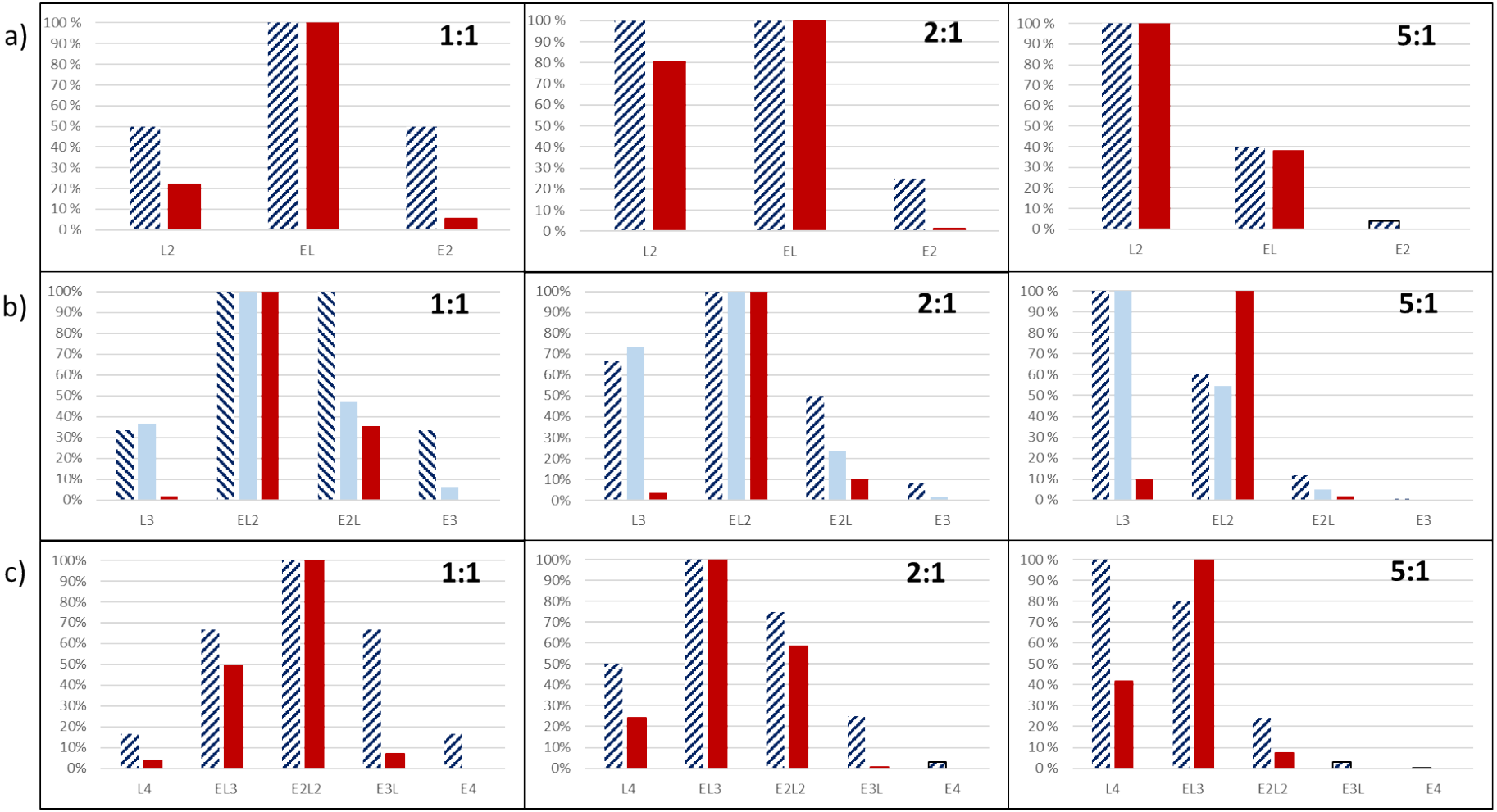

Figure S6. Comparison between the experimental peak intensity data (red bars) and expected distributions for random polymerization (hatched bars) for the different possible stoichiometries of a) dipeptides, b) tripeptides, c) tetrapeptides in systems with 1:1, 2:1 and 5:1 L:E molar ratios. For the tripeptides, the grey bars correspond to the expected peak intensities in the random scenario, taking into account the ionization efficiencies (cf. Figure 3).

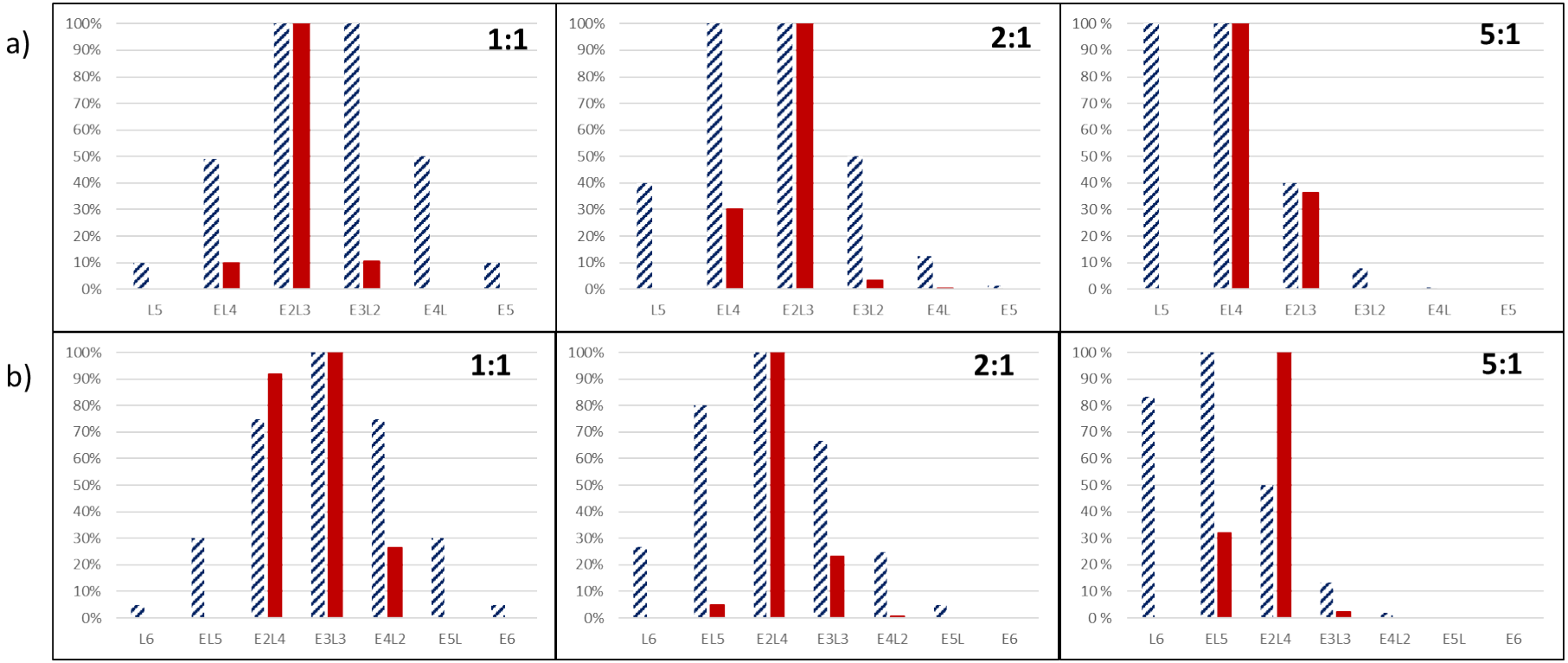

Figure S7. Comparison between the experimental peak intensity data (red bars) and expected distributions for random polymerization (hatched bars) for the different possible stoichiometries of a) pentapeptides, b) hexapeptides in systems with 1:1, 2:1 and 5:1 L:E molar ratios.

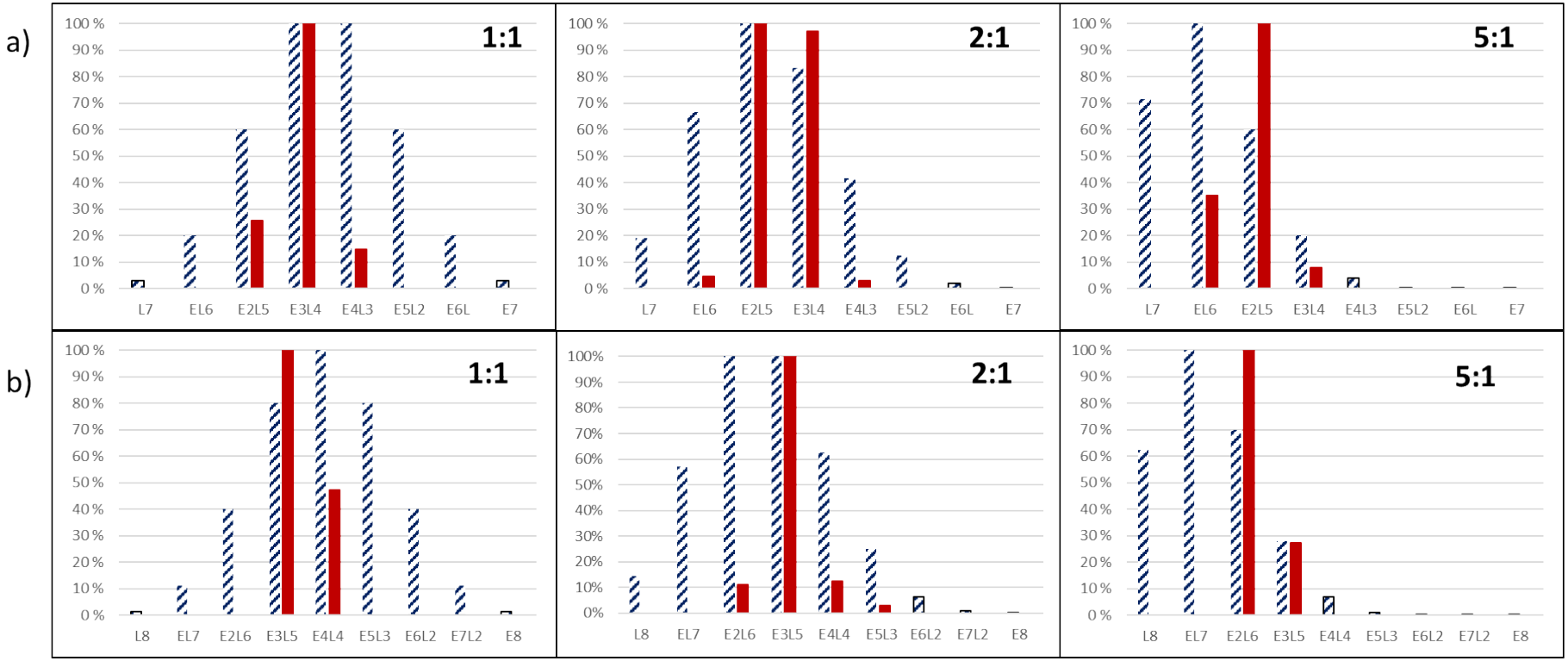

Figure S8. Comparison between the experimentally data (red distribution) on a) heptapeptides, b) octapeptides of different stoichiometries and expected values for random polymerization (hatched distribution) of different stoichiometries and expected values for random polymerization for the 1:1, 2:1 and 5:1 L:E molar ratios.

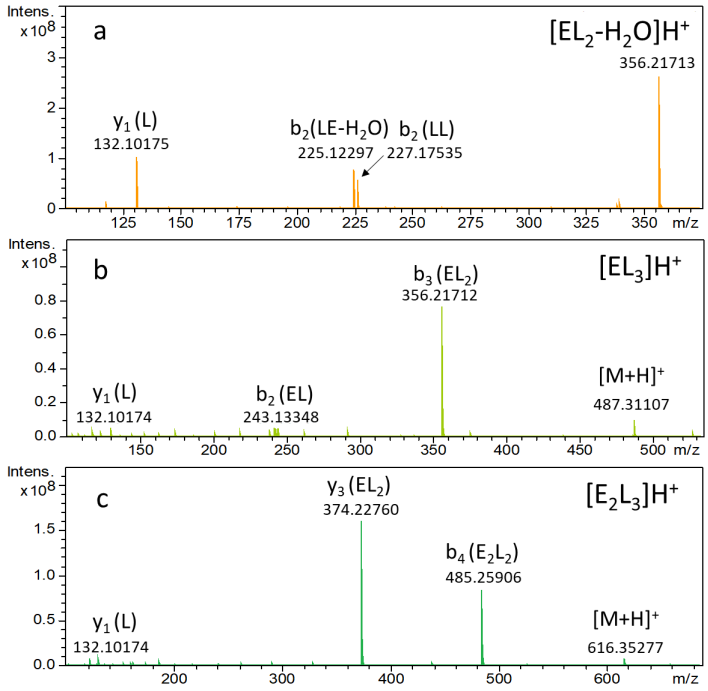

Figure S9. MS/MS spectra of precursor ions at (a) m/z 356.21713 corresponding to $[EL_2\text{-}H_2O]H^+$ tripeptides, (b) m/z 487.31107 corresponding to $[EL_3]H^+$ tetramer, (c) m/z 616.35277 corresponding to $[E_2L_3]H^+$ pentamer from the thermally activated Leu+Glu/SiO_2 system. Note that putative peptide stoechiometries were obtained from accurate mass measurements.

The fragmentation patterns detected for each peptide stoichiometry do not allow unambiguous sequence determination but give some clues about partial peptide sequencing.

a) Fragments ions were annotated as y1(L) at m/z 132 corresponding to a L residue at C-terminal, and two different b2 corresponding to LE-H_2O motif (or a EL-H_2O) and LL-H_2O at m/z = 225 and 227 respectively. This fragmentation pattern suggests that we are dealing with is a mixture of two or more possible sequences.
b) Fragments ions are annotated y1(L) at m/z 132 and b2(EL), b3(EL_2). It is not possible to distinguish the ELLL and the LELL possible sequences because of the lack of b1 and y3 fragments. One can eliminate LLLE and LLEL sequences as no corresponding b2 or b3 fragments ions are detected.
c) Fragments ions are annotated y1(L) at m/z 132, y3(EL_2), and b4(E_2L_2). The absence of b1, b2 and y2 does not allow a firm conclusion for a major sequence. Indeed, detected fragment ions could be produced from several sequences and/or a mixture of them.

Table SI 1: Assignment of main IR bands in non-activated Leu+Glu/SiO_2

Wavenumber (cm^{-1})	Assignment
1408	COO^- symmetric stretching ($\nu_{sym\ CO}$)
1473	CH_2 asymmetric bending ($\delta_{as\ HCH}$)
1500	NH_3^+ symmetric bending ($\delta_{sym\ HNH}$)
1595 (sh)	Mostly COO^- asymmetric stretching ($\nu_{as\ CO}$)
1627	NH_3^+ asymmetric bending ($\delta_{as\ HNH}$)
1718	C=O stretching, side chain COOH of Glu.