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Chiral Selectivity as a Bridge to Homochirality

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Introduction: In abiotic reactions, equal mixtures of L- and D- amino acid enantiomers are produced unless conditions that favor one enantiomer over the other are present. Understanding how the transition from racemic, abiotic chemistry to homochiral polymers used in proteins occurred is fundamental to our understanding of the origins of life on Earth and the search for signs of life elsewhere, but this transition is still poorly understood. We have begun investigations into whether enantiopure amino acid pools are a necessary condition, or if the polymerization process itself can impart some added degree of stereoselectivity. More specifically, we are exploring the polymerization behavior of chiral amino acids to determine if they show a preference for homochiral or heterochiral polymerization. We are also determining the effects of different amino acid chiral ratios ($L > D$) to determine at what level of enantiomeric enrichment homochiral peptides become predominant. These data will allow us to evaluate the plausibility of homochiral polymers arising by known abiotic mechanisms.

Methods: We used the prebiotically plausible salt-induced peptide formation (SIPF) reaction [e.g., 1, 2, 3, and references therein] to study the polymerization behavior of a suite of amino acids, with racemic, scalemic, and enantiopure starting mixtures. Peptides were analyzed by ultra-performance liquid chromatography with quadrupole-time of flight mass spectrometry (LC-MS).

Results: Preliminary work demonstrates both chiral and sequence selectivity. Racemic mixtures of alanine and valine show a dipeptide distribution of $AA = AV > VA \gg VV$. As shown in the left panel of figure 1, selectivity is more strongly observed in polymers formed by SIPF; similar experimental runs, using carbodiimide coupling agents do not show this selectivity. The favorability of AA over VV and the mixed dipeptides may be due to the steric differences between alanine and valine.

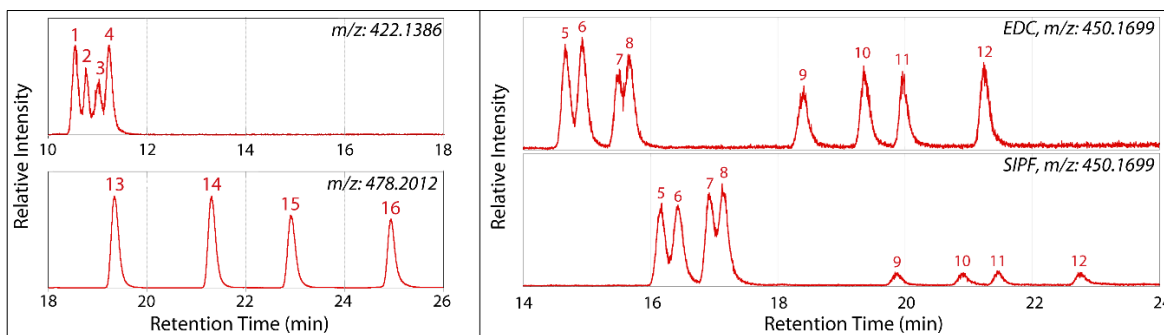


Figure 1. LC-MS extracted ion chromatograms ($M+H^+$) for OPA/NAC derivatives of dipeptides containing alanine and valine. Peak identifications are 1- $A_D A_L$, 2- $A_L A_L$, 3- $A_L A_D$, 4- $A_D A_D$ ($m/z=422.1386$); 13- $V_L V_L$, 14- $V_D V_D$, 15- $V_D V_L$, 16- $V_L V_D$ ($m/z=478.2012$); 5- $A_L V_D$, 6- $A_D V_L$, 7- $A_L V_L$, 8- $A_D V_D$, 9- $V_L A_L$, 10- $V_L A_D$, 11- $V_D A_D$, 12- $V_D A_L$ ($m/z=450.1699$). The right panel shows the strong preference for AV (peaks 5 – 8) over VA (peaks 9 – 12) in the SIPF reaction (bottom trace) compared with carbodiimide (EDC) coupling which shows no apparent sequence bias.

References: [1] Schwendinger MG and Rode BM (1989) *Analytical Sciences* 5:411-414. [2] Rode BM and Schwendinger MG (1990) *Origins of Life and Evolution of the Biosphere* 20: 401-410. [3] Fitz D et al. (2007) *Pure and Applied Chemistry* 79:2101-2117.