Japan Geoscience Union Meeting 2010
(May 23-28 2010 at Makuhari, Chiba, Japan)

BBG005-07 Room: 301B Time: May 23 11:10-11:25

Effects of pH and dissociation states on the polymerization rate of amino acid

Kasumi Sakata[1*], Norio Kitadai[1], Tadashi Yokoyama[1]

[1]Earth and Space, Osaka Univ.

Proteins are one of the fundamental components of life and are formed by polymerization of amino acids.The knowledge of the polymerization rates of amino acids under various conditions is important to determine the suitable environment for the chemical evolution in the early earth. Although it has been qualitatively known that the polymerization rates is strongly influenced by pH (Zamaraev et al.,1997), no study has quantitatively evaluated the effect of pH on polymerization rates. We examined the polymerization rates of glysine (Gly: NH_2-CH_2-COOH), one of the simplest amino acids, under various pH.
8.0 ml of 100 mM Gly solutions, having pH from 3.1 to 10.9, were inserted into Teflon bottles and heated at 140 degrees C from 1 to 14 days. After heating, the solutions were analyzed by a liquid chromatography (LC). The concentrations of glycylglycine (GlyGly) and diketopiperazine (DKP), which were formed from Gly, increased with heating time. The following four reaction pathways can be assumed: Gly to GlyGly, GlyGly to DKP, DKP to GlyGly and GlyGly to Gly. Each reaction has a different reaction constant. To obtain each rate constant, the results of heating experiments were fitted by the four reactions describing the above reactions. Polymerization rate of Gly was nearly constant at pH 3?7, increased with increasing pH from 7, reached a maximum value at around pH 9.8, and then decreased with further increasing pH.
Gly has three dissociation states (cationic state: Gly^+, zwitterionic state: Gly^0, anionic state: Gly^-) and the main existence forms of Gly at pH above 6 are $Gly^0$and Gly^-. The molar fraction of Gly^0 decreases and that of Gly^-increases with increasing pH from 6. Evaluation of the polymerization rates of each dissociation state revealed that the reaction between $Gly^0$and $Gly^-$is the fastest; the rate constant of the reaction between $Gly^0$and $Gly^-$is 9 times larger than that between $Gly^-$and Gly^- and 96 times larger than that between $Gly^0$and Gly^0. Therefore, overall polymerization rate of Gly is expected to increase with approaching the condition at which the molar fraction of $Gly^0$is low and those of $Gly^0$and $Gly^-$are similar, namely, pH approaches to 9.8. The reason of the different reactivity between each dissociation state appears to be the difference of the nucleophilicity of amino group and intramolecular or intermolecular electric interaction. These results show that the change of pH accompanying the change of the molar fractions of each dissociation state greatly influences the overall polymerization rate of Gly.

Keywords: amino acid, dissociation state, alkaline, hydrothermal system, origin of life