Report for MERIT Internship

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【Period】

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【Host】

Materials Characterization Support Team, Supramolecular Chemistry Division, Center for Emergent Matter Science (CEMS), Institute of Physical and Chemical Research (RIKEN)　(Team Leader: Dr. Daisuke Hashizume)

【Research Theme】

Mechanistic investigation for the oligomerization of glycine by using X-ray diffraction

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To know the structure of materials is the first step for understanding their nature, for controlling their properties, and for synthesizing them in practical ways. I have ever been working on the research on the structure analysis of small molecules by single crystal X-ray diffraction. It is one of the most powerful analysis methods in the viewpoint of revealing the molecular structures but the scope of this method is limited because single crystals, which are often difficult to get, are needed for this measurement. Actually, most of things around us are made from non-single-crystal, such as multicrystal, film, liquid crystal, amorphous and so on. Especially in the case of non-crystalline materials, not only the molecular structures but also the structures in larger scale such as the orientation, stacking manner affect strongly to their property. X ray diffraction gives us such high-level information. As I wanted to learn the methods for wide-ranged materials to obtain various structural information, I asked Dr. Hashizume, the specialist of X-ray analysis at RIKEN, to host me as a MERIT internship.

First, I learned about the basic experimental skills for powder and thin film X-ray diffraction. I measured powder samples of organic compounds and inorganic thin film on single-crystal substrate. I conducted the indentification, quantification and evaluation for the orientation and crystallinity. Moreover, I tried the structure analysis of an amino acid from the powder diffraction pattern by Rietveld method.

As an application of the method I learned through this internship, I worked on the research on the investigation of the mechanism of thermalcondensation of glycine by X-ray diffraction. Amino acids are the one of the major components of living things and are thought to have been produced by chemical evolution in early Earth. 19 α-amino acids except for glycine have one set of enantiomer, L-form and D-form, for each, and all the living things are composed of L-amino acids. The reason for that has not been clear though many hypotheses have been proposed such as "by chance hypothesis", magnetic field of Earth, and so on. All of them assume that amino acids are synthesized chemically from smaller molecule. On the other hand, recently another theory has proposed: First, polyglycine was synthesized, followed by chemical modifications and then decomposed into various amino acids. This means that the helicity of polyglycine is the origin of the chirality of each amino acid. This is because, if we assume polyglycine appeared firstly with only one of the helicity, the side chains can be modified chemically only from the direction perpendicular to the helical axis and thus to give sets of one of two enantiomer. However, the mechanism how polyglycine is made from glycine has not been revealed. So I decided to unveil the process by X-ray diffraction with the aid of mass spectrometry complementarily.

Glycine is known to have several polymorphs, so I first identified some different types of glycine samples by single crystal and powder X-ray diffraction. Next, I conducted thermal condensation experiments from powder in different phase or solution in various conditions. Mass spectrometry showed that only under the specific conditions did the oligomerization reaction proceed well. Temperature-dependent X-ray diffraction experiments suggested that the structural change was induced at the specific temperature: The lattice constant along with the direction of the hydrogen bond between hydroxyl and carboxyl groups of glycine molecules was shrunken. Under the specific condition, thermal condensation proceeded via pre-organization of glycine molecules into helical manner on the surface.

【Acknowledgement】

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