学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Experimental and Simulation Studies on Crystal Growth and Crystallinity Evaluation of Organic Materials and Polymers
（有機材料および高分子の結晶成長と結晶化度の評価に関する実験とシミュレーションによる研究）

Functional materials refer to materials that have specific functions through the treatment of light, electricity, magnetism, heat, chemistry, biochemistry, etc. and their crystal growth is very important to improve the properties and performance. The author has studied the crystal growth of organic semiconductors, characterization of crystallinity evolution of polymers in composites from experiments and simulations.

The dissertation is composed of five chapters.

Chapter one is general introduction and describes the background of this research. Experimental and computational techniques and materials are also explained in this chapter.

Chapter two is about the crystal growth of pentacene by "naphthalene flux method". Pentacene is an important organic semiconductor material which belongs to organic functional material. The naphthalene flux method is a technique recently developed in collaboration with the author. It is a technique to grow crystals of molecules from a solution of naphthalene and can be applied to large aromatic molecules that are insoluble to ordinary solvents. The determined the solubility of pentacene in naphthalene by optical absorption at elevated temperatures and crystals with more than 1 cm size was obtained. The crystals were characterized by Laser microscopy, X-ray diffraction and X-ray pole figure to analyze the crystals. The author succeeded the scaling up of the naphthalene flux method using a vacuum-tight stainless steel vessel with two rooms. The X-ray analysis revealed that the pentacene crystal is composed of microscopic twins, and the polytype was "bulk type".

Chapter three describe a new phenomenon discovered during the attempt to grow C_{60} crystals by naphthalene flux method. The removal of naphthalene from C_{60} was not successful because the vapor pressure of naphthalene was substantially decreased by adding C_{60}. The author measured the naphthalene vapor concentration by optical absorption of the vapor (wavelength 270 nm) in a quartz tube. From the control experiment, it was found that this phenomenon was specific to C60. To elucidate the mechanism, the author used molecular dynamics (MD). It was found that naphthalene and C_{60} did not mix when melt, and C_{60} was expelled out from the naphthalene liquid. The author proposed a model in which C_{60} flows at the surface of naphthalene liquid as a layer and prevents evaporation.

Chapter four describes the new method to predict and understand the vibrational spectroscopy, which is applied to Poly (ether ether ketone) (PEEK) crystallization. PEEK is an engineering plastic frequently used as composites with inorganic filler. The local crystallization behavior of PEEK is important for applications and it is evaluated with micro Raman spectroscopy. One peak shows a characteristic increase in intensity during the crystallization but the mechanism was not understood. I developed a new method to use MD simulation and Fourier transform to estimate the local vibrational spectra. I found the characteristic peak is related to intermolecular interaction. The computational time is very short compared with the first principle calculation and this technique is applicable to evaluate the vibrational spectra of complex large systems such as composite.

Chapter five is a general conclusion and future prospects. The author succeeded the growth of pentacene crystals with unprecedented size by developing the scaling-up of naphthalene flux method, found a new phenomenon to prevent the vaporization, and developed a new method to obtain vibrational spectrum from MD simulations, and successfully identified the experimental low-frequency peaks that have not been done.