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論文題目: Development of Effective Method for Catalytic Fixation of Carbon Dioxide into Polymers

Title of this thesis is "Development of Effective Method for Catalytic Fixation of Carbon Dioxide into Polymers" with 5 chapters. Herein, efficient fixation of carbon dioxide (CO_2) into materials including polymers is described. CO_2-fixation reaction with propargylamine derivativies and its polymers were efficiently transformed to corresponding poly(oxazolidinone)s using various metal- or organo- catalysts.

In chapter 1, "Introduction", the author described CO_2-fixation reactions for fabricating the valuable materials and polymers to reveal the purpose and meaning of this thesis.

In chapter 2, "CO_2-fixation reaction of poly(propargylamine)s using Cu-macrocycle catalyst.", the author demonstrated the CO_2-fixation reaction with propargylamines and its polymers using copper macrocycle catalyst. At first, propargylamine compounds and various copper catalysts bearing phenanthroline ligand were prepared. CO_2-fixation reaction was performed with propargylamine. It was shown that copper catalyst and DABCO played synergistic roles in activating both the alkyne and the amino group of propargylic amines in the reaction. Based on this result, polymer bearing propargylamine moiety was synthesized by the Sonogashira-Hagihara coupling reaction of an AB-type monomer. Obtained polypropargylamine was effectively transformed to polyoxazolidinone.

In chapter 3, "Base-mediated highly efficient CO_2-fixation to propargylamines and polypropargylamine", the author described the CO_2-fixation reaction with propargyl amines using base-catalysts. Various base-catalysts were used for CO_2 fixation reaction. Among them, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) showed best catalytic ability. The solvent effect and substituent effect were revealed. It was found that the propargylamines bearing pyridine moiety reacted with CO_2 in high efficiency under mild conditions, which required only five minutes at room temperature in the presence of DBU under CO_2 atmosphere (0.1 MPa) in DMSO as a solvent. To demonstrate the electronic effect and clarify the reaction mechanism, DFT calculation was performed. This reaction proceeded quantitatively even under atmospheric air condition at room temperature. Moreover, transformed poly(oxazolidinone)s showed excellent thermal stability.

In chapter 4, "Metal- and solvent-free CO_2-fixation to polypropargylamine", the author described the CO_2-fixation reaction with various polypropargylamines in solvent-free condition. It was found that the polypropargylamine bearing 2-pyridyl moieties reacted with CO_2 to poly(oxazolidinone)s in the presence of DBU under CO_2 atmosphere (0.1 MPa) without a solvent. Additionally, polymethacrylate type polymers were synthesized. Since this polymer system can be modified by copolymerization, catalytic functional group was

introduced. This copolymer showed positive effect for CO_2-fixation reaction.

In chapter 5, "Conclusion" summarized the results obtained in this work along with its future prospect. To establish the CO_2 incorporation into the polymers, the author designed novel poly(propargylamine)s bearing propargylamine moiety. Synthesized propargylamines and its polymers are efficientyl transformed to poly(oxazolidinone)s by CO_2-fixation reaction under the Cu-macrocycle catalyst/DABCO system. Introduction of electron withdrawing group to poly(propargylamine)s transformed to corresponding poly(oxazolidinone)s within few minutes in the presence of DBU. In addition, poly(propargylamine)s were transformed to poly(oxazolidinone)s even open-air condition at room temperature. And also, the solvent free CO_2-fixation reaction were performed. Additionally, side-chain type polymers were synthesized. This polymer system can be modified by copolymerization. Thus, the present study will give the environmentally friendly versatile methods and the useful entry enough to reduce CO_2 content in air and to derive to value-added materials in the future.