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論文要旨

THESIS SUMMARY

専攻： Department of	有機・高分子物質　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
学生氏名： Student’s Name	金　南均 (Kim Nam-Kyun)	指導教員（主）： Academic Supervisor(main)	
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要旨（英文800語程度）
Thesis Summary（approx.800 English Words ）

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 efficiantly transperformed to corresponding poly(oxazolidinone)s using various metal- or organo- catalysts.

In chapter 1, "Introduction", the author described the various strategy for CO_2-fixation reaction into 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 the copper macrocycle catalyst were prepared. Because copper has good interaction with alkyne group and also it is usefull transition metal for preparing macrocycle catalyst. And then CO_2-fixation reaction was performed with propargylamines and polypropargylamine. 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. It was possible to obtained polymers, which has propargylamine moiety in the main chain. A variety of molecular weight polymers were synthesized by controlling reaction temperature and time. It was found that the copper macrocycle catalyzed polymer transformation reaction of high molecular weight was faster than low molecular weight polymer, although same amount of copper macrocycle catalyst was used for CO_2-fixation reaction. These results indicate the possibility that the macrocycle catalyst formed pseudo-rotaxane structure with polymer. Because of this interlocked structure, macrocycle catalyst continuously react with next propargylamine group. Which is rotaxane-based catalystic system that is consisted with mechanical axle-wheel linkage. The axle component bearing propargylamine was efficiently translated by CO_2-fixation reaction by copper macrocycle as a wheel component.

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. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) showed good catalytic ability for CO_2-fixation reaction. And also the solvent effect and substituent effect were revealed. It was found that the propargylamines bearing pyridine moieties reacted with CO_2 to poly(oxazolidinone)s 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 demonstrated that electronic effect and clarify the reaction mechanism, DFT calculation was performed. This transformation was confirmed by NMR and IR. *E* / *Z* conformation of the double bond of the oxazolidinone moiety was determined by NOE correlation, suggesting the preferential formation of *Z*-isomer under the conditions. The transformation of alkyne group to double bond was clearly indicated by appearance of carbonyl and double bond stretching signal in the IR spectra. This reaction proceeded quantitatively even under atmospheric air condition at room temperature. Morover, transformed poly(oxazolidinone)s were showed ecellent thermal stability (T_{d5}: 350 °C).

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. After preparation of polypropargylamines bearing 2-pyridyl group, CO_2-fixation reaction was performed without solvent. It was found that the polypropargylamine reacted with CO_2 to polyoxazolidinones in the presence catalytic amount of DBU under CO_2 atmosphere (0.1 MPa) without a solvent. Additionally, side-chain type polymers were synthesized by via the typical free-radical polymerization using AIBN as an initiator in toluene. Since this polymer system can be modified by copolymerization, catalytic functional group was introduced. Copolymerization of methacrylate bearing propargylamine moiety and propargyl (diethylamino)ethyl methacrylate (DEMA) was prepared. This copolymer containing DEMA showed acceleration of solvent-free CO_2-fixation reaction in the presence catalytic amount of DBU under CO_2 atmosphere (0.1 MPa).

In chapter 5, "Conclusion" summarized the results obtained in this work along with its future prospect.

In summary, 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. It was found that the copper macrocycle catalyzed polymer transformation reaction system showed pseudo-rotaxane catalyst system. Especially, the propargylamines bearing pyridine moieties transformed to corresponding poly(oxazolidinone)s in high efficiency. In the atmospheric CO_2 pressure and temperature, synthesized poly(propargylamine)s were fixed the CO_2 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. Finally, incorporation of catalytic functional group into the poly(propargylamine) was demonstrated.