

氏名	片岡 頌治
学位の種類	博士 (工学)
学位記番号	博理工第 579 号
学位授与年月日	平成 31 年 3 月 26 日
学位授与の要件	学位規則第 5 条第 1 項該当
学位論文題目	ポリフルオロシクロペンテンの反応性を利用する機能性含フッ素化合物への展開
審査会	委員長 福元 博基 委員 久保田俊夫 委員 吾郷 友宏 委員 桑原 純平

論文内容の要旨

1. Introduction

Fluorine has the highest electronegativity among all elements, and its atomic radius is small. In addition, since the C - F bond is short and the binding energy is large, it has a strong and stable bond. Fluorine-containing organic compounds having many C-F bonds show excellent chemical stability and heat resistance, high water, oil repellency, high electron acceptability and low refractive index, which are not seen in non-fluorine organic compounds. For example, polytetrafluoroethylene (PTFE) developed by DuPont has a structure in which all hydrogen of polyethylene (PE) is substituted with fluorine. Thus, PTFE is insoluble and infusible resistant polymer with the melting point of 327 °C, whereas the melting point of high density PE is in the range from 120 to 140 °C. Further, the fluoropolymer has high transparency in a wide region from visible to ultraviolet and is also used as a transparent material. In particular, Cytop® (AGC) and Teflon AF® (DuPont) are known as amorphous perfluoropolymers having a cyclic structure with little light scattering. In addition to extremely high light transmittance, they have the lowest refractive index as a polymer, and therefore they are applied in information fields such as antireflection coating of flat panel displays (FPD) such as optical fibers and plasma displays.

We discovered that fluorine-containing phenanthrenes can be efficiently obtained by combination of nucleophilic addition-defluoride reaction¹⁾ of octafluorocyclopentene (OFCP) and aryl lithium and the following Mallory reaction²⁾. We also reported the intermolecular π - π interaction between phenanthrene units and the control of molecular arrangement in crystal by interaction between fluorine substituents in the phenanthrene molecule³⁾. In order to develop these fluorinated phenanthrenes as functional materials, it is considered that introduction of functional group into aromatic rings is effective. For example, nucleophilic addition and defluorination between OFCP and a lithium reagent bearing hydroxy groups proceeds to give a fluorine-containing diarylethene with hydroxy groups on aromatic rings, and the following intramolecular photocyclization of the obtained compound can be the monomer for polyestefication.

In this study, synthesis of fluorinated phenanthrene with hydroxy groups on aromatic ring and its polyestefication was described (Chapter 2). In addition, reactivity and application of heptafluorocyclopentene (HFCP), of which the structure is similar to that of OFCP, and application of was also described (Chapter 3).

2. Synthesis and polymerization of fluorinated phenanthrene with hydroxy groups

First of all, 4-bromophenol (**1**) in which the hydrogen group was protected with a methoxyethoxymethyl (MEM) group were converted to its lithium salt (**2**). Next, nucleophilic addition-defluorination of PFCP with **2** in 1:2 molar ratio afforded the diarylethene **3**. Finally, the Mallory reaction of **4**, obtained by deprotection of the MEM group in **3**, proceeded to give fluorinated phenanthrene having a hydroxy group at the 2 and 9 position (**5**) in high yield. Polyesterification of **4** and **5** with various carboxylic acid dichlorides was carried out. Among the diarylethene-type polymers (**Poly-1-Poly-6**), **Poly-2** and **Poly-6** show good solubility in organic solvents such as chloroform, while other diarylethene-type or phenanthrene-type polyesters are insoluble because the polymer chains are more rigid than those of **Poly-2** and **Poly-6**. It was confirmed that the obtained polymer showed high heat resistance by TGA measurement.

3. Reactivity of heptafluorocyclopentene (HFCP) as an electrophile

The sp^2 carbon bonded hydrogen in heptafluorocyclopentene (HFCP) is known to be reactive so that replacement of the hydrogen with lithium cation easily proceed. In this study, reactivity of the cation species of HFCP with various electrophiles such as aldehyde and ketone were carried out to give the corresponding secondary alcohol in high or moderate yield. Many of the obtained products reacted with nucleophiles on another sp^2 carbon with elimination of fluoride ion, affording disubstituted

hexafluorocyclopentene. On the other hand, mono-substituted hexafluorocyclopentene, which was synthesized by reaction of HFCP with nucleophiles (e.g., phenyllithium), were not converted to the corresponding lithium salt.

4. Summary

In this study, we have investigated the synthesis of novel fluorinated compounds using OFCP or HFCP and the development of heat resistant polymers starting from fluorinated phenanthrene derivatives obtained. In addition, we have found that HFCP reacts both nucleophiles and electrophiles to give mono- and disubstituted perfluoroalkenes. Through this study, the author has proved that polyfluorocyclopentene has possibility as an excellent building block of fluorine-containing compounds.

5. Reference

- 1) S. Yamada, T. Konno, T. Ishihara, H. Yamanaka *J. Fluorine. Chem.*, **2005**, *126*, 125-133.
- 2) (a) F. B. Mallory, C. S. Wood, *J. Org. Chem.*, **1964**, *29*, 3373-3377. (b) F. B. Mallory, C. S. Wood, J. T. Gordon *J. Am. Chem. Soc.*, **1964**, *86*, 3094-3102.
- 3) H. Fukumoto, M. Ando, T. Shiota, H. Izumiya, T. Kubota *Macromolecules*, **2017**, *50*, 865-871.

論文審査の結果の要旨

片岡頌治氏の申請した博士学位論文（ポリフルオロシクロペンテンの反応性を利用する機能性含フッ素化合物への展開）について、以下のような手順で審査を行った。

まず公聴会（平成31年2月4日13:00）において、学位論文の内容に関する発表ならびに会場の傍聴者との質疑応答を約1時間行った。本研究の目的や開発する化合物の分子設計指針など、研究の細部だけにとどまらず、本研究を俯瞰的に捉えているかどうかについての質疑もいくつか寄せられた。

その後の審査会にて、本研究科の博士学位論文の評価基準に基づいて審査を行い、研究内容の独創性、有用性についての明確な記述と実験データの分析・解析の適切性については全審査委員が評価した。一方、一部の審査委員から、研究目的と当該研究分野における位置づけの明確な記述ならびに説明がやや不十分である、といった指摘が上がった。この点について慎重に審査した結果、指摘事項を修正することで博士学位論文に値すると判断した。

また、申請者の当該研究分野ならびに周辺分野に関する学力・幅広い知識力を確認するために、同日に最終試験として約30分間の口頭試問を行った。審査委員からの質問の意図を正確に把握し、明確に回答していたことから、申請者の研究遂行能力は十分に備わっていると判断した。以上の通り、審査会ならびに最終試験の結果に基づいて総合的に審査を行い、申請者が提出した博士学位論文に対して合格の判定を下した。