様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　　元 年　　６ 月 １２ 日現在

機関番号：１６３０１
研究種目：若手研究(B)
研究期間：2016～2018
課題番号：１６Ｋ１７９１６

研究課題名（和文）ジアゾ酢酸エステルの精密重合を可能とする新規開始剤系の開発

研究課題名（英文）Development of new initiating system enabling controlled polymerization of diazoacetate

研究代表者

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愛媛大学・理工学研究科（工学系）・講師

研究者番号：４０６２５５９７

交付決定額（研究期間全体）：（直接経費）　　3,100,000円

研究成果の概要（和文）：本申請研究では、遷移金属錯体を用いたジアゾ酢酸エステルの重合においていまだ達成されていない（i）リビング重合可能な開始剤系の開発と（ii）立体特異性重合可能な開始剤系の開発を目標として研究に取り組んできた。種々の検討の結果、立体構造の比較的制御されたポリマーを与える新規Pd開始剤系の開発に成功した。

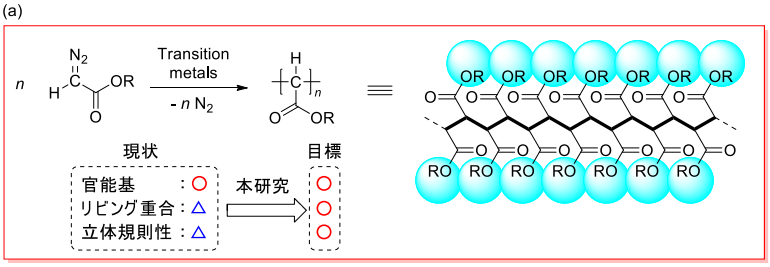
研究成果の学術的意義や社会的意義
ジアゾ酢酸エステルをモノマーとする重合によって、すべての主鎖炭素上に置換基を有するポリ(置換メチレン）を合成することができる。本研究の結果、これまで困難であったポリマーの立体構造を比較的制御できるようになった。本結果は、この重合法の一般性を高める成果であり、今後はより優れた高分子材料開発に向けた応用展開が期待される。

研究成果の概要（英文）：Polymerization of diazoacetates is a useful method to prepare C-C main chain polymers bearing an ester substituent on each main chain carbon atom. We tried to develop new Pd-based initiating systems for polymerization of diazoacetates. As a result, we have successfully developed a new Pd complex which can afford polymers with high stereoregularity.

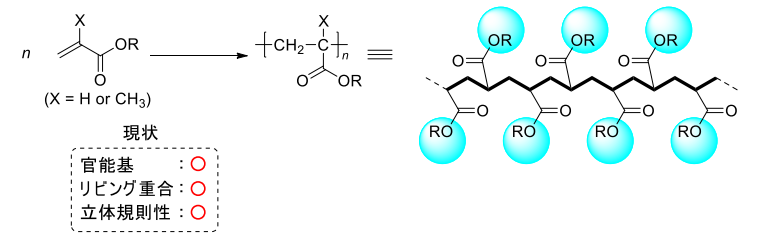
研究分野：高分子合成

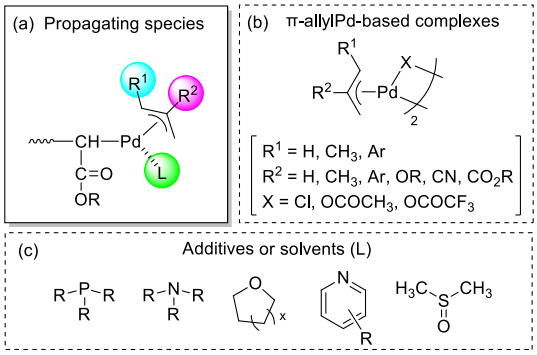
キーワード：高分子合成　遷移金属錯体　立体構造　精密重合

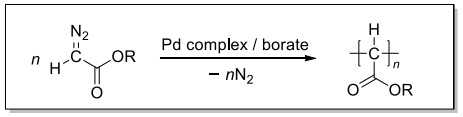
(a)

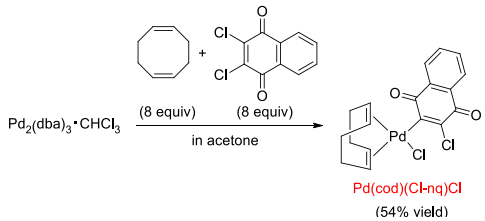

n
N2
H
C
OR
O
Transition metals
- n N2
H
C
n
O
OR
現状
官能基 ：○
リビング重合：△
立体規則性 ：△
本研究
目標
○
○
○
OR
RO
O

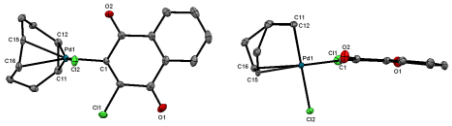
(b)

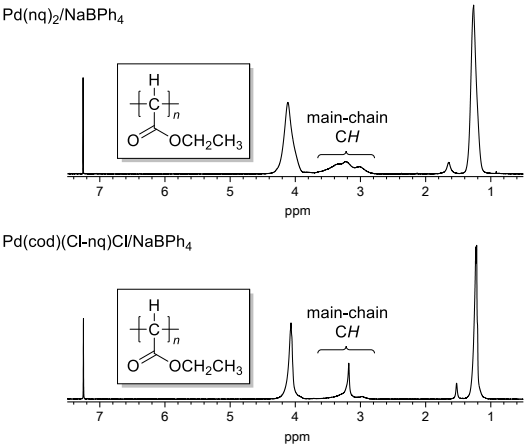

n
X
OR
O
(X = H or CH3)
CH2
C
n
現状
官能基 ：○
リビング重合：○
立体規則性 ：○
OR
RO
O


(a) Propagating species
(b) π-allylPd-based complexes
(c) Additives or solvents (L)


Pd complex / borate
以前の研究
本研究
Pd(nq)2
Pd(NHC)(NQ)
Pd(cod)(Cl-nq)Cl


(8 equiv)
(8 equiv)
in acetone
Pd(cod)(Cl-nq)Cl
(54% yield)





□ □ "Polymerization of Diazoacetates: New Synthetic Strategy for C-C Main Chain Polymers"
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"Excited-State Dynamics of Pyrene Incorporated into Poly(substituted methylene)s: Effects of Dense Packing of Pyrenes on Excimer Formation"
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1. Fluorinated Poly(substituted methylene)s Prepared by Pd-Initiated Polymerization of Fluorine-Containing Alkyl and Phenyl Diazoacetates: Their Unique Solubility and Postpolymerization Modification"
Shimomoto. H.; Kudo, T.; Tsunematsu, S; Itoh, T.; Ihara, H.
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[illegible]
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Solid State Ionics **2016**, *292*, 1-6.

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[illegible] 2017 ″ 11 v

[illegible]

[illegible] 2017 ″ 11 v

[illegible]

[illegible] 2017 ″ 9 v

Advances in Pd-initiated polymerization of diazoacetates: From variety of functional groups, living polymerization system, to high stereoregularity
Hiroaki Shimomoto
66 2017 9

(quinone)Pd/borate
66 2017 9

10)
66 2017 9

11)
66 2017 9

12) (NHC)Pd/borate
63 2017 7

13) Pd
63 2017 7

14) /Pd
66 2017 5

15) Pd
66 2017 5

16) "Advances in Pd-initiated polymerization of diazoacetates: From variety of functional groups, living polymerization system, to high stereoregularity"
Hiroaki Shimomoto, Eiji Ihara
253rd American Chemical Society National Meeting & Exposition, San Francisco, 2017 4

17)
31 2016 11

18) Pd
2016 2016 11

19)
65 2016 5

20) Pd

CMC 2018

http://www.ach.ehime-u.ac.jp/poly/index.html