アカデミックプログラム［B講演］ | 18. 高分子：口頭B講演

2025年3月29日(土) 13:00 ~ 15:10 [F]2404(第4学舎 2号館 [4階] 2404)

[[F]2404-4pm] 18. 高分子

座長：松岡 慶太郎、東原 知哉

日本語
13:00 ~ 13:20

[[F]2404-4pm-01]

半導体高分子の精密合成と有機エレクトロニクス材料への応用

○東原 知哉[1]、西山 滉哉[1]、Cheng-Liang Liu[2] (1. 山形大、2. 台湾大)

日本語
13:20 ~ 13:40

[[F]2404-4pm-02]

マロン酸エステル合成の重合反応への展開: 炭素鎖ポリマーの繰り返し構造の精密制御

○松岡 慶太郎[1,2]、目野 泰地[2]、相内 達真[3]、土屋 竣資[2]、佐田 和己[1,2] (1. 北大院理、2. 北大院総化、3. 北大理)

日本語
13:40 ~ 14:00

[[F]2404-4pm-03]

セルロース熱分解物から誘導したエポキシドを用いた新規高分子の合成

○綾川 陽斗[1]、高 添 [2]、山本 拓矢[2]、李 灃[2]、磯野 拓也[2]、佐藤 敏文[2,3] (1. 北大院総合、2. 北大院工、3. 北大ICReDD List-PF)

14:00 ~ 14:10

休憩

英語
14:10 ~ 14:30

[[F]2404-4pm-04]

2,6-ジヒドロキシベンゾエートから誘導される高活性ニッケル触媒を用いた種々の不飽和モノマーの配位重合挙動

○Yao Taidong[1]、一二三 遼祐[1]、冨田 育義[1] (1. 東京科学大学)

英語
14:30 ~ 14:50

[[F]2404-4pm-05]

ビニルボロン酸誘導体の立体特異的ラジカル重合による立体規則性PVAの自在合成

○鈴木 宏史[1]、西川 剛[1]、大内 誠[1] (1. 京大院工)

日本語
14:50 ~ 15:10

[[F]2404-4pm-06]

末端に水酸基を持つ多分岐ポリアクリレートのラジカル重合による構造制御合成とその物性

○仝 天翔[1]、登阪 雅聡[1]、松宮 由実[1]、渡辺 宏[1]、山子 茂[1] (1. 京大化研)

半導体高分子の精密合成と有機エレクトロニクス材料への応用

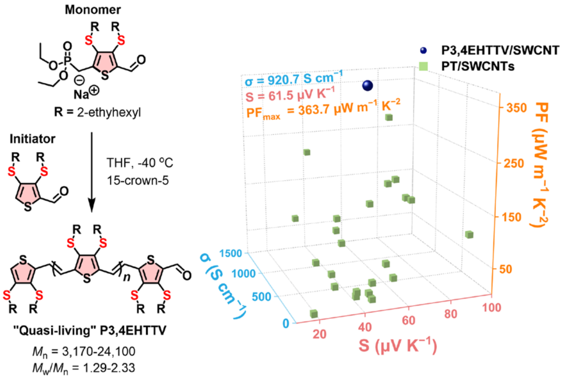
（山大院有機 [1]・台湾大材料 [2]）○東原 知哉 [1]・西山 浩哉 [1]・劉振良 [2]

Controlled Synthesis of Semiconducting Polymers Suited for Organic Electronics

([1]*Graduate School of Organic Materials Science, Yamagata University*, [2]*Department of Materials Science and Engineering, National Taiwan University*) ○Tomoya Higashihara,[1] Koya Nishiyama,[1] Cheng-Liang Liu,[2]

Semiconducting polymers are lightweight, low cost, and easy to manufacture, making them promising candidates for application in electronic devices. In this study, poly(thienylene vinylene) (PTV) with alkylthio side chains, poly[3,4-bis(2-ethylhexylthio)thienylene vinylene] (P3,4EHTTV), was successfully synthesized using an environmentally friendly polymerization system employing neither transition-metal catalysts nor halogens. The polymerization proceeded *via* a chain-growth mechanism, exhibiting a “quasi-living” nature. P3,4EHTTV was then combined with single-walled carbon nanotube (SWCNT) to fabricate nanocomposite thin films with thermoelectric (TE) properties. The P3,4EHTTV/SWCNT composite system showed favorable charge distribution and improved alignments in the energy levels, contributing to considerably improved TE properties, with a record-breaking power factor of 363.7 μW m^{-1} K^{-2}. These findings highlight the importance of structural design in PTV and alkylthio side-chain engineering for optimizing TE performance.

Keywords : Semiconducting Polymer; Living Polymerization; Environmentally Friendly; Carbon Nanotube; Thermoelectric.



★ Chain-growth condensation polymerization system
★ Excellent dispersant for SWCNT
★ High performance as thermoelectric materials

本研究では、遷移金属触媒やハロゲンを用いない環境に優しい縮合的連鎖重合法に基づき、アルキルチオ側鎖を有するポリ［3,4-ビス（2-エチルヘキシルチオ）チエニレンビニレン］（P3,4EHTTV）を精密合成することに初めて成功した [1)]。P3,4EHTTV と単層カーボンナノチューブ（SWCNT）とからなるナノコンポジット薄膜を用いた有機熱電変換素子を作製・評価したところ、半導体高分子/CNT 系ナノコンポジット材料における世界最高水準のパワーファクター値（363.7 μ W m^{-1} K^{-2}）を示し、本開発ポリマーが高い熱電変換機能を有する SWCNT 分散材料として有望であることが分った。

1) Environmentally Friendly Controlled Synthesis of Poly(thienylene vinylene) with Alkylthio Side Chains and Application to Thermoelectric Materials. K. Nishiyama, Y.-T. Hsiao, W.-N. Wu, J.-M. Lin, S.-H. Tung, C.-L. Liu, T. Higashiharaa, *J. Mater. Chem. A* **2024**, *12*, in press.

マロン酸エステル合成の重合反応への展開: 炭素鎖ポリマーの繰り返し構造の精密制御

（北大院理 [1]・北大院総化 [2]・北大理 [3]）○松岡 慶太郎 [1]・目野 泰地 [2]・相内 達真 [3]・土屋 竣資 [2]・佐田 和己 [1,2]

Expansion of Malonic Ester Synthesis into Polymerization Reaction: Precise Control of Repeating Unit in Carbon Chain Polymers

([1]*Faculty of Science, Hokkaido University*, [2]*Graduate School of Chemical Sciences and Engineering, Hokkaido University*, [3]*School of Science, Hokkaido University*) ○ Keitaro Matsuoka[1,2], Taichi Meno[2], Tatsuma Aiuchi[3], Shunsuke Tsuchiya[2], Kazuki Sada[1,2]

Carbon chain polymers with backbones composed of sp^3 carbon-carbon bonds could be designed for their function by controlling the number of backbone carbons and the arrangement of side chains in repeating units. Although various polymerization reactions have been developed, it has remained challenging to precisely control the spacing and arrangement of side chains within the repeating units. In this study, we developed the malonic ester synthesis-type polymerization method to control the backbone carbon numbers one by one. Malonic ester synthesis, the nucleophilic substitution reaction of malonate and haloalkane, is one of the classical sp^3 carbon-carbon bond formation reactions in organic synthesis. Polycondensation reaction of the dimalonic ester monomers and the dibromoalkane monomers with NaH afforded carbon chain polymers (up to M_n=2.8×10^4). In the presentation, details of the polymerization reaction and control of the repeating structure will be discussed.

Keywords : Malonic Ester Synthesis, Polymerization, Precise Control, Repeating Unit, Sequence

ビニルポリマーに代表される主鎖が sp^3 炭素-炭素結合からなる炭素鎖ポリマーは、繰り返し構造の主鎖炭素数/側鎖配置を制御することで機能が設計される。これまでに、合成可能な繰り返し構造の範囲を拡張すべく様々な重合反応が開発されてきたが、繰り返し構造における側鎖の間隔や配列を精密に制御することは依然として困難だった。本研究では、繰り返し構造の主鎖炭素数が炭素 1 個単位で制御された炭素鎖ポリマーの合成を目指し、マロン酸エステル合成型重合法を開発した。マロネートとハロアルカンの求核置換反応であるマロン酸エステル合成は、有機合成化学における古典的な sp^3 炭素-炭素結合形成反応である [1)]。ジマロン酸エステルモノマーとジブロモアルカンモノマーを NaH 存在下重縮合させることで、最大 M_n=2.8×10^4 程度の炭素鎖ポリマーが得られた。発表では、重合反応の詳細や繰り返し構造の制御について議論する。

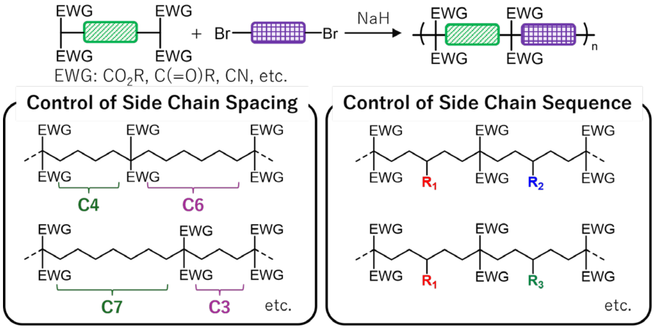


Figure 1. Malonic Ester Synthesis-type Polymerization with controllable spacing and sequence of side chains.

1) Gao, L.; Cong, H. *et al. RSC. Adv.* **2019**, *9*, 40455.

セルロース熱分解物から誘導したエポキシドを用いた新規高分子の合成

（北大院総合[1]・北大院工[2]・北大 ICReDD List-PF[3]）○綾川 陽斗[1]・髙 添乐[2]・山本 拓矢[2]・李 澧[2]・磯野 拓也[2]・佐藤 敏文[2]

Synthesis of Novel Polymers with the Epoxide Derived from Cellulose Pyrolysate

([1]*Grad. Sch. of Chem. Sci. Eng., Hokkaido Univ.*, [2]*Faculty of Eng., Hokkaido Univ.*, [3]*ICReDD List-PF, Hokkaido Univ.*) ○Hiroto Ayakawa,[1] Tianle Gao,[2] Takuya Yamamoto,[2] Feng Li,[2] Takuya Isono,[2] Toshifumi Satoh[2,3]

In this research, we aim to develop functional polymer materials by utilizing naturally abundant non-edible biomass resources. As shown in Figure 1, a novel class of epoxide monomers was synthesized through a one-step Corey-Chaykovsky reaction using cellulose-derived compounds, levoglucosenon (LGO) and dihydrolevoglucosenon (Cyrene™). The resulting epoxide monomers underwent ring-opening polymerization (ROP) to produce polyethers, as well as ring-opening alternating copolymerization (ROAC) with cyclic anhydrides to yield polyesters. Both polymerization systems were achieved in a well-controlled manner. The bicyclic acetal structure in the monomers not only serves as a bulky moiety, contributing to the high glass transition temperatures of the polymers, but also offers potential for further post-polymerization modification.

Keywords : Biomass; Epoxide; Polymerization; Polyether; Polyester

本研究では天然に豊富に存在する非可食バイオマス資源を用いた機能性高分子材料の合成を目的とした。Figure 1 に示すように、セルロース由来の化合物であるレボグルコセノン (LGO) とジヒドロレボグルコセノン (Cyrene™) を用いて、一段階のコーリー-チャイコフスキー反応により新規エポキシドモノマーを合成した。得られたエポキシドモノマーから、開環重合によりポリエーテルを、環状無水物との開環交互共重合によりポリエステルを生成した。モノマーの嵩高い二環式アセタール構造は、ガラス転移温度の上昇に寄与するだけでなく、重合後の変換反応にも応用可能である。

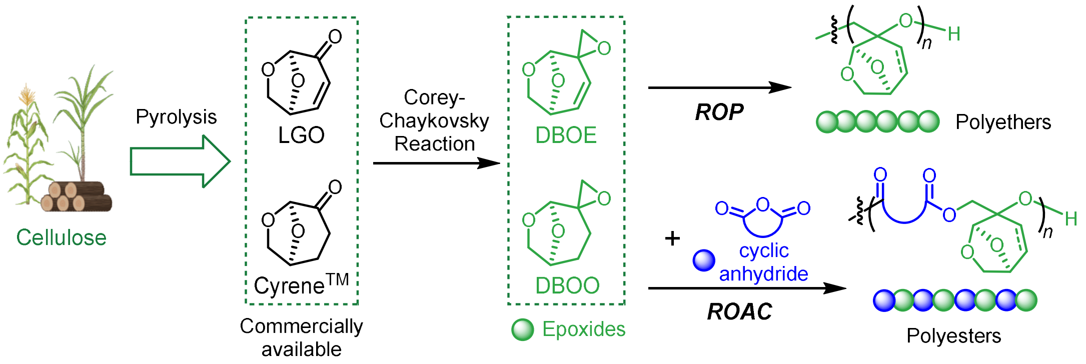


Figure 1. The outline of this research.

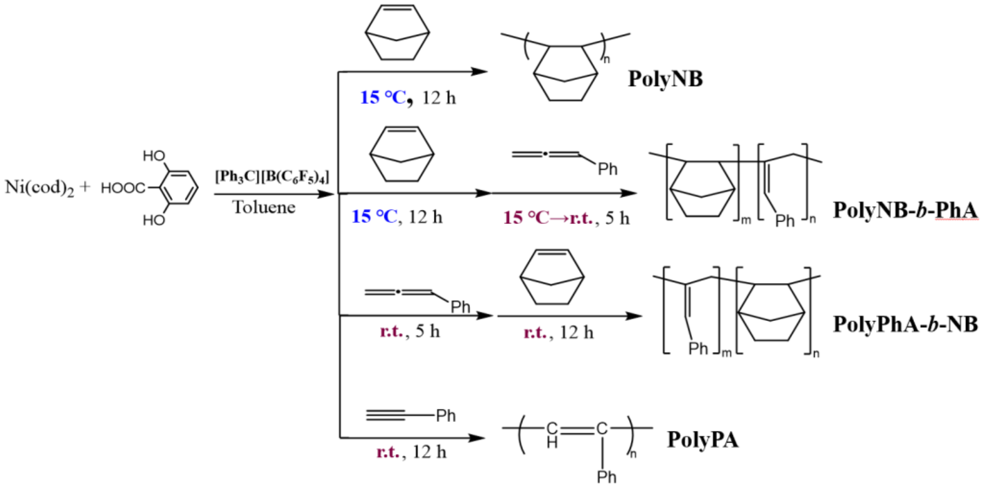
Coordination Polymerization Behavior of Various Unsaturated Monomers by Highly Active Nickel Catalysts Derived from 2,6-Dihydroxybenzoate

([1]*School of Materials and Chemical Technology, Institute of Science Tokyo*)
○Taidong Yao,[1] Ryoyu Hifumi,[1] Ikuyoshi Tomita[1]

Keywords: *Coordination polymerization, Nickel catalysts, Unsaturated Monomers, Norbornenes, Acetylene Derivatives*

Coordination polymerization of unsaturated monomers such as norbornene (NB), allene, diene, and acetylene derivatives have drawn attention due to the excellent performance and functions of the resulting polymers suitable for versatile applications. For example, polynorbornene features a rigid cyclic structure with excellent thermal stability and optical properties, polyacetylenes with rigid π-conjugated backbones provides optoelectronic functions, and so on.[1,2] Accordingly, catalyst systems capable of conducting the coordinating polymerization of various unsaturated monomers holds significant industrial and scientific implications.

We have described that the nickel-catalyzed living coordination polymerization of allenes can produce well-defined polymers containing various functional groups.[3] Additionally, nickel catalysts bearing 2,6-dihydroxybenzoate ligands efficiently accelerate the living coordination polymerization.[4] Herein, on the basis of the highly active nickel catalysts, we described the polymerization of NB and the copolymerization of NB and phenylallene (PhA) in the presence of a small amount of co-catalysts such as $[Ph_3C][B(C_6F_5)_4]$ (Scheme 1). The living polymerization of NB can take place accompanying the nice control of the molecular weight even with larger amounts of NB (500~1000 equiv.) to produce polymers in high yields (Scheme 1). Further, the block copolymers of NB and PhA were obtained effectively through a living mechanism irrespective of the order of monomer additions. The polymerization behavior of other unsaturated monomers such as acetylene derivatives will also be described.



Scheme 1 Coordination (co)polymerization of unsaturated monomers by Highly Active Nickel Catalysts

1) M.V. Bermeshev, P.P. Chapala, *Prog. Polym. Sci.*, **84**, 1 (**2018**). 2) Eugene Y-X. Chen, *Chem. Rev.*,**109**, 5157 (**2009**). 3). T. Kino, M. Taguchi, A. Tazawa, I. Tomita, *Macromolecules*, **39**, 7474 (2006). (4) (a) I. Tomita, K. Kikuchi, *Polym. Prepr.. Jpn.*, **56**, 2547 (2007). (b) T. Shono, I. Tomita, *The 90th Ann. Meeting Chem. Soc. Jpn.*, 2G4-17 (2010).

Versatile Synthesis of Tacticity-Controlled PVA via Stereospecific Radical Polymerization of Vinylboronic Acid Derivatives

(*Graduate School of Engineering, Kyoto University*) ○Hiroshi Suzuki, Tsuyoshi Nishikawa, Makoto Ouchi

Keywords: *Boron, Radical Polymerization, Post-Polymerization Transformation, Tacticity, Poly(vinyl alcohol)*

Poly(vinyl alcohol) (PVA), a widely used synthetic polymer bearing hydroxy groups on the main chain, exhibits unique properties such as hydrophilicity and crystallinity. The tacticity is known to have a huge impact on the properties, and a considerable effort has been devoted for the stereoselective radical polymerization of vinyl acetate (VAc) and their derivatives, which are typical precursor monomers of PVAs.[1] However, rigorous condition such as cryogenic temperature is needed for tacticity control, and thus the comprehensive control over the primary structures (e.g., tacticity and molecular weight) still remains challenging.

Recently, we revealed that radical (co)polymerization of alkenyl boronates and post-polymerization oxidation of boron pendant to synthesize various PVA derivatives.[2] Given the tunable reactivity of organoboron compounds by boron protecting-group, we came up with exploration of the boron-protecting group design in vinylboron monomers for controlling the resultant polymer structure. In this work, we designed various monomers protected by anthranilamides bearing various alkyl groups on the nitrogen atom of the amide group toward synthesis of tacticity-controlled PVA via radical polymerization and subsequent oxidation (Figure 1). Consequently, tacticity of the obtained PVAs was dependent on the alkyl group: bulky alkyl substituents such as isobutyl and neopentyl groups afforded isotactic PVAs in contrast to small ones such as methyl and *n*-butyl leading to atactic tacticity. Interestingly, tetrahydrofurfuryl group-containing monomer allowed regulation of syndiotacticity. In the presentation, the mechanism of tacticity control and the stereospecific controlled polymerization for comprehensive structural control will be also described.

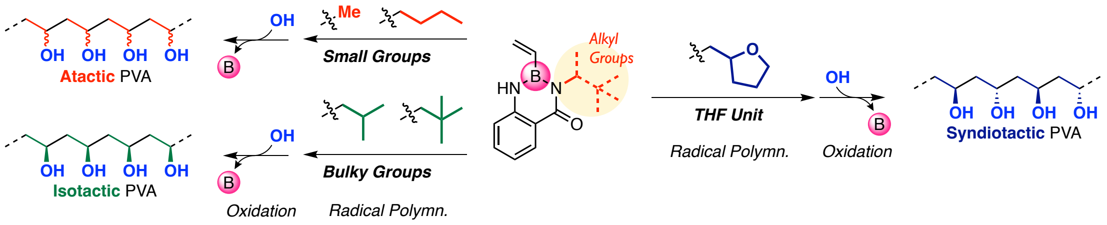


Figure 1. Design of protecting group in vinylboron monomers for syntheses of tacticity-controlled PVAs.

1) K. Satoh, M. Kamigaito, *Chem. Rev.* **2009**, *109*, 5120-5156. 2) T. Nishikawa, *Polym. J.*, **2024**, *56*, 873-886..

末端に水酸基を持つ多分岐ポリアクリレートのラジカル重合による構造制御合成とその物性

（京大化研 [1]）○仝 天翔 [1]、登阪 雅聡 [1]、松宮 由実 [1]、渡辺 宏 [1]、山子 茂 [1]

Synthesis of structurally controlled hyperbranched polyacrylate with end hydroxyl groups by radical polymerization and their properties

([1]Institute for Chemical Research, Kyoto University) ○TIANXIANG TONG[1], Masatoshi Tosaka[1], Yumi Matumiya[1], Hiroshi Watanabe[1], Shigeru Yamago[1]

The formation of condensed polymer materials has relied exclusively on the “entanglement” of linear polymer chains until now. In contrast, we became interested in the possibility of reversible formation and degradation of polymer materials by using end-functionalized hyperbranched polymers (HBPs), which have limited entanglement with multiple polymer-end groups. Therefore, we have synthesized end-functionalized HBPs (Figure 1) based on the recently reported method developed by our group and have examined their properties[1]. As a result, this HBP reversibly forms polymer materials through the interaction of the terminal functional groups. We also found that this HBP also exhibits high self-healing properties.

Keywords: Hyperbranched polymer; Organotellurium-mediated radical polymerization; End-group interaction; Polymer recycling; Self-healing polymers

これまで凝縮系高分子材料の形成は、線状高分子鎖の「絡み合い」が専ら利用されてきている。しかし、その方法の限界がプラスチック問題として顕在化してきている。すなわち、絡み合った高分子鎖を高分子一分子へとリサイクルできないことから、高分子材料のリサイクルは破壊・分離に基づく物理的リサイクル法と、モノマーまで分解する高エネルギープロセスである化学的リサイクル法に限られている。我々は、絡み合いが限定的である多分岐ポリマー（HBP）に多数存在する末端基の相互作用を利用することで、可逆的に高分子材料の形成と分解を行える可能性に興味を持った。そこで、最近報告した制御ラジカル重合法 TERP を用いる HBP 合成法を用い[1]、HBP 末端に水酸基を導入したブロック共重合体を合成した（図 1）。その結果、この HBP が末端官能基の相互作用により、可逆的に凝縮状態を形成すると共に、高い自己修復性を示すことを明らかにしたので報告する。

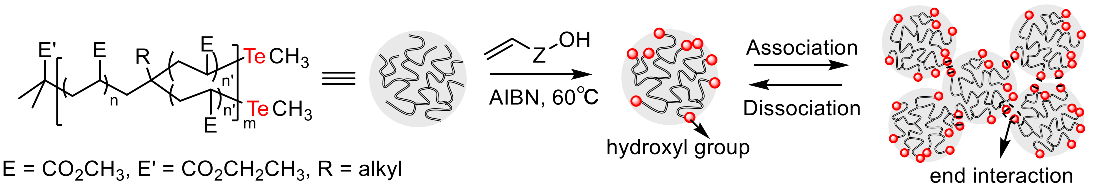


図 1. TERP により合成した HBP を用いる可逆的な高分子材料創製

[1] a) Yamago, S. *Polymer J.*, **2021**, *53*, 847. b) Lu, Y. *et. al. Nat. Commun.* **2017**, *8*, 1863. c) Tosaka, M. et. al. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305127. d) Jiang, Y. *et. al.Angew. Chem. Int. Ed.* **2023**, *62*, e202306916. e) Tong, T. et al., *Polymer Prepr. Jpn*. **2024**, *73*, 2C16.