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研究課題名（和文） Synergistic catalysis for the sustainable synthesis of semiconducting polymers

研究課題名（英文） Synergistic catalysis for the sustainable synthesis of semiconducting polymers

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研究成果の概要（和文）：近年、半導体ポリマーは、OLED、OFET、OPV、さらに生物医学センサーやバイオエレクトロニクスへの応用に大きな関心を集めています。しかし、これらの材料の合成はコストと時間がかかり、環境的に持続不可能です。私たちはCDC重合とKCTPを用いて合成効率を向上させました。主な成果は、テトラフルオロベンゼンと組み合わせたフランやチオフェンと組み合わせたジフルオロベンゾチアジアゾールなどの新モノマーの特定、5倍の速度加速を実現するDA型モノマーの開発です。これにより、半導体ポリマーの効率的で持続可能な合成プロセスが可能となり、有機電子デバイスの性能向上に貢献します。

研究成果の学術的意義や社会的意義

Our research enhances the synthesis of semiconducting polymers, crucial for applications in OLEDs, OFETs, OPVs, and bioelectronics. Our findings improve efficiency, cost-effectiveness, and sustainability, driving broader and enhanced applications in organic electronics.

研究成果の概要（英文）：Semiconducting polymers are crucial for organic electronics like OLEDs, OFETs, OPVs, and biomedical sensors. Recent advancements stem from complex polymer syntheses, often costly and unsustainable. Our research focused on improving synthesis through cross-dehydrogenative coupling (CDC) and KCTP.
Key achievements: (1) Monomer Scope Expansion: New monomers, such as furan with tetrafluorobenzene and difluorobenzothiadiazole with thiophene, for CDC polymerization, (2) Donor-Acceptor Monomers: DA-type monomers for living polymerization, enhancing scalability and environmental friendliness, with a 5x rate increase over traditional methods, (3) Kinetics Understanding: Highlighted the impact of monomer structure on reactivity, emphasizing the need for accurate kinetic data for better copolymer design.
These insights are crucial for efficient, cost-effective, and sustainable synthesis processes, enhancing the performance of semiconducting polymers in organic electronics.

研究分野： Polymerization mechanisms of conjugated polymers

キーワード： Polymers　Conjugated Polymers　Semiconducting Polymers　CH activation　Polymerization kinetics　KCTP　CDC　OECTs

１．研究開始当初の背景

In recent years, semiconducting polymers have attracted much interest in a wide range of applications in organic electronics, including organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and more recently, in biological applications including biomedical sensors and bioelectronics. We have now reached a stage where the quantum efficiencies of OLEDs outperform those of inorganic LEDs, the highest charge mobilities reached are 24 cm^2/Vs for polymer-based FETs, and massive growth has been observed in the power conversion efficiencies of OPVs where 18% has been achieved. The advances made in performance of these materials can largely be attributed to the synthesis of ever more complex polymers, which can be costly, time consuming, and environmentally unsustainable. Another issue related to the synthesis of complex polymers is the introduction of defects, e.g., homocoupling, that can occur.

To address the issues related to environmentally sustainability, several research groups have focused on adopting C-H functionalization, using green solvents, replacing the toxic and scarce metal catalysts with earth abundant first row transition metal catalysts, reducing energy consumption in the synthesis, and using naturally sourced building blocks. To address the issue of defects, several research groups have explored the development of monomers and catalysts to reduce the defects, but have also investigated controlled/living polymerizations to control molecular weights.

I aimed to tackle both issues – I sought to develop synthetic methodologies of semiconducting polymers that improve environmental sustainability while also achieving higher degree of control over sequence specificity, and ultimately, molecular weight in the synthesized polymers.

２．研究の目的

In recent years, direct arylation polymerization (DArP) has attracted significant interest as a more atom economical approach to synthesize semiconducting polymers. Typically, semiconducting polymers are synthesized using metal-catalyzed cross-coupling reactions such as Stille, Suzuki-Miyaura, Negishi, and Kumada coupling reactions (Figure 1 – middle arrows). In DArP, only one of the coupling partners needs to be functionalized (i.e., halogenated) and one can avoid the pre-metalation step, reducing the total number of steps required to synthesize the polymers, and eliminating the need to use a stoichiometric amount of a(n) (organo)metallic reagent (Figure 1 – top arrow). In this project, I aimed to go one step further by investigating cross-dehydrogenative coupling (CDC) reactions, commonly also referred to as oxidative C-H/C-H coupling or Oxi-DArP (Figure 1 – bottom arrow). CDC polymerizations completely eliminate the need to prefunctionalize the monomers making the synthesis even more atom economical.

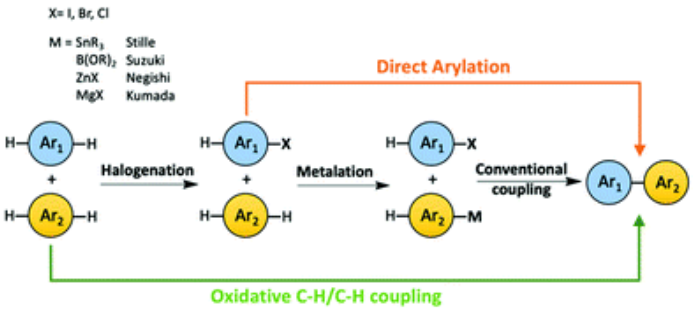

Figure 1. Schematic comparison of conventional cross-coupling, direct arylation, and oxidative C-H/C-H coupling to synthesize organic semiconductors

CDC polymerizations, however, have added complications compared to conventional coupling methods and DArP. Specifically, chemo- and regioselectivity become of greater concern and care must be taken to avoid homocoupling and to ensure only cross-coupling occurs. Thus far, limited studies have been published on this topic. Monomer scope remains highly limited, and no study has reported molecular weight control using CDC polymerization.

A secondary goal of this project was to conduct a comprehensive and quantitative comparison of the copolymerization kinetics in the Kumada catalyst-transfer polymerization (KCTP) of polythiophenes. Specifically, the research focused on measuring the reactivity ratios and polymerization rate constants of 3-hexylthiophene with various thiophene comonomers. By adapting the Mayo-Lewis equation and analyzing the first-order kinetic behavior of the chain polymerization, the study aims to provide detailed kinetic information that highlights the significant impact of monomer structure on reactivity. This data is crucial for accurately predicting the copolymer structures formed during equimolar batch copolymerizations, allowing for better experimental design and more precise control over the synthesis of copolymers. Furthermore, the project sought to understand how different monomer structures influence the overall polymerization process, which is vital for the design of copolymers with desired properties. The investigation includes characterizing the monomer consumption rate and the resulting copolymer structure, thus verifying the obtained reactivity values. The ultimate aim is to enhance the efficiency of polymer synthesis by reducing the trial-and-error approach currently prevalent in the field. By providing a systematic and quantitative study of the kinetic behavior of thiophene monomers, the research contributes to the development of more efficient, cost-effective, and sustainable synthetic processes for producing high-performance semiconducting polymers.

A final goal of the paper was to elucidate the mechanistic influences of ethylene glycol side chains on the polymerization process of glycolated polythiophenes, particularly focusing on the formation of the active Grignard monomer species during Kumada catalyst-transfer polymerization (KCTP). The study aims to understand how the content, length, and proximity of oxygen atoms in the ethylene glycol side chains affect the polymerization kinetics and the resulting polymer structure and properties. By investigating these parameters, the research seeks to develop a reproducible and efficient synthetic strategy for high-performing organic electrochemical transistor (OECT) materials, specifically targeting the synthesis of P3MEEMT with controlled molecular weight and regioregularity

３．研究の方法

KCTP Kinetics

Homopolymerisation Kinetics Studies via NMR

The kinetics of homopolymerization were studied using 1H-NMR. Monomer 3HT was mixed with an internal standard (TMB), degassed, and dissolved in anhydrous THF under nitrogen. The polymerization was initiated by adding i-PrMgCl and Ni(dppp)Cl_2 at room temperature. Aliquots were taken at various time intervals, quenched with HCl, extracted with chloroform, and analyzed using 1H-NMR to determine the degree of polymerization.

Copolymerisation Kinetics Studies via GC-MS

For copolymerization studies, different ratios of monomers 3HT and 3DDT were prepared and reacted with i-PrMgCl in THF. The reaction mixture was stirred and aliquots were taken at specific intervals, quenched, and analyzed by GC-MS to study monomer consumption and polymer composition.

Equimolar Batch Copolymerisation

Equimolar mixtures of monomers (e.g., 3HT and 3DDT) were degassed, dissolved in THF, and reacted with i-PrMgCl. Ni(dppp)Cl_2 was then added to initiate polymerization. The reaction was monitored by taking aliquots at different times, quenching with HCl, and extracting with chloroform. The resulting copolymers were characterized using NMR, GC-MS, and MALDI-TOF to validate copolymer structures and compositions.

Characterization of Monomer Consumption and Copolymer Structure

Monomer consumption during polymerization was monitored using NMR and GC-MS. The copolymer structures were characterized using MALDI-TOF mass spectrometry and the composition was confirmed by comparing the relative intensities of specific peaks corresponding to different monomer units.

Examination of Failed Chain Polymerisation

To investigate failed polymerizations, dispersity changes and molecular weight growth were studied. Homopolymers and copolymers were synthesized and characterized by MALDI-TOF to understand the differences in polymerization kinetics and to explore the impact of steric hindrance and other structural factors on polymerization.

P3MEEMT Study

Grignard Metathesis Reaction

The active Grignard monomer was obtained in situ from the dihalomonomer via Grignard metathesis with isopropylmagnesium chloride (iPrMgCl) in THF. The reaction conditions were optimized to achieve high regioselectivity for the formation of the desired isomer. The Grignard metathesis reaction was carried out in the presence of a turbo Grignard reagent to enhance the completeness of the Mg/Br exchange reaction.

Polymerization Studies

Polymerization of the monomers was conducted using KCTP with Ni(dppe)Cl_2 as the catalyst. Polymerization studies were performed at room temperature with varying monomer concentrations to determine the optimal conditions for controlled polymerization. The kinetics of the polymerization process was monitored by taking aliquots at different time intervals and analyzing them using gel permeation chromatography (GPC) to determine the molecular weight and dispersity of the resulting polymers.

Characterization

The polymers were characterized using 1H NMR spectroscopy and GPC. The molecular weight and dispersity were determined relative to polystyrene standards using THF as the eluent. Additional characterization included MALDI-TOF mass spectrometry to analyze the end groups and polymer composition, as well as GC-MS for monomer consumption rates during copolymerization.

４．研究成果

CDC Study

The key findings from the CDC study are as follows:

Expansion of monomer scope that can be used in the CDC polymerization. One new donor monomer (furan) paired with tetrafluorobenzene and one new acceptor (difluorobenzothiadiazole) paired with thiophene have been identified.

Development of donor-acceptor (DA monomers) to facilitate the transition towards achieving a living polymerization. In addition to atom economy, minimizing time and energy input in the synthetic process of D-A semiconducting polymers is an essential part of improving the environmental friendliness and scalability of D-A semiconducting polymer production. Based on our prior results that a rate enhancement was observed as the chain extended, DA-type monomers were synthesized hypothesizing that these would lead to more rapid polymerizations. The data show that the DA-type monomer leads to a rate acceleration of 5x compared to the polymerization of a D monomer and an A monomer.

KCTP Kinetics Study

The study investigated the copolymerization kinetics of polythiophenes using Kumada catalyst-transfer polymerization (KCTP), focusing on 3-hexylthiophene (3HT) and four thiophene comonomers: 3-dodecylthiophene (3DDT), 3-(6-bromo)hexylthiophene (3BrHT), 3-(2-ethylhexyl)thiophene (3EHT), and 3-(4-octylphenyl)thiophene (3OPT) (Figure 2). The reactivity ratios and polymerization rate constants were measured using the Mayo-Lewis equation and first-order kinetic behavior. The study aimed to understand the impact of monomer structure on reactivity and predict copolymer structures accurately. The results highlighted the necessity of accurate kinetic data for better copolymer design and revealed significant differences in reactivity based on monomer structure.

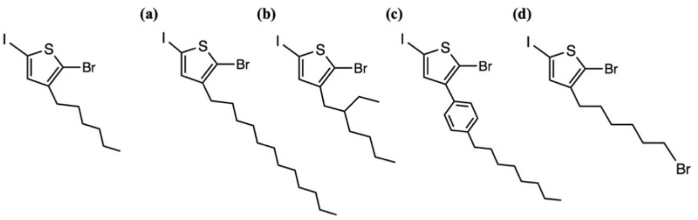

Figure 2. Thiophene monomer structures. (a) 2-bromo-3-dodecyl-5-iodothiophene (3DDT); (b) 2-bromo-3-(2-ethylhexyl)-5-iodothiophene (2EHT); (c) 2-bromo-3-(4-octylphenyl)-5-iodohtiophene (3OPT); (d) 2-bromo-3-(6-bromohexyl)-5-iodothiophene (3BrHT)

The homopolymerization kinetics showed that monomers with linear side chains (3HT, 3DDT, 3BrHT) had similar rate constants, while 3OPT exhibited significantly lower reactivity due to steric hindrance from the phenyl ring. 3EHT failed to homopolymerize at room temperature, requiring elevated temperatures for successful polymerization. These findings demonstrated that increasing side chain steric hindrance lowers the homopolymerization rate constants, affecting the overall polymerization behavior.

In copolymerization studies, 3DDT and 3BrHT displayed nearly equivalent reactivity with 3HT, resulting in random copolymers. The reactivity ratios for 3HT:3EHT and 3HT:3OPT indicated preferential consumption of 3HT over the bulkier comonomers, leading to gradient copolymers and highlighting the challenges in achieving controlled copolymerization with bulky monomers. The study also identified the need to build up a 3HT block before introducing 3EHT in semi-batch polymerizations for better control over the copolymer structure.

Characterization of the copolymers using NMR, GC-MS, and MALDI-TOF confirmed the predicted structures based on the kinetic data. For instance, the 3HT:3DDT copolymer showed a random distribution, while the 3HT:3EHT copolymer exhibited a gradient composition. The study emphasized the importance of understanding the impact of monomer structure on polymerization kinetics for efficient design and synthesis of semiconducting polymers. Future research will focus on optimizing experimental conditions, such as temperature and catalyst selection, to improve the control and efficiency of polymerization processes involving bulky comonomers.

P3MEEMT Study

The study explored the influence of ethylene glycol side chains on the polymerization kinetics of glycolated polythiophenes, particularly focusing on 3MEEMT, a high-performing OECT material. The results showed that the polymerization of P3MEEMT via KCTP is highly sensitive to monomer concentration, with a minimum of 0.15 M required to obtain the polymer. Below this concentration, no polymerization occurred, indicating the critical role of monomer concentration in achieving successful polymerization. This sensitivity highlights the challenges in synthesizing glycolated polythiophenes compared to other polythiophenes, like P3HT.

The study also investigated the Grignard metathesis step, crucial for forming the active monomer species. The presence of ethylene glycol side chains significantly influenced the regioselectivity of the Mg/Br exchange reaction. For instance, 3MEEMT produced two regioisomers in a 1:2 ratio (Table 1), whereas monomers with modified side chains, like 3MEEBT and 3PAAT, showed improved selectivity. The study found that using a turbo Grignard reagent (iPrMgCl.LiCl) enhanced the completeness of the Mg/Br exchange, crucial for subsequent polymerization steps. However, the presence of water scavengers adversely affected polymerization, underlining the need for careful control of reaction conditions.

Table 1. Overview of regioisomers formed upon Grignard metathesis with monomers.

	A (%)	B (%)	Unexchanged Monomer (%)
2,5-dibromo-3-hexylthiophene	80	20	NA
3MEEMT	28[a]	56[a]	15[a]
	35[b]	65[b]	NA
3PAAT	49	51	NA
3MEEBT	75	25	NA

[a] upon metathesis with *i*PrMgCl

[b] upon metathesis with *i*PrMgCl.LiCl for 2 h.

Polymerization studies revealed that the polymerization of 3MEEMT is extremely fast, leading to uncontrolled chain growth. This behavior contrasts with the controlled synthesis typically observed in the polymerization of poly(3-hexylthiophene) (P3HT). GPC analysis showed a rapid decline in the number average molecular weight (Mn) after just one minute, with the appearance of insoluble material after ten minutes. This suggests that the coordination of oxygen atoms in the ethylene glycol side chain with Li or Mg may play a role in the rapid polymerization kinetics, potentially leading to a radical-mediated polymerization pathway.

Overall, the study provided critical insights into the polymerization mechanisms of glycolated polythiophenes. The findings emphasize the importance of controlling monomer concentration and reaction conditions to achieve successful polymerization. These insights are crucial for developing efficient synthetic strategies for high-performance OECT materials, with the potential to enhance the performance and reproducibility of organic electronic devices.

５．主な発表論文等

〔雑誌論文〕　計3件（うち査読付論文　3件／うち国際共著　2件／うちオープンアクセス　3件）

１．著者名 Bakry, A.; Yadav, P.; Chen, S. Y.; Luscombe, C.K.	４．巻 250
２．論文標題 The unexpected fast polymerization during the synthesis of a glycolated polythiophene	５．発行年 2024年
３．雑誌名 Faraday Discussions	６．最初と最後の頁 74-82
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D3FD00146F	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

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オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

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７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
米国	Stanford University	Cornell University	University of Chicago	他3機関