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28日(金) 15:55 ~ 17:15 [F]2404(第4学舎 2号館 [4階] 2404)

[[F]2404-3vn] 18. 高分子

座長：古賀 智之、高橋 明

日本語
15:55 ~ 16:15
[[F]2404-3vn-01]

5員環環状ケテンアセタールと自己組織化ペプチドマクロモノマーのラジカル開環共重合挙動の検討

○西村 慎之介[1]、Miki Hasegawa[1]、上田 捷也[1]、古賀 智之[1] (1. 同志社大学)

日本語
16:15 ~ 16:35
[[F]2404-3vn-02]

MOFのナノ空間を利用した高分子束状構造の構築

○亀谷 優樹[1]、植村 卓史[1] (1. 東大院工)

英語
16:35 ~ 16:55
[[F]2404-3vn-03]

ポリマーメカノラジカルと1,1-ジアリールエチレン誘導体のメカノケミカル酸化開裂反応

○小髙 彬[1]、杉田 一[1]、高橋 明[1]、大塚 英幸[1] (1. 東京科学大学)

英語
16:55 ~ 17:15
[[F]2404-3vn-04]

耐熱性を有する蛍光性メカノフォアの開発とメカノクロミックポリマーへの応用

○内田 優斗[1]、杉田 一[1]、高橋 明[1]、大塚 英幸[1] (1. 科学大物質理工)

5 員環環状ケテンアセタールと自己組織性ペプチドマクロモノマーのラジカル開環共重合挙動の検討

(同志社大理工 [1]) ○西村 慎之介 [1]・ミキ ラウノイス ハセガワ [1]・上田 捷也・古賀 智之 [1]

Radical Ring-Opening Polymerization of Five-Membered Cyclic Ketene Acetal with Self-Assembling Peptide Macromonomer ([1]*Faculty of Science and Engineering, Doshisha University*) ○Shin-nosuke Nishimura,[1] M. L. Hasegawa,[1] K. Ueda,[1] Tomoyuki Koga[1]

In this study, we demonstrate the novel synthesis of a self-assembling peptide-grafted polyesters. The graft copolymers were prepared via radical ring-opening polymerization (RROP) of 2-methylene-1,3-dioxolane (C5), a five-membered cyclic ketene acetal, and tetraleucine peptide macromonomers (MA-Leu$_4$-Am) with various feed compositions, and their structures were characterized by ^{1}H NMR, SEC, and FT-IR analyses. The ring-opening ratio (R_{op}) of C5 units were almost constant at 70–85% regardless of the feed compositions. In contrast, the values of the grafting ratio of the peptide chain (G_{r}) were remarkably higher than the values calculated from the feed composition of C5 and MA-Leu$_4$-Am ($G_{\mathrm{r,feed}}$), reflecting their monomer reactivities. To characterize the copolymerization behavior in detail, density functional theory (DFT) calculations were performed to elucidate the copolymerization mechanisms. These calculations demonstrated that radicals derived from C5 preferentially react with the peptide macromonomer, which was supported by the calculated reaction rate constants and monomer reactivity ratios.

持続可能な開発目標 (SDGs) の観点から、汎用高分子に置き換わるバイオマス由来の生分解性ポリエステルの開発が近年重要な課題となっている。本研究では、生分解性高分子の機能化を念頭に、自己組織化ペプチドをグラフトに有するポリエステルを新規に設計した (Figure 1)[1)]。テトラロイシンペプチドマクロモノマー (MA-Leu$_4$-Am) をコモノマーに用いた 2-メチレン-1,3-ジオキソラン (C5) のラジカル開環重合 (RROP) によって合成した。得られたポリマーの構造ならびに分子量は ^{1}H NMR、SEC、FT-IR 分析により評価した。ポリマー中の C5 に由来するユニットの開環率 (R_{op}) はモノマー仕込み組成に関わらず 70–85%の範囲でほぼ一定であった。一方、ペプチド鎖のグラフト率 (G_{r}) は、C5 と MA-Leu$_4$-Am の仕込み比から計算した値 ($G_{\mathrm{r,feed}}$) よりも著しく高かった。共重合挙動を詳細に検討するために、密度汎関数理論 (DFT) 計算を行い、各成長反応の速度定数を算出した。C5 に由来する成長ラジカルは速やかに開環する一方で、開環の有無に関わらずペプチドマクロモノマーと優先的に反応することがわかった。

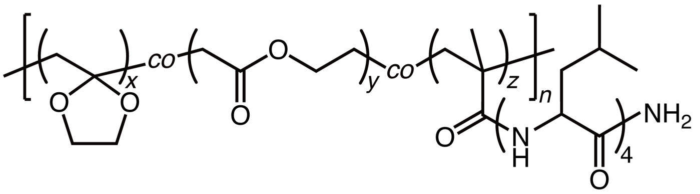


Figure 1. Chemical structure of tetraleucine-grafted aliphatic polyester obtained via RROP of C5 with the peptide macromonomer.

1) S. Nishimura, M. L. Hasegawa, K. Ueda, T. Koga, *New J. Chem.*, **2024**, *48*, 19691-19699.

MOF のナノ空間を利用した高分子束状構造の構築

（東大院工）〇亀谷　優樹・植村　卓史

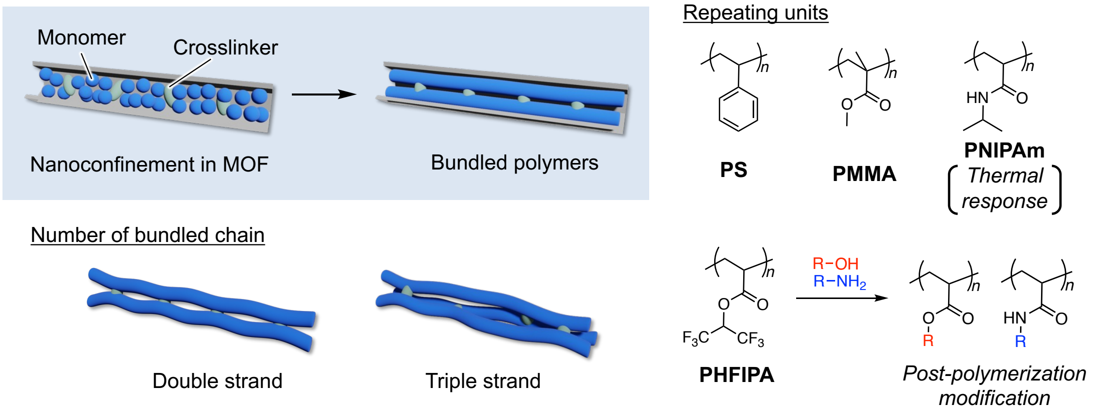
Fabrication of bundled polymers mediated by nanochannels of metal-organic frameworks

(*Graduate School of Engineering, The University of Tokyo*)
〇Yuki Kametani, Takashi Uemura

In this work, we synthesized bundled polymers using the one-dimensional pores of metal-organic frameworks (MOFs) as confined reaction fields for crosslinking polymerization. The nanochannel of the MOF regulated the conformation of formed polymers into an extended state and ensured that the cross-linking occurred exclusively within a pore. This spatially controlled polymerization does not require specialized monomer units, enabling the synthesis of bundled polymers consisting of common vinyl polymers, as shown in the figure. We also explored the potential to regulate the number of polymer chains in a bundle by tuning the pore size of MOF templates. Bundled polymers potentially show distinctive properties arising from restricted mobility and conformation, as well as proximity effects between the parallelly bundled chains.

Keywords : Radical polymerization; Metal-organic frameworks; Crosslink; Polystyrene; Polymethyl methacrylate

本研究では金属有機構造体（MOF）の一次元細孔を反応場として架橋重合を行うことで、生成する高分子鎖のコンフォメーションを引き伸ばされた状態に制御しつつ、細孔内部でのみ架橋を進行させ、束状高分子を合成した。この空間的に重合を制御する手法では、特別な繰り返し単位を必要としないため、図に示すような一般的なビニル高分子からなる束状高分子を合成できた。さらに、用いる MOF の細孔径を調整することで、束を構成する高分子鎖の本数の制御についても検討した。束状高分子は鎖の運動性や取りうる形態が制限されることや、鎖間の近接効果などに基づく特性が期待される。



1) M. Abe, Y. Kametani, T. Uemura, *J. Am. Chem. Soc.* **2023**, *145*, 2448-2454.

Mechanochemical Oxidative Cleavage of 1,1-Diarylethylene Derivatives Using Polymeric Mechanoradicals

([1]*Department of Chemical Science and Engineering, Institute of Science Tokyo*) ○Akira Kodaka,[1] Hajime Sugita,[1] Akira Takahashi,[1] Hideyuki Otsuka[1]

Keywords: Mechanochemistry; Mechanoradical; Electron paramagnetic resonance; Polymer reactions; Oxidative cleavage reactions

Polymer chains with molecular weights above a certain threshold undergo homolytic cleavage under mechanical stimuli, producing active radical species called mechanoradicals. While their use in polymer functionalization has been reported,[1] their application as radical sources in small-molecule organic reactions remains largely unexplored.[2]

1,1-Diarylethylene (DAE) undergoes oxidative cleavage catalyzed by azobisisobutyronitrile-derived carbon radicals in solution under an oxygen atmosphere, forming 1,1-diaryl ketones (DAK).[3] In this study, we investigated the oxidative cleavage of DAE derivatives under solid-state conditions using polymer chains as radical sources (**Fig. 1**).

DAE derivatives with various substituents were ground in the presence of a common polymer using a ball mill. ^{1}H NMR confirmed the formation of the corresponding 1,1-diaryl ketones for all derivatives, while the electron-poor derivatives also afforded 1,1-diaryloxiranes (**Fig. 1b**). Solid-state electron paramagnetic resonance (EPR) revealed the formation of oxyradicals (**Fig. 1c**), suggesting oxidation of the formed DAE-derived carbon radicals.

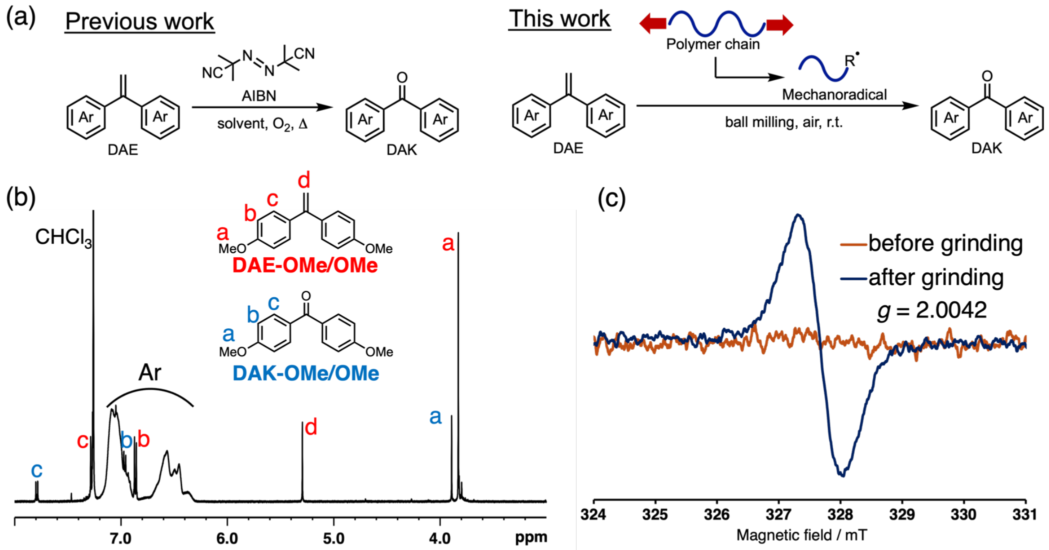


Fig. 1. (a) Conceptual illustration of previous work and this work. (b) ^{1}H NMR spectrum of the ground mixture of **DAE-OMe/OMe** and polystyrene ($CDCl_3$, 500 MHz). (c) ESR spectra of the mixture of **DAE-OMe/OMe** and polystyrene before and after grinding.

1) T. Nakajima, J. P. Gong et al., *Science*, **2019**, *363*, 504. 2) K. Kubota, H. Ito et al., *J. Am. Chem. Soc.*, **2024**, *146*, 1062. 3) H. Xu et al., *J. Org. Chem.*, **2014**, *79*, 7220.

Development of a Thermally Stable Fluorescent Mechanophore and Its Application to Mechanochromic Polymers

(*Department of Chemical Science and Engineering, Institute of Science Tokyo*) ○Yuto Uchida, Hajime Sugita, Akira Takahashi, Hideyuki Otsuka

Keywords: Mechanochemistry; Mechanochromism; Mechanophores; Stimuli-responsive polymers; Fluorescent radicals

Color-changing polymeric materials that respond to mechanical stimuli have great potential for various applications such as stress-sensing. A common approach for these materials is the incorporation of mechanophores into polymer chains. Radical-type mechanophores (RMs), which generate colored and/or fluorescent radical species via homolysis of a specific C–C bond, allow not only visualization of mechanical stress but also quantitative evaluation of the homolysis by electron paramagnetic resonance spectroscopy. However, most RMs also respond to thermal stimuli, limiting their range of applications. For example, tetraarylsuccinonitrile (TASN) is a valuable mechanophore as it mechanically generates fluorescent diarylacetonitrile (DAAN) radicals (**Fig. 1a**), but is also susceptible to temperature change.[1,2] In this study, we investigated diarylacetonitrile-α-carboxylic ester (DAANAC) derivatives as new RM units with high thermal stability.

A DAANAC-containing dimethacrylate cross-linker was synthesized and subjected to free-radical copolymerization with methyl acrylate (MA) to afford a DAANAC-cross-linked PMA (**CP$_{\text{DAANAC}}$**) (**Fig. 1b**). Elongation of **CP$_{\text{DAANAC}}$** showed yellow fluorescence under UV irradiation, demonstrating the generation of DAAN radical (**Fig. 1c, d**). These results suggest that the DAANAC skeleton can serve as a thermally stable RM, which can visualize mechanical stress by the generation of fluorescent DAAN radicals.

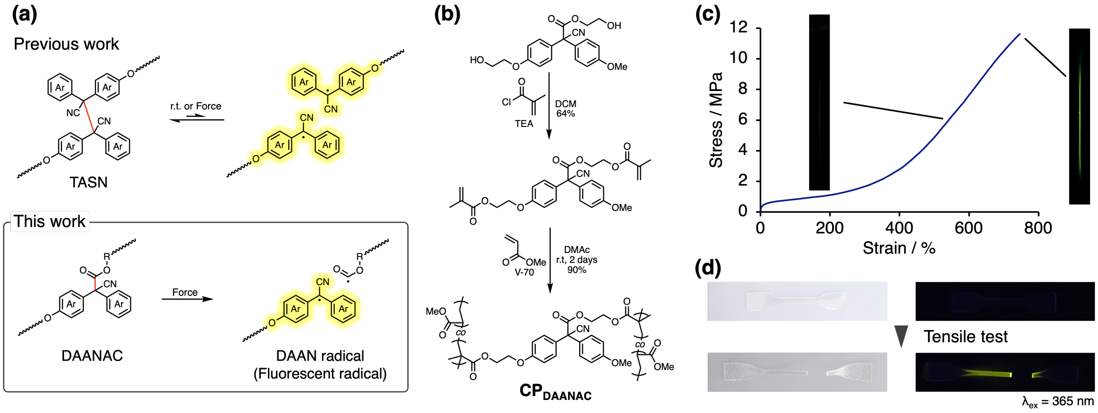


Fig. 1 (a) Conceptual illustration of this work. (b) Synthetic routes of **CP$_{\text{DAANAC}}$**. (c) Representative stress–strain curve of **CP$_{\text{DAANAC}}$** (10 mm/min). (d) Photographs of **CP$_{\text{DAANAC}}$** under room light (left) and UV irradiation (right) before (top) and after tensile test (bottom).

1) H. Otsuka *et al.*, *Chem. Commun.* **2017**, *53*, 11885.
2) H. Otsuka *et al.*, *Nat. Commun.* **2021**, *12*, 126.