

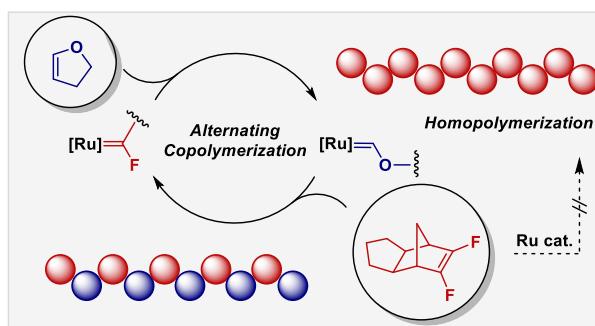
フルオロアルケンの開環メタセシス重合による交互共重合の開発

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 Development of Alternating Copolymerization by Ring-Opening Metathesis Polymerization of
 Fluoroalkenes
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Ring-opening metathesis polymerization (ROMP) has become one of the most powerful methods to synthesize diverse functional polymers from cycloalkenes. Norbornene derivatives (NBEs) are highly strained and therefore commonly used as substrates for not only homopolymerization but also copolymerization. Alternating copolymerization is distinguished by the ability to control the sequence of two monomers, a beneficial feature which allows the polymer bulk properties to be adjusted according to the sequence order. To the best of our knowledge, completely alternating ROMP of NBEs has not been reported, though other highly-strained cycloalkenes (cyclobutene,¹⁾ cyclopropene,²⁾ and oxanorbornene³⁾) have been used for alternating ROMP. In the present study, inspired by the cross metathesis of fluoroalkenes and enol ethers,⁴⁾ copolymerization of fluorinated NBEs and dihydrofuran was conducted. The introduction of fluorine atoms at the carbon-carbon double bond prevents homopolymerization of NBEs, thereby ensuring a completely alternating sequence.

Keywords : Ring-Opening Metathesis Polymerization, Alternating Copolymerization

開環メタセシス重合は、環状アルケンから多様な機能性ポリマーを合成する最も有力な方法の一つである。ノルボルネン誘導体は、その大きな環歪みゆえに多くの単独重合に加え共重合にも利用される。中でも交互共重合は二種類のモノマーの規則的な配列を実現することで物性を制御できる優れた手法と言える。シクロブテン¹⁾、シクロプロパン²⁾、オキサノルボルネン³⁾の交互開環メタセシス重合が報告される一方で、ノルボルネン誘導体の完全な交互開環メタセシス重合は報告例がない。本研究では、フルオロアルケンとエノールエーテルのクロスマタセシスに着想を得て⁴⁾、炭素-炭素二重結合にフッ素原子を導入することによりノルボルネン誘導体の単独重合を抑え、ジヒドロフランとの開環メタセシス重合により完全な交互共重合体を合成した。



- 1) Song, A.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2009**, *131*, 3444–3445. 2) Elling, B. R.; Xia, Y. *J. Am. Chem. Soc.* **2015**, *137*, 9922–9926. 3) Pal, S.; Alizadeh, M.; Kong, P.; Kilbinger, A. F. M. *Chem. Sci.* **2021**, *12*, 6705–6711. 4) Mori, K.; Akiyama, M.; Inada, K.; Imamura, Y.; Ishibashi, Y.; Takahira, Y.; Nozaki, K.; Okazoe, T. *J. Am. Chem. Soc.* **2021**, *143*, 20980–20987.