

The Fluorocarbene Exploit: Enforcing Alternation in Ring-Opening Metathesis Polymerization

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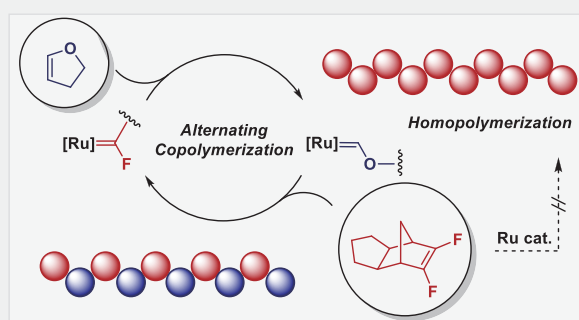
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ABSTRACT: Fluoroalkenes are known to be notoriously reluctant substrates for olefin metathesis due to the generation of thermodynamically stable Fischer-type fluorocarbene intermediates, which invariably fail to undergo further reaction. In the present disclosure, we find that fluorine substitution on the sp^2 carbon also strictly suppresses homopolymerization of norbornene derivatives (NBEs), and this can be harnessed to achieve alternating ring-opening metathesis polymerization (ROMP) with an appropriately electron-rich comonomer. Dihydrofuran (DHF) is thereby shown to undergo alternating ROMP with fluorinated norbornenes, the perfectly alternating structure of the resulting copolymer having been unambiguously elucidated by 1H , ^{19}F , and ^{13}C NMR analyses. Furthermore, we find that the degradability of the resultant copolymers in acidic media via hydrolysis of enol ether moieties in the backbone can be predictably modulated by the number of fluorine atoms present in the NBE comonomer, affording an opportunity to engage with the desirable physical properties of fluorinated polymers while limiting their attendant environmental degradability issues.



INTRODUCTION

Ring-opening metathesis polymerization (ROMP) has become one of the most powerful methods to synthesize diverse functional polymers from cycloalkenes.^{1,2} Norbornene derivatives (NBEs) are particularly performative due to their highly-strained nature and are therefore commonly used. ROMP of NBEs readily proceeds without chain transfer to produce low-dispersity homopolymers with controlled molecular weight. In addition to homopolymerization, a number of examples of ring-opening metathesis copolymerization have been reported.^{3–5} Since the nanostructure of a polymer affects its bulk properties, sequence-controlled copolymers are highly desired. Alternating copolymerization is distinguished by the ability to perfectly control the sequence of two monomers.⁶ Many efforts toward alternating ring-opening metathesis polymerization (AROMP) of NBEs with other cycloalkenes have been reported, including the use of NBEs with bulky substituents or electron-deficient groups,^{7,8} or by employing unsymmetrical ruthenium catalysts.^{9,10} However, in these examples, one or both of the monomers can still undergo limited homopolymerization, which leads to the undesirable outcome of irregular and statistically random homoaddition runs in the polymer chain.

The most reliable way to achieve AROMP is to use two “single addition monomers”, which can react with a ruthenium catalyst only once and which therefore cannot undergo homopolymerization. In 2009, Sampson et al. disclosed the

AROMP of 1-carboxylate-cyclobutene and cyclohexene.^{11–18} Homopolymerization of the former is strictly suppressed by its steric hindrance, while that of the latter, particularly under diluted conditions, lacks the driver of ring strain. Later, Xia et al. explored living AROMP using sterically hindered cyclopropene derivatives.^{19–22} More recently, single addition and AROMP of oxanorbornene derivatives were also demonstrated by Kilbinger et al.^{23,24} In the case of NBEs, single addition of 7-isopropylidene-2,3-dicarbomethoxynorbornadiene and AROMP using its analogues have been reported by Schrock et al. using molybdenum catalysts.^{25–27} However, the prior art reveals no precedent for Ru-catalyzed AROMP of NBEs. While the introduction of a bulky substituent proximal to the double bond might be expected to suppress NBE homopolymerization, it also unfortunately thwarts copolymerization, as has been reported for methyl norborn-2-ene-2-carboxylate, the steric hindrance of which is great enough to prevent cycloaddition with a Grubbs third-generation catalyst.²⁸

Herein, we wish to highlight a different approach, which focuses instead on fluoroalkenes, especially which have fluorine

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