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Spotlight

Turnaround in use of enol ether opens the door to degradable plastics

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While ring-opening metathesis polymerization (ROMP) is a robust method to construct polymers, monomer systems for degradable ROMP polymers are limited. Existing systems suffer from lengthy synthesis and/or uncontrolled polymerization. Xia and coworkers demonstrated the synthesis of degradable ROMP copolymers from the commercially available monomers in a controlled manner.

Enol ethers are considered 'troublesome' substrates in olefin metathesis because they rapidly react with the Ru alkylcarbene to form a thermodynamically stable electron-rich alkoxycarbene: a typical Fischer carbene that is regarded as inert or unreactive towards further metathesis (Figure 1A) [1]. In fact, the unique stability of the Ru Fischer carbene makes enol ethers effective quenching agents for olefin metathesis [1–4]. Nevertheless, metathesis reactions between enol ethers and certain substrates, such as strained cycloalkenes [3,5], alkynes [2], fluoroolefins [6,7], and some electron-rich olefins [1] have been observed. For example, Ozawa [5] and Rainier [3] reported the ring-opening cross metathesis of strained norbornene derivatives (NBEs) with enol ethers (Figure 1B). The intermolecular enyne metathesis between terminal alkynes and enol ethers was demonstrated by Diver and coworkers (Figure 1B) [2]. In addition, Grubbs and Louie demonstrated that the Ru Fischer carbenes are reactive enough to initiate the polymerization of the highly strained NBEs at room temperature (Figure 1C) [1].

Despite the demonstrated reactivity in metathesis, it was unclear whether a cyclic enol ether can be used as a monomer for ROMP until Xia and Feist first demonstrated the ROMP of a five-membered cyclic enol ether, that is, 2,3-dihydrofuran (DHF) in 2020 (Figure 1D) [8]. Due to the low ring strain of DHF, the resulting poly (enol ether) can be depolymerized to recycle the DHF monomer in the presence of a Ru catalyst under elevated temperature [8]. Moreover, the acid-labile enol ether moiety enables the polymer to be degraded into small molecules under acidic conditions. Meanwhile, Gutekunst and coworkers reported the alternating copolymerization of enynes and DHF (Figure 1D) and the resulting polymer is also degradable due to the incorporation of the enol ether group on the backbone [9].

In a more recent work, Xia and coworkers explored the copolymerization of NBEs and DHF (Figure 1D) and obtained polymers with controlled molecular weight (which was not achieved in their previous work on the homopolymerization of DHF [8]) and the resulting polymers can be degraded efficiently into small molecules under acidic conditions [10]. The efficient degradation suggests balanced distribution of both NBEs and DHF on the polymers: homoaddition of NBE is effectively suppressed. Note that predominant homoaddition of NBEs would be expected for the copolymerization of NBEs and a low-strain monomer, such as cyclohexene and cyclopentene. Since the ring strain of DHF is comparable with that of cyclopentene [8], the suppressed homoaddition here can therefore be attributed to the unique reactivity of enol ether: an alkylcarbene (resulted from the metathesis between an NBE and the Ru at a polymer chain end) would prefer reacting with DHF over an NBE (Figure 2). The favorable reactivity of DHF over NBE is supported by kinetic studies of polymerization, which showed zeroth- and first-order kinetics with respect to DHF and NBE, respectively. However, the homoaddition of DHF is unfavorable thermodynamically due to the low ring strain of the monomer (Figure 2). Taken together, both the high reactivity of enol ether and the low ring strain energy of the five-membered ring play important roles in the uniform incorporation of enol ether in the copolymerization.

Besides providing a uniform distribution of the degradable moiety, the use of enol

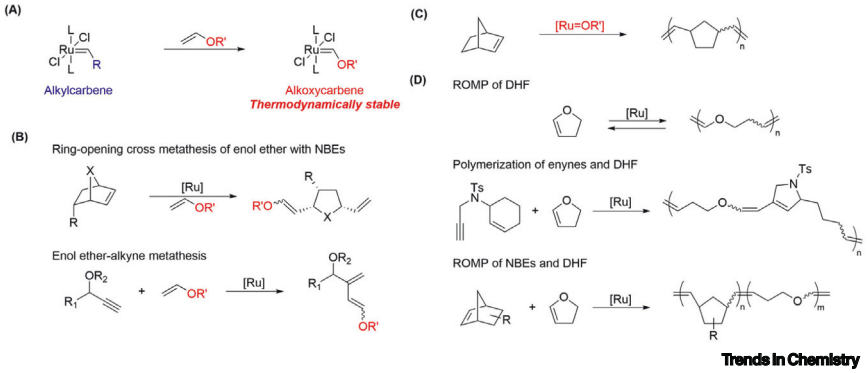

Figure 1. An overview of olefin metathesis that involves enol ethers. (A) Enol ether reacts with Ru alkylcarbene and forms the thermodynamically stable alkoxycarbene. (B) Examples of metathesis reactions between enol ether and highly reactive substrates, such as norbornene derivatives (NBEs) and alkynes. (C) Ru alkoxycarbene used as an initiator for ring-opening metathesis polymerization (ROMP). (D) Cyclic enol ether 2,3-dihydrofuran (DHF) used as a monomer for ROMP.

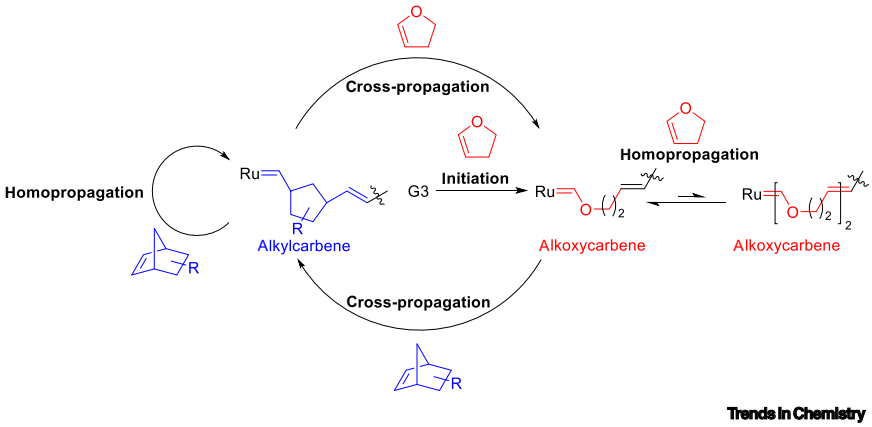

Figure 2. Proposed mechanism for the copolymerization of 2,3-dihydrofuran and norbornene derivatives.

ether in copolymerization also leads to an improved functional group tolerance because of the low reactivity of the Ru Fischer carbene formed *in situ*. For example, while acrylic pendant group does not survive a typical ROMP condition due to its selective cross-metathesis with electron neutral olefins, it was found to be compatible with the reaction conditions for copolymerization of DHF and NBEs and was successfully incorporated. The pendant acrylic group provides an opportunity for further functionalization and crosslinking of the polymers.

Given the availability of NBEs with various functionalities, identifying the key monomer DHF for copolymerization with NBEs thus opens the door to degradable polymers with a broad range of material properties. As a proof of concept, the authors developed copolymers of DHF with various functionalities on the NBE building block, including esters, imides, and water-soluble oligo(ethylene glycol) to achieve diverse material properties. In addition, DHF is commercially available at a low cost, which adds economic value for using it to prepare degradable plastics that can potentially replace the current nondegradable counterparts and address the corresponding challenges in sustainability.

Declaration of interests

No interests are declared.

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