

Catalytic Living Ring-Opening Metathesis Polymerization using Vinyl Ethers as Effective Chain Transfer Agents

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Abstract: A catalytic living ring-opening metathesis copolymerization (ROMP) method is described that relies on a degenerative, reversible and regioselective exchange of propagating Fischer-carbenes. All characteristics of a living polymerization such as narrow dispersity, excellent molar mass control and the ability to form block copolymers are achieved by this method. The method allows the use of up to 200 times less ruthenium complex than traditional living ROMP. We demonstrate the synthesis of ROMP-ROMP diblock copolymers, ATRP from a ROMP macro-initiator and living ROMP from a PEG-based macro chain transfer agent. The cost-effective, sustainable and environmentally friendly synthesis of degradable polymers and block copolymers enabled by this strategy will find various applications in biomedicine, materials science, and technology.

Introduction

Ring-opening metathesis polymerization (ROMP) is one of the most widely used methods to construct an extensive variety of structurally and functionally diverse polymers, finding applications in numerous fields.^[1,2,3,4] Since ROMP polymers typically consist of non-degradable backbones, recent efforts have been directed toward expanding the family of degradable polymers accessible via olefin metathesis polymerization for their potential applications in biomedicine, lithography, energy storage, electronics, as well as for environmental sustainability.^[5,6,7] Over the past decades, several strategies have been exploited in olefin metathesis to incorporate degradable bonds into polymer backbones. These include special monomer designs, polymerization via entropy-driven ROMP or combining a low strain cycloolefin with cleavable units with a high strain monomer to impart ROMP systems with degradable linkages.^[8,9,10,11,12,13,14,15,16,17,18,19]

Although vinyl ethers are commonly used as terminating agents for ROMP due to the formation of a thermodynamically stable alkoxymethylidene complex,^[20,21,22] Xia and co-workers recently illustrated the ROMP of commercially available 2,3-dihydrofuran (DHF) to form degradable poly-DHF exploiting the surprising metathesis activity of the Fischer carbene.^[23] Afterwards, the

Gutekunst group demonstrated the alternating copolymerization behavior of cyclic enol ethers with enyne monomers.^[24,25] Furthermore, a very recent report showed the copolymerization of DHF with traditional norbornene monomers to synthesize degradable polymers (Figure 1A).^[26]

However, it is also noteworthy that all of the examples of degradable polymers discussed here utilized a stoichiometric amount of ruthenium-based metal catalyst, which bestow a ruthenium carbene on each polymer chain during the polymerization. This often results in high catalyst loading, which is quite expensive and leads to toxic metal contaminants in the synthesized polymers, potentially hindering the industrial and biomedical applications of these materials.^[27,28] To overcome this drawback, numerous methods have been developed gradually to reduce the catalyst level in the final products. Initially, methods relying on irreversible chain-transfer agents (CTAs) were developed to produce homotelechelic polymers under a thermodynamically driven catalytic process.^[29,30,31,32,33,34,35,36] Pulsed addition of monomer was another technique for synthesizing polymers with a sub-stoichiometric amount of metal complex.^[37,38,39] A method based on a kinetically controlled chain transfer mechanism is also a straightforward approach of achieving ROMP polymers with a catalytic amount of ruthenium complex.^[40,41,42,43,44] Moreover, our group has recently reported a catalytic living ROMP exploiting a new degenerative reversible chain transfer mechanism.^[45,46]

However, all these ROMP strategies are limited to non-degradable polymers. It would, however, be very interesting as well as beneficial to develop new methods to synthesize degradable ROMP polymers using only catalytic amounts of transition metal complexes. Very recently our group has reported a kinetically controlled catalytic ROMP using vinyl ethers as CTAs to synthesize degradable polymers via copolymerization of DHF with Vince lactam and its derivatives (Figure 1B).^[47] There, the synthesized polymers are non-living with broad dispersity and are unable of forming block copolymers via re-initiation due to a mechanistic necessity. Finding a catalytic ROMP protocol that will facilitate the synthesis of living and degradable polymers has always been a challenging issue.

Herein, we report for the first time a catalytic living ROMP mechanism using vinyl ethers as CTAs to synthesize narrowly dispersed degradable polymers by copolymerizing 2,3 -

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dihydrofuran (DHF) with several norbornene derivatives (Figure 1C).

We have recently explored the ultrafast and regioselective metathesis activity of vinyl ethers [48,49,50,51,52] in the catalytic synthesis of degradable copolymers relying on a kinetically controlled chain transfer process (Figure 1B). [47] In that report, we have investigated the potential of vinyl ethers as efficient CTAs during the catalytic copolymerization of DHF with Vince lactam and its derivatives. As these monomers contain an amide bond, the partial double bond character of the C-N bond makes them more strained and hence highly reactive under the ROMP conditions. A one-pot copolymerization of M1 and DHF using CTA1 in the presence of a catalytic amount of G2 yielded a polymer with broad dispersity and controlled molar mass (equal to the [monomer]:[CTA1] ratio). [47] This is only possible when the rate of chain transfer to CTA1 is on the same order of magnitude

as that of the monomer propagation rate, one of the requirements for a kinetically controlled chain transfer mechanism. Our group has recently described a mechanism for catalytic living ROMP based on a degenerative exchange using reversible chain transfer agents (rCTA). [45,46] In that process, a substoichiometric amount of ruthenium complex initiates the polymerization of a strained monomer which is continuously added to the reaction mixture containing the catalyst and rCTA. As described previously, [45] due to the low monomer concentration, the propagation reaction, as well as the reaction with the rCTA, becomes equally favorable leading to a reversible chain transfer equilibrium in which the propagating ruthenium carbene chain end of the polymer exchanges rapidly with the other chain ends. As a result, all the chains appear to grow quasi-simultaneously yielding polymers with controlled molar mass and narrow dispersity.

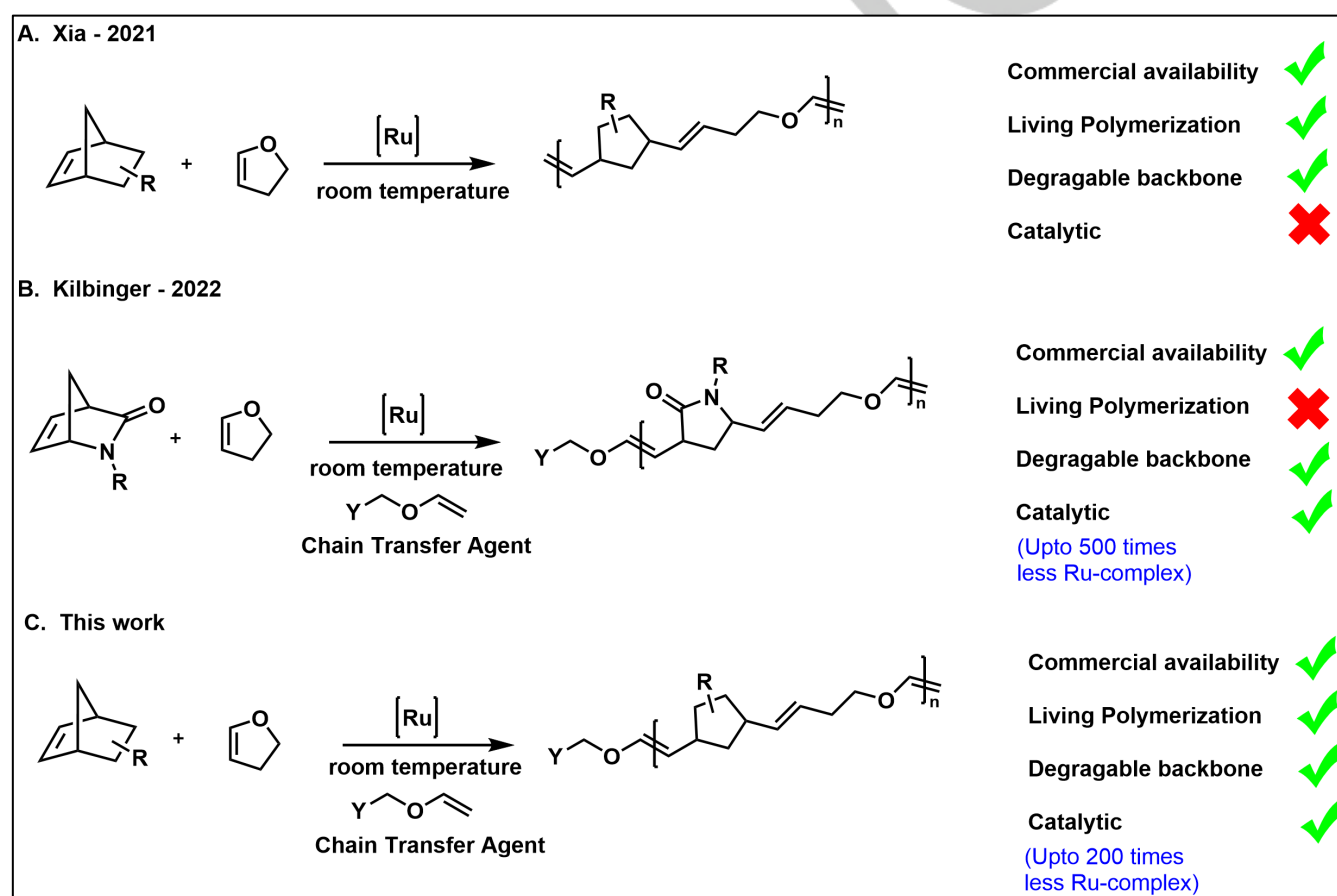


Figure 1. (A.) Syntheses of degradable polymers via classical living ROMP. (B.) Catalytic syntheses of degradable polymers using vinyl ethers as CTAs. (C.) Syntheses of degradable polymers via catalytic living ROMP using vinyl ethers as CTAs.

Results and Discussion

Based on our previous knowledge we hypothesized that adding a mixture of monomers M1 and DHF slowly to a solution containing CTA1 and a catalytic amount of G2 could lead to a living polymerization. We believed that the low concentration of monomer as well as very fast and regioselective chain transfer between the propagating Fischer carbene and the vinyl ether of CTA1 would fulfill the requirement of a fast reversible chain transfer equilibrium (Figure 2A). Once all of CTA1 has been transferred to the polymer chain ends, a degenerative, reversible and regioselective Fischer-carbene exchange of the end groups would occur faster than monomer propagation under slow monomer addition conditions. Hence, all polymer chains should form in a quasi-living polymerization (Figure 2B). This quasi-simultaneous growth of all chains would lead to polymers with controlled molar mass (determined by the [monomer]:[CTA] ratio) and narrow dispersity. To prove our hypothesis, we added a mixture of M1 and DHF (1:2)^[47] in DCM (0.15 M with respect to DHF) slowly (1 mL/h) to a solution containing G2 and CTA1 (1:15). As expected, the molar mass of the produced polymer P1 appeared to be controlled by the monomer to CTA ratio ($M_{n,SEC}(\text{DMF}) = 12.34 \text{ kDa}$, $M_{n,theo.} = 11.40 \text{ kDa}$) and, the polymer showed a narrow dispersity ($\mathcal{D} = 1.35$, SI, Table S2, entry 1 and Fig S16). This result was in support of our hypothesized living copolymerization based on a Fischer-carbene to Fischer-carbene exchange. After that, we changed the [M1]:[CTA1] ratio to prepare a series of degradable and telechelic copolymers (SI, Table S2, entry 2-5) which were characterized by SEC (DMF) (SI, Fig S17-S19) and ¹H NMR spectroscopy (SI, Fig S47-S49). A linear correlation between apparent molecular weight and [M1]:[CTA1] ratio was observed as expected for a living copolymerization (Figure 5A).

Furthermore, a kinetic analysis also confirmed the living nature of the polymerization. Here, aliquots taken at different time intervals during the copolymerization of M1 and DHF with CTA1 were analyzed by SEC (SI, Table S4). As expected, a gradual increase in molar mass over time was observed with a constant low dispersity as expected for a living polymerization.

This result further prompted us to exploit the behavior of a more traditional monomer in this living copolymerization. We next chose norbornene (M2) and copolymerized it with DHF using CTA1 under identical catalytic living ROMP condition as described above (SI, Table S2, entry 6). This yielded the desired polymer P5 with good molar mass control ($M_{n,SEC}(\text{CHCl}_3) = 3.56 \text{ kDa}$) and narrow dispersity ($\mathcal{D} = 1.30$, SI, Fig S20).

A critical requirement for this type of living polymerization is a fast exchange of the propagating chain ends compared to the rate of propagation. We anticipated that instead of adding the monomer slowly to the polymerization mixture, a slower propagating co-monomer might allow the polymerization to be carried out in one pot. We, therefore, chose norborneneimide derivatives (some of the most popular monomers in ROMP) which are less prone to be ring-opened by the propagating Ru Fischer carbene.^[26]

To test this proposition, a one-pot copolymerization using a ratio of [G2]:[CTA1]:[M3]:[DHF] of 1:10:100:200 was performed. ¹H NMR spectroscopy revealed > 95 % of M3 conversion within 24h (SI, Table S3, entry 1). SEC analysis of the precipitated copolymer (P6) showed a monomodal distribution with a molar mass of 9.68 kDa (determined by [monomer]:[CTA1] ratio) and a dispersity of 1.20 (SI, Fig S21, Fig S4, Fig S52).

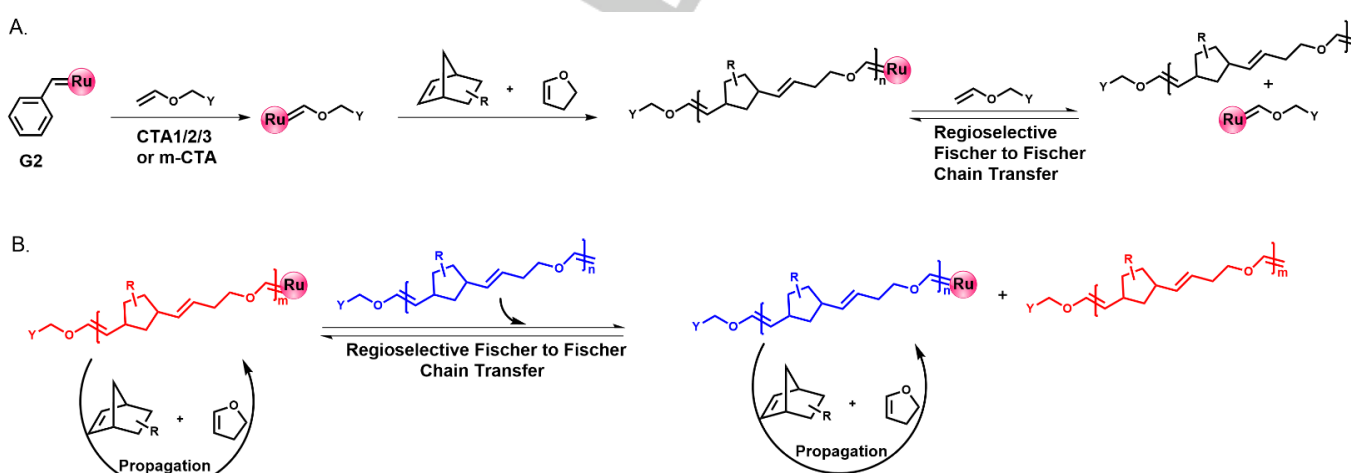


Figure 2. Proposed mechanism of catalytic living ROMP for the syntheses of degradable polymers using vinyl ethers as CTAs.

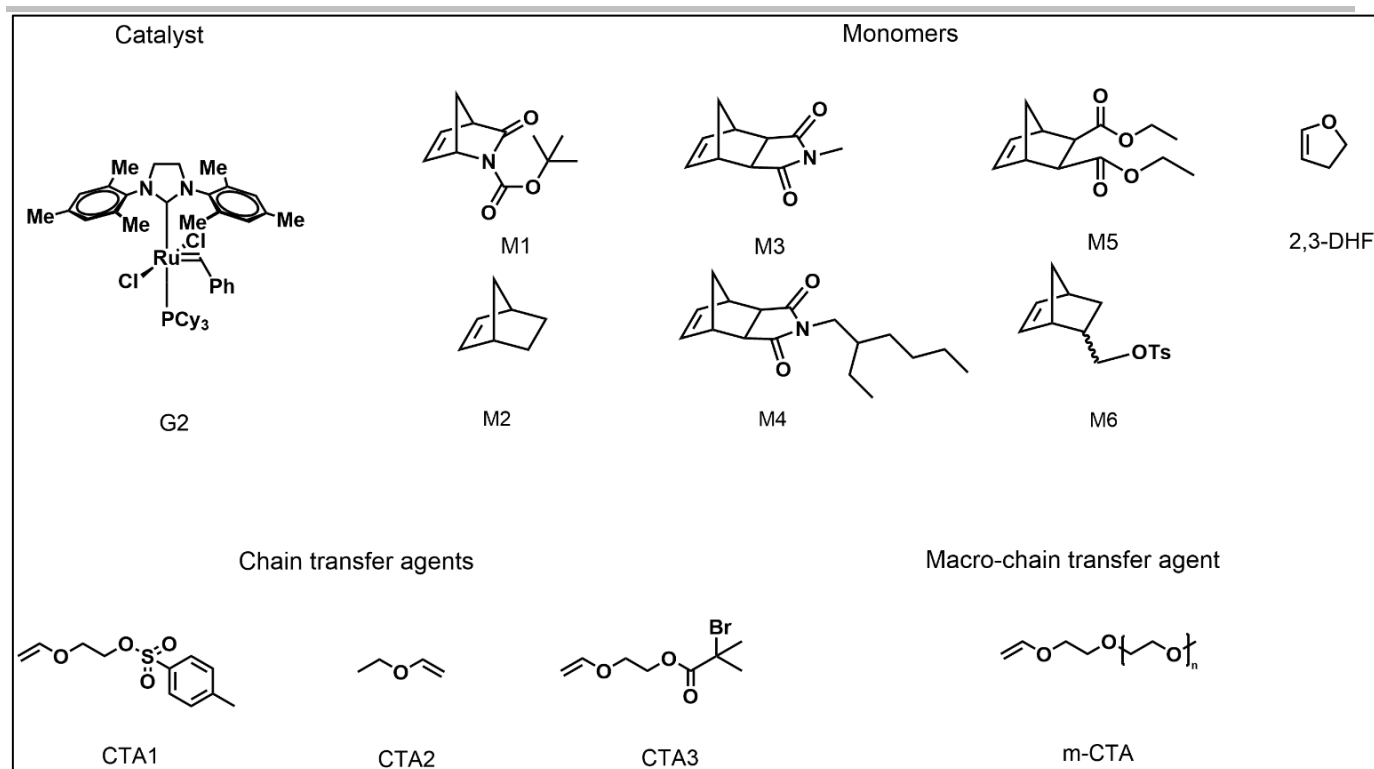


Figure 3. Structures of the catalyst, monomers, and CTAs used in this report.

A ^1H NMR experiment showed that all of CTA1 was consumed within the first 2 h of the polymerization whereas only 30 % of M3 was consumed at that time which is also in agreement with our proposed living mechanism (SI, Fig S3). Next, to prove that the [monomer]:[CTA] ratio determines the molar mass and that the polymerization fulfills living characteristics, a series of copolymers were synthesized in one pot by changing the [M3]:[CTA1] ratio (SI, Table S3, entry 2-4) and fully characterized by SEC and ^1H NMR (SI, Fig S22-S24, Fig S54, S56, S57). As predicted, a linear correlation between molar mass and the [M3]:[CTA1] ratio was obtained (Figure 5B). Furthermore, a kinetic analysis also revealed the living nature of the polymerization. Aliquots taken at different time intervals during a one-pot copolymerization using a ratio of [G2]:[CTA1]:[M3]:[DHF] of 1:10:300:600 were analyzed for conversion and molecular weight by ^1H NMR and SEC respectively to show a linear increase in molar mass with conversion (Figure 5C, SI Table S5).

Then, a narrowly dispersed copolymer P12 (> 92% monomer conversion) was synthesized by using $1/200^{\text{th}}$ of the classically required amount of ruthenium catalyst (SI, Table S3, entry 7). Notably, we synthesized P12 (540 mg) by using only 1 mg of Grubbs 2nd generation catalyst whereas in a traditional living ROMP experiment one would have required 200 mg of the costly

and cytotoxic ruthenium catalyst to synthesize the same amount of this polymer. We believe that this high reduction in catalyst loading will make this method very beneficial in potential biomedical or even industrial applications. After that, commercially available CTA2 and alpha-bromoester functionalized CTA3 were employed to synthesize the degradable copolymers P13 and P14 respectively (SI, Table S3, entry 8-9). Next, to show the versatility of this one pot catalytic living copolymerization method, other monomers M4, M5 and M6 were copolymerized with DHF in the presence of CTA1 producing narrowly dispersed degradable copolymers with high monomer conversion and controlled molar mass (SI, Table S3, entry 10-12). Thermal properties (Differential Scanning Calorimetry measurement) of these copolymers were also investigated (the glass transition temperatures [T_g] exhibited by the synthesized copolymers in this report range from 10 °C to 60 °C) (SI, Fig S81-S85) and are comparable with the previous literature report ($T_g = 20\text{ °C} - 70\text{ °C}$).^[26]

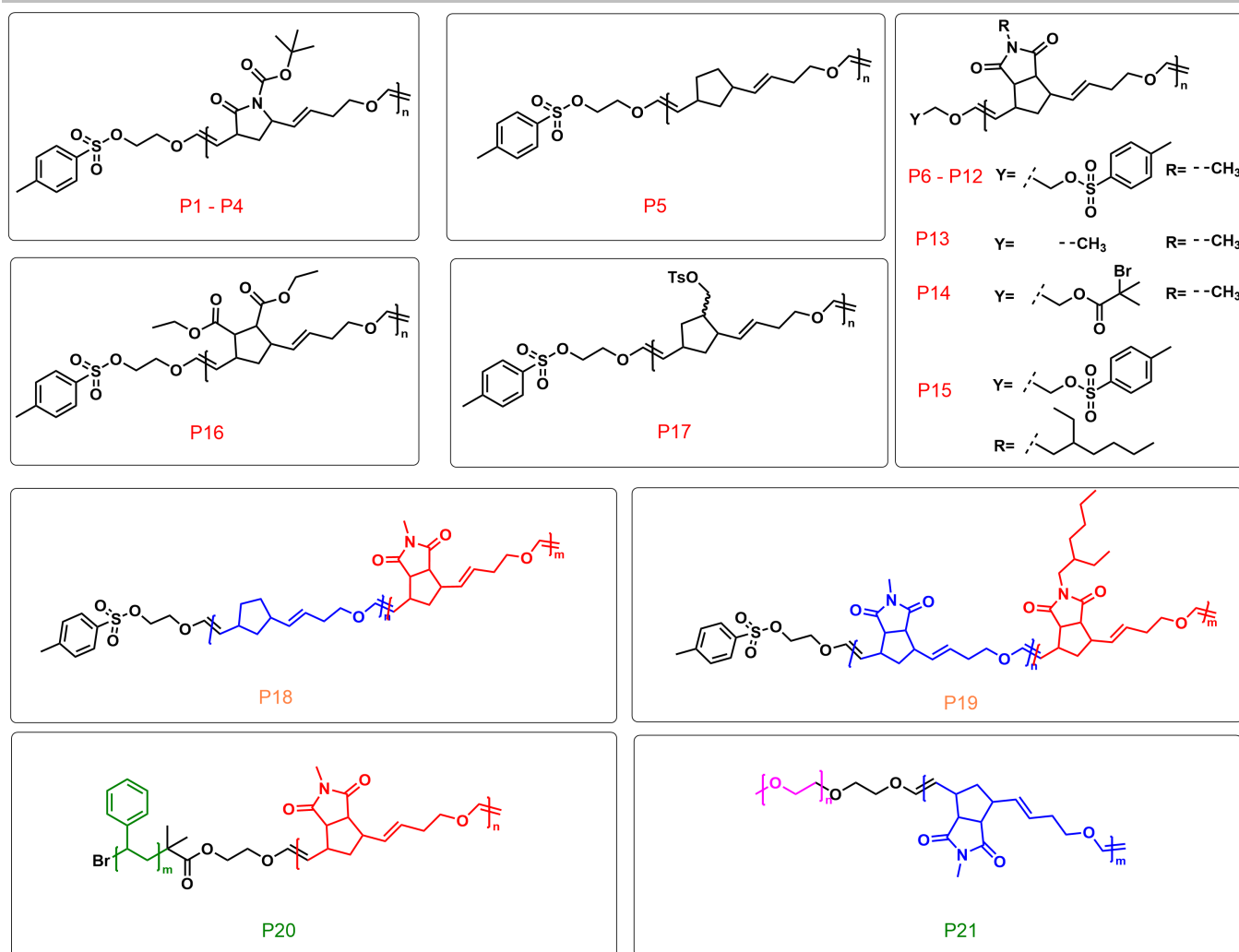


Figure 4. Structures of the polymers synthesized in this report.

The ability to prepare block copolymers is one of the important features of a living polymerization. When polymer P5 was redissolved in DCM along with M3, DHF, and a catalytic amount of G2, a diblock copolymer P18 was formed, as observed by the shift of the SEC trace to higher molar mass (SI, Fig S7). In a similar manner, block copolymer P19 was synthesized via reinitiating polymer P10 with a catalytic amount of G2 and adding a mixture of monomers M4 and DHF. Here, also, SEC analysis showed a complete shift of the first block to give a poly(M3-DHF)-*b*-poly(M4-DHF) diblock copolymer (P19, Figure 5D). Besides, DOSY NMR spectra further confirmed the formation of diblock copolymers (SI Fig S8, Fig S10). The formation of these block copolymers via re-initiation is rigorous proof of our proposed mechanism. Next, alpha bromoester end-functionalized polymer

P14 was used as a macro-initiator to grow a polystyrene block using the CuBr/PMDETA catalyst system. SEC and DOSY characterization confirmed the formation of a diblock copolymer (P20) ($M_{n,SEC}(\text{CHCl}_3) = 14.03 \text{ kDa}$, $\text{Đ} = 1.18$) with excellent efficacy (Figure 6A, 6B, SI Fig S12). This shows that this new method allows us to prepare suitably end-functionalized and narrowly dispersed degradable polymers using catalytic amounts of a ruthenium metal catalyst, that could act as macro-initiators for further polymerization via different mechanisms such as ATRP or RAFT.

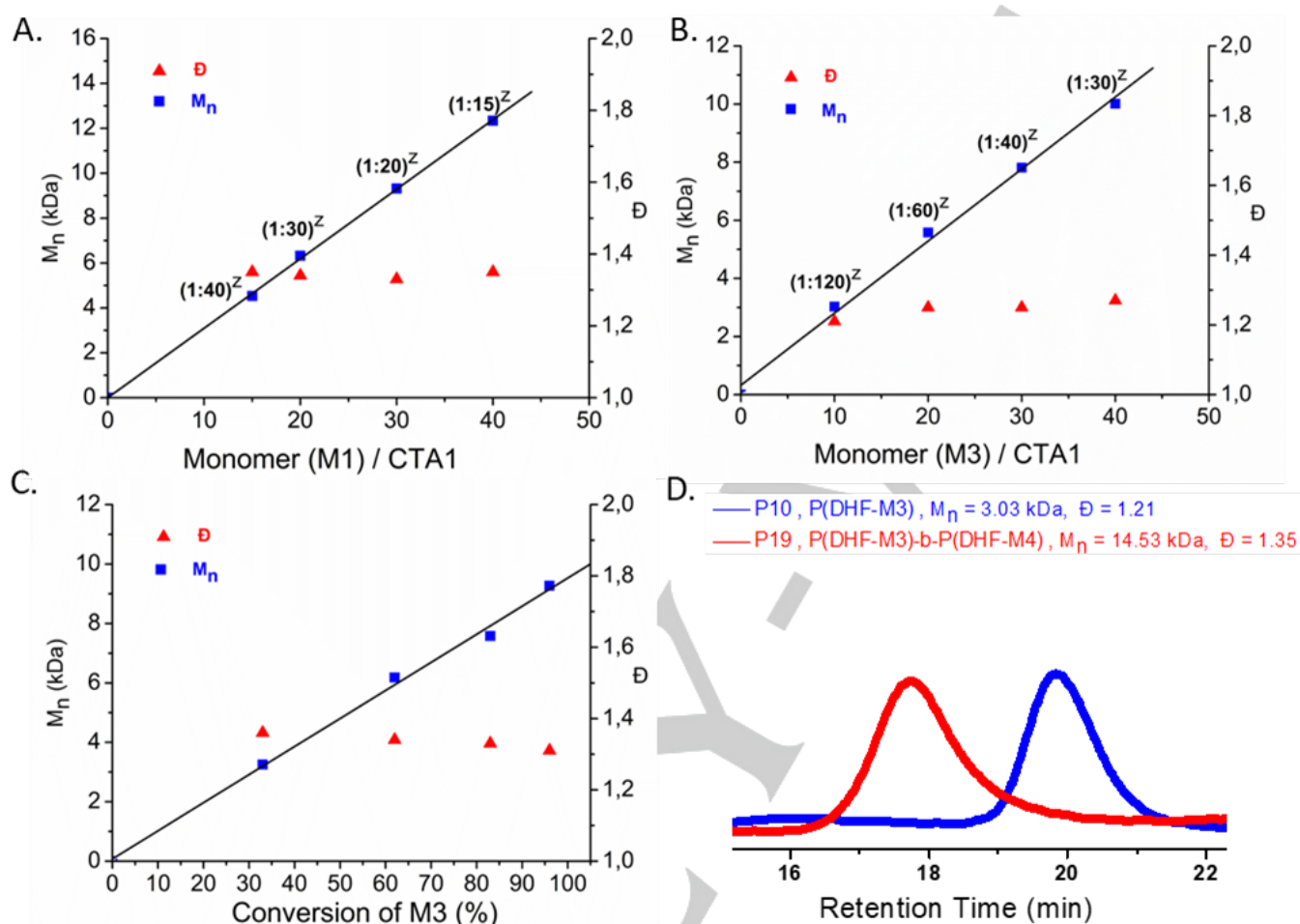


Figure 5. (A.) Plot of the number average molar mass (M_n , SEC (DMF) and dispersity (\bar{D}) versus [M1]:[CTA1] ratio showing a linear correlation. The ratios reported in brackets (z) denote the [G2]:[CTA1] ratio. (B.) Plot of the number average molar mass (M_n , SEC (CHCl₃) and dispersity (\bar{D}) versus [M3]:[CTA1] ratio showing a linear correlation. The ratios reported in brackets (z) denote the [G2]:[CTA1] ratio. (C.) Plot of the number average molar mass (M_n , SEC (CHCl₃) versus the conversion (%) of M3 showing a linear correlation. (D.) SEC (CHCl₃) traces of the first block P10 (P-(M3-DHF), blue) and the diblock copolymer P19 (red).

After that, the high metathesis activity of vinyl ethers prompted us to investigate a macro-CTA under catalytic living ROMP conditions. In an analogous manner as described above, M3 and DHF were copolymerized using the PEG-based macro-CTA (m-CTA) and G2 with a ratio of [G2]:[m-CTA]:[M3]:[DHF] of 1:40:3200:6400 to obtain a low dispersity di-block copolymer P21. SEC analysis showed a monomodal distribution (M_n , SEC (DMF) = 21.82 kDa, \bar{D} = 1.34) with a clear shift from the first block to the di-block copolymer in the SEC elugram (Figure 6C, 6D). Moreover, DOSY NMR spectroscopy also revealed the successful synthesis of a block copolymer (SI Fig S15).

Next, due to the presence of acid-labile vinyl ether motifs in the main chain of these copolymers,^[26] treatment of P12, P16 and

P18 with dilute HCl resulted in complete degradation within 30 min suggesting a uniform incorporation of the DHF units throughout the polymer backbone (SI Fig S33, S34, S35). Also, when PEG-based diblock copolymer P21 was subjected to dilute acidic conditions, a SEC measurement revealed that the homopolymer PEG did not degrade under these conditions (SI Fig S36).

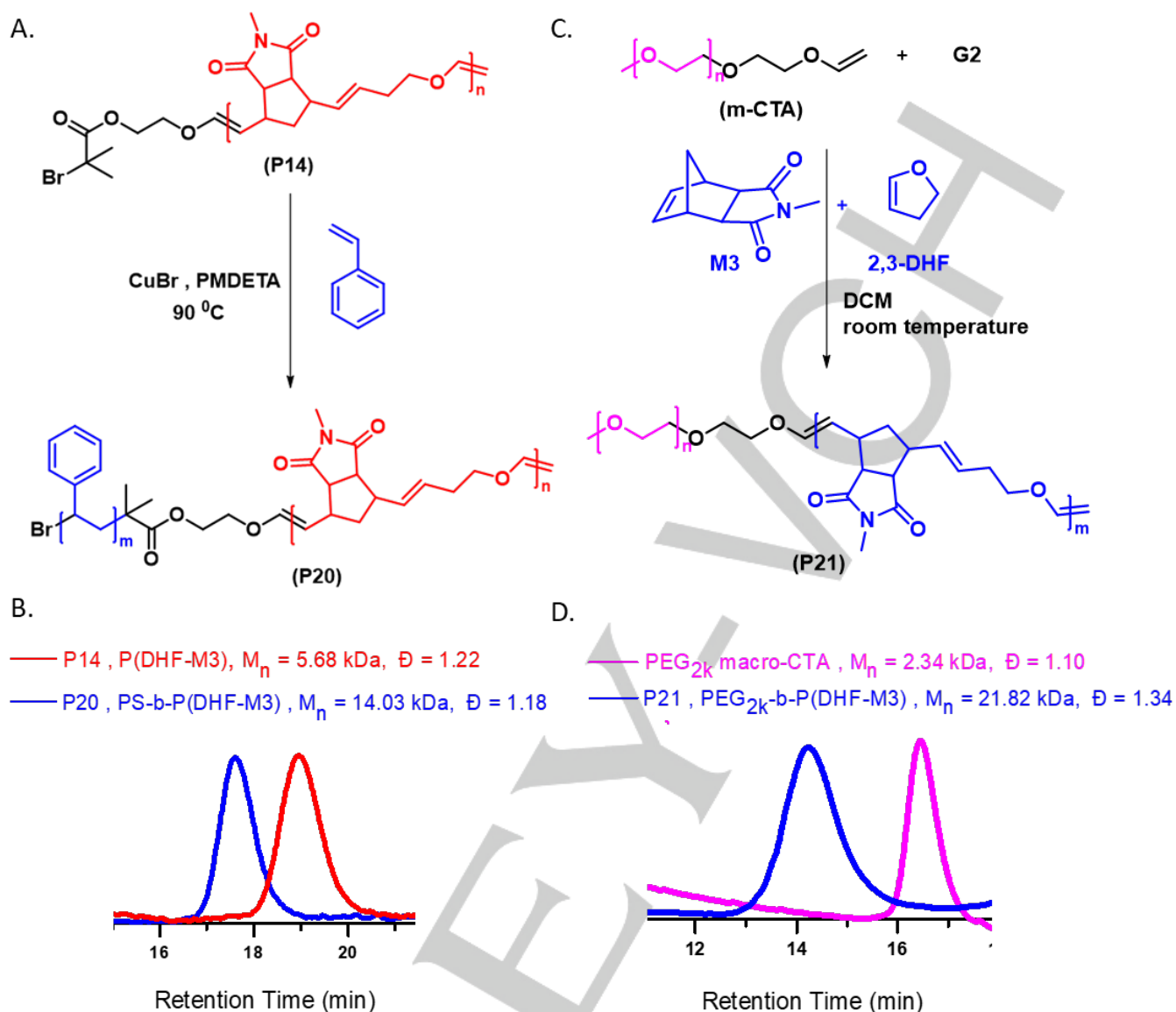


Figure 6. (A.) Synthesis of ROMP-ATRP diblock copolymer (B.) SEC (CHCl_3) traces of the first block P14 (P-(M3-DHF), red) and the diblock copolymer P20 (blue). (C.) Synthesis of PEG-ROMP diblock copolymer (D.) SEC (DMF) traces of the first block PEG_{2k} macro-CTA (magenta) and the diblock copolymer P21 (blue)

Conclusion

In conclusion, we have successfully developed a simple yet powerful strategy for the synthesis of degradable and living telechelic copolymers catalytically (up to 200 times less Ru complex) using vinyl ethers as CTAs. A one-pot approach was demonstrated for the copolymerization of commercially available DHF with different norbornene derivatives in a living fashion using only catalytic amounts of ruthenium

initiator for the very first time. This method allowed us to synthesize narrowly dispersed ROMP-ROMP (P18, P19) and ROMP-ATRP (P20) diblock copolymers using sub-stoichiometric amounts of ruthenium complex. Moreover, a PEG-based macro CTA was also used to synthesize a PEG-ROMP diblock copolymer (P21) under this catalytic living ROMP condition. We believe that this versatile method will provide a more economical and greener way for the synthesis of degradable polymers to find widespread applications in bordering fields.

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Keywords: Living and degradable copolymers • Macro-chain transfer agent • Vinyl ethers as chain transfer agents • Catalyst – economical syntheses • Block copolymers

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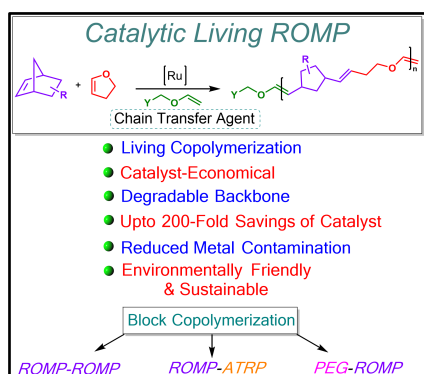
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A new catalytic polymerization mechanism (relying on a regioselective Fischer to Fischer-carbene exchange) to prepare living and degradable ring opening metathesis polymers in one pot is reported here. This method also allowed us to synthesize ROMP-ROMP, ROMP-ATRP, PEG-ROMP diblock copolymers with controlled molecular weights and narrow dispersities using sub-stoichiometric amounts of costly and toxic ruthenium catalyst quite straightforwardly.

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