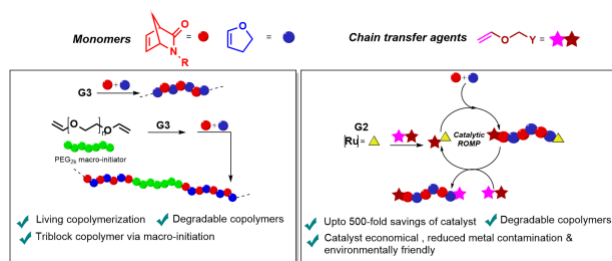# Catalytic syntheses of degradable polymers via ring opening metathesis copolymerization using vinyl ethers as chain transfer agents

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ABSTRACT: Commercially available Vince lactam and its derivatives are copolymerized with 2,3-dihydrofuran (DHF) in a living fashion based on the unique reactivity of Ru Fischer carbene. The resulting copolymers can be fully degraded into small molecules under mildly acidic conditions suggesting a uniform incorporation of the DHF units throughout the polymer backbone. The regioselective and ultrafast chain transfer of **G3**-benzylidene to vinyl ethers enabled us to synthesize a narrowly dispersed triblock copolymer via macro-initiation from poly(ethylene glycol) divinyl ether. This high metathesis activity and regioselectivity of vinyl ethers was further exploited in a kinetically controlled catalytic synthesis of degradable copolymers using vinyl ethers as effective chain transfer agents. This strategy paves the way for a one-pot synthesis of degradable ROMP polymers from easily accessible monomers and chain transfer agents. We report a catalytic copolymerization in which up to 500-fold savings in the expensive and toxic ruthenium carbene complex can be achieved than in a conventional ROMP. We believe that this cost-effective and environmentally friendly synthesis of degradable polymers will be highly useful for many biomedical applications as well as for environmental sustainability.

Introduction

Ring opening metathesis polymerization (ROMP) has emerged as one of the most efficient techniques to synthesize a wide variety of structurally and functionally diverse polymers from cyclic olefin monomers, finding applications in material science, industry, medicine and academia.[1, 2,3] Since most of the ROMP polymers lack backbone degradability, recent efforts have been directed towards synthesizing degradable metathesis polymers for their wide spread applications in drug delivery, therapeutics, as well as in technology.[4,5,6] Many strategies have been developed to incorporate labile or degradable functionalities into the polymer backbone but most of them require special monomer designs via multistep syntheses and often result in uncontrolled polymerizations.[7,8,9,10,11] An alternative approach is the combination of a low-strain cycloolefin (which generally displays poor homopolymerization behaviour) containing a labile functionality with a high strain monomer to incorporate degradable units in the backbone due to random or alternating copolymerization.[12,13,14,15,16,17]

In a typical ROMP procedure vinyl ethers are often used to quench the propagating Grubbs ruthenium complex by forming an electron rich and deactivated alkoxymethylidene Fischer carbene (thermodynamically more stable and much less reactive than Grubbs alkylidene complexes). However, there are some cases where this less reactive Fischer carbene exhibits metathesis activity with highly strained monomers.[18,19,20,21,22] In 2020, the Xia group demonstrated that in-situ formed Ru Fischer carbenes can catalyze the ROMP of 2,3-dihydrofuran (DHF) to form the degradable polyDHF.[23]

Afterwards, the Gutekunst group reported an alternating cascade copolymerization of DHF and alkynes.[24,25] A very recent report showed the synthesis of degradable polymers via ROMP of DHF with norbornene derivatives.[26] Our group has also reported alternating metathesis copolymerization of DHF with terminal alkynes.[27] However, in all these cases, just like in conventional living ROMP, a stoichiometric amount of ruthenium initiator with respect to the polymer chains is required. This often leads to high catalyst loadings, which is quite expensive, as well as difficult as far as removing the toxic metal contaminants from the synthesized polymers is concerned. It furthermore renders the process unattractive for industrial and biomedical applications.[28,29]

For this reason, numerous methods are developed gradually for synthesizing ROMP polymers with reduced catalyst loadings. Initially, several irreversible chain transfer agents were developed which can produce homotelechelic polymers under a thermodynamically driven catalytic process.[30,31,32,33,34,35,36] Pulsed addition ROMP is another method for synthesizing polymers with sub-stoichiometric amounts of ruthenium initiator.[37,38,39] Recently, our group has reported a catalytic living ROMP based on a degenerative reversible chain transfer mechanism.[40,41] Another way of synthesizing ROMP polymers with catalytic amounts of ruthenium initiator relies on a kinetically controlled chain transfer mechanism. Katayama et. al exploited the regioselective chain transfer of heteroatom-substituted vinylic compounds in synthesizing ROMP polymers under a kinetically controlled catalytic process.[42,43,44] Later our group reported the synthesis of heterotelechelic polymers of

norbornene derivatives via a kinetically controlled procedure based on the regioselective cross-metathesis of Grubbs´ first-generation catalyst with cinnamyl alcohol derivatives.[45]

However, in all these reports, the synthesized polymers typically consist of non-degradable all-hydrocarbon backbones. It would be very interesting and important to synthesize degradable ROMP polymers using catalytic amounts of ruthenium complexes making the process more environmentally friendly as well as more useful and attractive for biomedical or technological applications.

Herein, we report a kinetically controlled catalytic ROMP (upto 500 times catalytic) using vinyl ethers as chain transfer agents to synthesize easily degradable polymers via copolymerization of **DHF** with commercially available (1R,4S)-2-azabicyclo[2.2.1]hept-5-en-3-one, which is often referred to as Vince lactam and its derivatives. Besides, we also demonstrate the synthesis of degradable living copolymers using stoichiometric amounts of Grubbs´ third generation catalyst (**G3**). Also, a Fischer carbene macro-initiated triblock copolymer from poly(ethylene glycol) divinyl ether was synthesized for the very first time. We chose this monomer because of its commercial availability and the ease with which derivatives can be synthesized.[46] Furthermore, the partial double bond character of the C-N-bond of the amide, renders the bicycle more strained and hence more reactive in ROMP.

Results and Discussion

We first investigated the homopolymerization of Vince lactam **M2** with **G3**.[46] Addition of **G3** (1 equiv.) to a solution of 30 equiv. of **M2** in DCM led to > 98% conversion of the monomer within 6 h. A SEC measurement (SI, Fig S9) of the precipitated polymer (**P0**) in diethyl ether indicated a good control over molecular weight as well as dispersity. ($M_{n(theo)}$ = 6.27 kDa, **P0**: $M_{n,SEC}$ (DMF) = 6.38 kDa, Đ = 1.19).Next we performed a set of polymerization reactions varying the monomer to **G3** ratio. (SI, Table S1). In all cases, SEC analyses (SI, Fig S10 and S11) confirmed the excellent control over molecular weight and dispersities. Furthermore, a block copolymer was also synthesized by the sequential polymerization of *exo-N*-methylnorborneneimide (MNI) (30 equiv.) followed by addition of 100 equiv. of **M2**. SEC measurements of the first ($M_{n,SEC}$ (DMF) = 5.36 kDa, Đ = 1.09) and after the second block revealed the formation of a diblock copolymer **P8** ($M_{n,SEC}$ (DMF) = 24.21 kDa, Đ = 1.31) with excellent efficacy(SI, Fig S1).
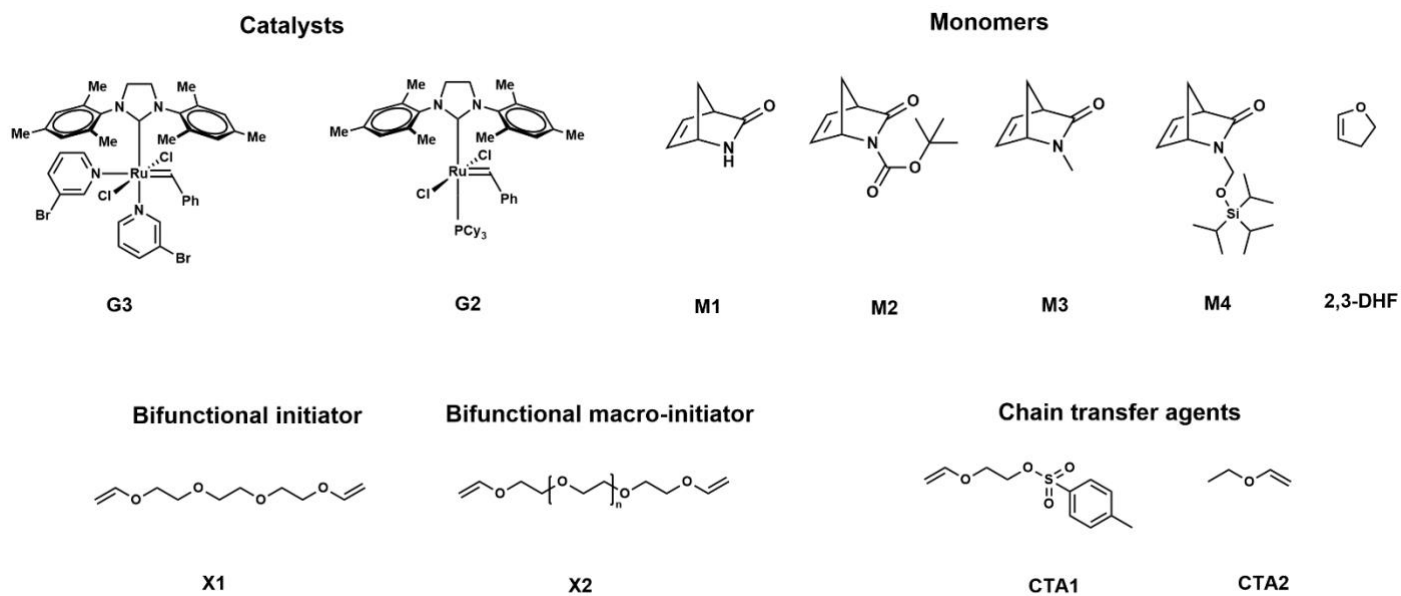
Fig 1: Structures of catalysts, monomers, bifunctional initiator, bifunctional macro-initiator and chain transfer agents used in this report.
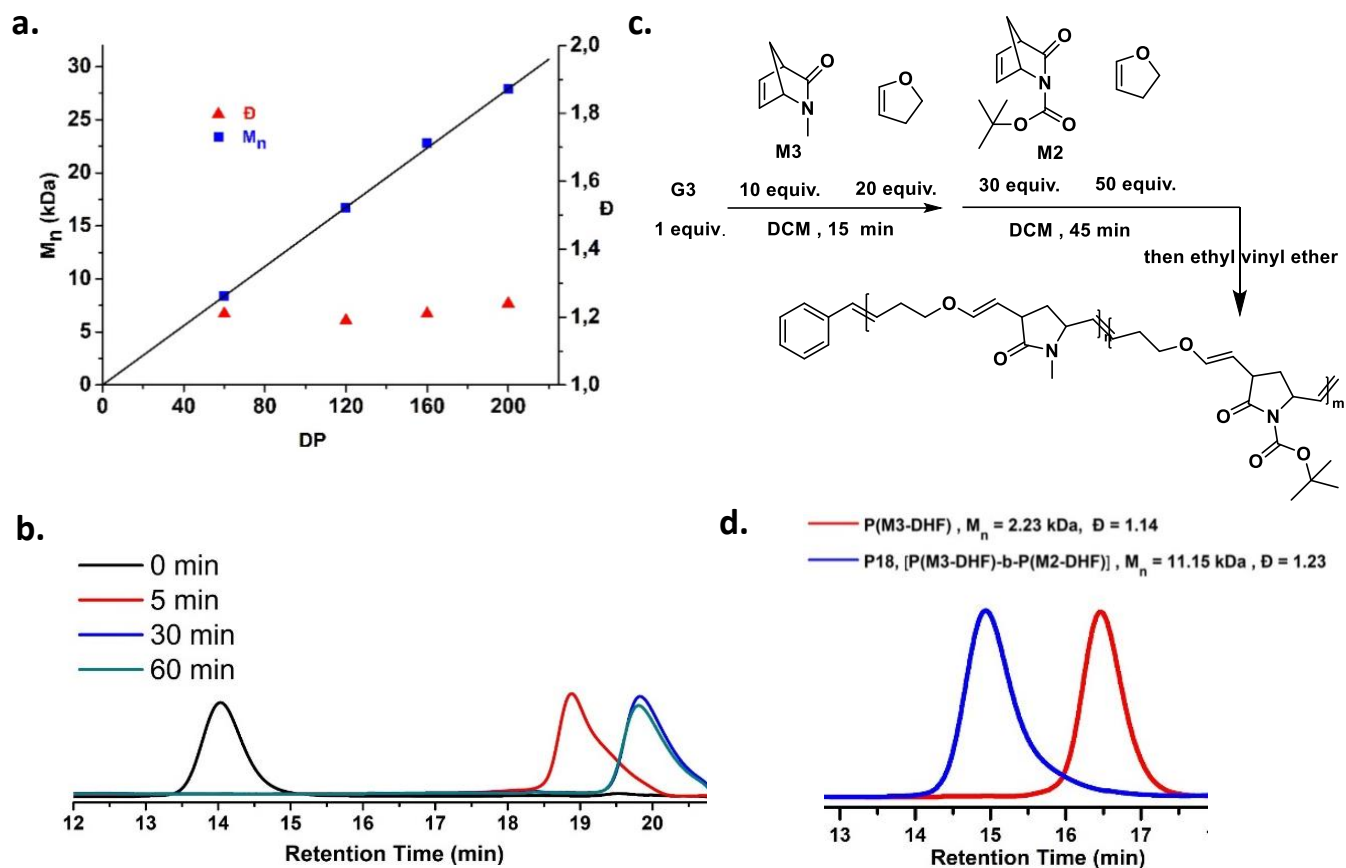
Fig 2: (a.) Plot of the number average molecular weight (M_n, SEC (DMF) and molecular weight dispersity ($Đ$) versus the degree of polymerization (DP) showing a linear correlation. Catalyst **G3** and monomers **M2** and **DHF** were employed for this polymerization. (b.) SEC (DMF) analyses for degradation of **P12** under mild acidic condition. (c.) Synthesis of diblock copolymer **P18** through sequential monomer addition (d.) SEC (DMF) traces of the first block (P-(**M3-DHF**), red) and the diblock copolymer **P18** (blue).

Next in the similar manner, homopolymerization of **M3** (SI, Table S2) and **M4** (SI, Table S3) were also investigated with different monomer to **G3** ratios. In all cases, SEC measurements (SI, Fig S12–S16) confirmed excellent control over molecular weights with narrow dispersities. Interestingly, the homopolymerization rate of **M2** was low, but **M3** and **M4** were quite fast (completed within 15 min), we believe that the coordination of ruthenium to the carbonyl oxygen of the BOC group is responsible for the slow propagation of **M2**. (SI, Fig S121)

After that we explored the living ring opening metathesis copolymerization of **2,3-DHF** with Vince lactam and its different derivatives (**M1-M4**). First, **G3** (1 equiv.) was added to a solution of **M2** (30 equiv.) and **DHF** (60 equiv.) in DCM (0.2 M with respect to **DHF**). ^{1}H NMR spectroscopy revealed that both monomers were reacted during copolymerization and within 30 minutes 98% of **M2** conversion was achieved(SI, Table S4, entry 1). The polymerization was quenched with excess ethyl vinyl ether [26] and precipitated into cold diethyl ether. SEC analysis (SI, Fig S17) of the copolymer indicated a controlled polymerization with narrow dispersity (**P9**: $M_{n,SEC}$ (DMF) = 8.91 kDa, Đ = 1.21). Analysis of the ^{1}H NMR spectra (SI, Fig S2) of poly(**DHF**), poly(**M2**) and poly(**DHF-M2**) (**P9**) showed around 90-93 % alternating character in the synthesized copolymer(SI, Fig S70).To supress the homoropagation of Vince lactam monomer as much as possible, a 1:2 ratio of Vince lactam and DHF was used instead of 1:1 (SI, Table S4). Next a series of copolymers was synthesized by changing the **M2** to initiator ratio for a degree of polymerization (DP) up to 200 (SI, Table S4). A linear relationship was obtained between the number average molecular weights with respect to the degrees of polymerization as expected for a living polymerization (Fig 2a). SEC and ^{1}H NMR analyses further confirmed the excellent control over molecular weights with narrow dispersities and high degree of alternation (SI, Fig S18, S19, S72, S74). Next **M1** (150 equiv.) and **DHF** (300 equiv.) were copolymerized analogously to obtain the copolymer **P13** with controlled molecular weight and dispersity (**P13**, $M_{n,SEC}$ (DMF) = 27.87 kDa, Đ = 1.26). Although the homopolymer of **M1** is insoluble in most of the common organic solvents the synthesized copolymer (**P13**,DP=300) was highly soluble in DCM, chloroform and DMF. After that, to expand the efficacy of this method, other monomers **M3** and **M4** were polymerized with **DHF** for different DPs (SI, Table S4, entry 5-8). Similarly to the procedure described above the copolymers (**P14-P17**) were obtained with high monomer conversion, good degree of alternation, (SI, Fig S3, S4) controlled molecular weights and narrow dispersities. (SI, Fig S21-S24)

To further prove the living character of this copolymerization method, a block copolymer was synthesized by the sequential polymerization of **M3** (10 equiv.) with **DHF** (20 equiv.) followed by **M2** (30 equiv.) with **DHF** (50 equiv.) to give the diblock copolymer **P18** (Fig 2c). SEC analysis showed a complete shift of the first block to give a poly(**M3-DHF)-**b**-poly(M2-DHF)** diblock copolymer (**P18**)(Fig 2d).

Next, as these copolymers contain the acid-labile vinyl ether motifs[26], addition of dilute HCl to a solution of copolymers **P12,P13,P16,P17** (Fig 2b, SI, Fig S42-S44)in DCM showed a complete degradation within 30 minutes which also suggested the uniform distribution of DHF units throughout the backbone.

After that, the rapid and highly regioselective chain transfer of vinyl ethers with **G3**[20,47,48] was exploited in a bifunctional initiation and bifunctional macro-initiation. First, commercially available tri(ethylene glycol) divinyl ether (**X1**) (1 equiv.) was dissolved in CDCl₃ in an NMR tube. A solution of **G3** in CDCl₃ (1 equiv.) was added and a ^{1}H NMR spectrum was recorded within 5 minutes. All the **G3** benzylidene protons (which are found around 19.07 ppm) shifted to a new peak around 13.56 ppm (Fischer carbene) (SI, Fig S6b). Simultaneously, there the generation of 1 equiv. of styrene was observed (characteristic

peaks at 5.25 ppm, 5.75 ppm, SI, Fig S6b). After that, addition of 1 additional equiv. of **G3** to the above solution showed the complete disappearance of the double bond protons (SI, Fig S6c) of the bifunctional initiator **X1**. This shows the ultra-fast reaction of the Grubbs catalyst with vinyl ethers driven by the formation of a thermodynamically more stable Fischer carbene from a **G3** benzylidene. Thereafter, repetition of the same procedure under Schlenk conditions followed by addition of a mixture of monomer **M2** (30/100 equiv.) and **DHF** (60/200 equiv.) yielded the copolymer **P19** and **P20** with an excellent control over molecular weight and dispersity (SI, Table S5, Fig S25, S26).

Encouraged by the above result, we next reacted 1 equiv. of PEG_{2k} divinyl ether (**X2**) with 2 equiv. of **G3**. Here also, ^{1}H NMR spectroscopy revealed the ultra-fast transfer of the Grubbs catalyst to the bifunctional macro-initiator (**X2**) within 5 minutes (i.e. complete shift of the ruthenium benzylidene signals to those of the Fischer carbene along with the disappearance of the double bond protons of **X2**, SI, Fig S7). In a similar manner, addition of **M2** (100 equiv.) and **DHF** (200 equiv.) resulted in the formation of a PEG_{2k}-macro-initiated triblock copolymer **P21** (Fig 3a). SEC analysis after the completion of the copolymerization showed a complete shift in the SEC trace compared to the PEG macro-initiator confirming the block copolymer formation (Fig 3b).

Thereafter, this regioselective and ultrafast reactivity of the vinyl ethers impelled us to investigate the catalytic synthesis of such copolymers exploiting a kinetically controlled chain transfer process. A comparable rate of monomer propagation to that of the chain transfer to the CTA is the key step for such a mechanism. Ideally, the molecular weight of the resulting polymer will be determined by the monomer to CTA ratio, and not by the monomer to catalyst ratio. Because of the high metathesis activity and regioselectivity, we hypothesized that vinyl ethers can be used as efficient CTAs to react regioselectively with the propagating polymer chain thereby regenerating the initiating species making the whole process catalytic. (Fig 4a). Furthermore, in a catalytic process the initiation kinetics of the ruthenium complex are less important than in a living polymerization. We, therefore, chose **G2** (Figure 1) for the next experiments.
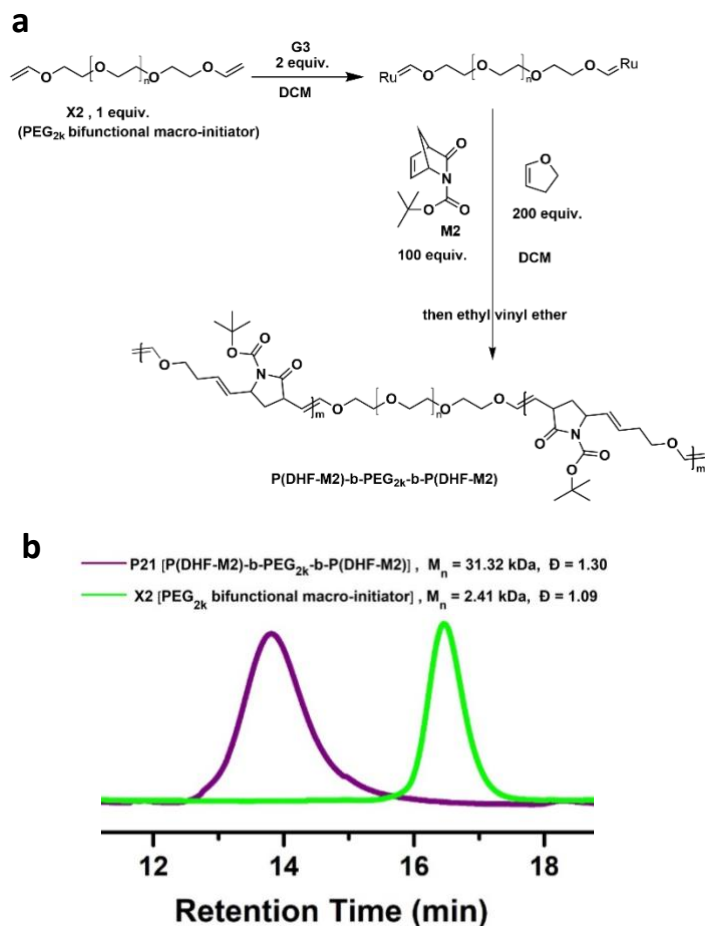
Fig 3: (a) Synthesis of triblock copolymer **P21** via macro-initiation from PEG$_{2k}$ divinyl ether (**X2**) (b) SEC (DMF) traces of the bifunctional macro-initiator **X2** (green) and the triblock copolymer **P21** (purple).

To prove our hypothesis, a one-pot copolymerization using a ratio of **G2:CTA1:M2:DHF** of 1:20:600:1200 was performed in DCM. Within 2h, >98% conversion of **M2** was achieved. (Table S1**,** entry 1**)** SEC analysis (SI, Fig S27) of the precipitated copolymer (**P22**) showed a monomodal distribution with a molecular weight of 9.68 kDa (determined by monomer/**CTA1** ratio) and dispersity of 1.74 which is in agreement with mechanistic considerations.[42,44,45] Under identical condition , **G3** also yielded a polymer with controlled molecular wight and dispersity ($M_{n,SEC}$ (DMF) = 10.32 kDa, Đ = 1.79). Also, the correct matching of the end groups with respect to the backbone protons is shown in the ^{1}H NMR spectrum of the copolymer **P22** (SI, Fig S93). This is possible via a catalytic copolymerization relying on a very fast and efficient chain transfer to **CTA1** in a kinetically controlled manner. Then, a series of telechelic copolymers were synthesized by varying the **M2/CTA1** ratio (Table S1, entry 2-5**)** and characterized by SEC (DMF) (SI, Fig S28-S31) and ^{1}H NMR (SI, Fig S95, S97, S98, S100). A linear correlation between the molecular weight (M_n) and the **M2/CTA1** ratio was obtained as expected (Fig 4b).

To further elucidate the mechanism, a kinetic SEC experiment was performed where a mixture of **M2** (15000 equiv.) and **DHF** (30000 equiv.) was treated with a solution of **CTA1** (100 equiv.) and **G2** (1 equiv.). At different time intervals, a small amount of sample was taken from the polymerization mixture, precipitated in cold diethyl ether and analysed by SEC (DMF). The almost constant molecular weight (M_n) and dispersity throughout the polymerization reaction strongly indicated a catalytic copolymerization under a kinetically controlled chain transfer mechanism (SI, Fig S8).

Then, a catalytic synthesis of a telechelic copolymer **P27** (**Table 1,** entry 6) was achieved with a high monomer conversion using a 1/500 [th] of the classically required amount of Grubbs catalyst **G2**. Notably, in this synthesis there is a 500-fold saving of the costly and toxic ruthenium catalyst compared to a traditional ROMP, which, to the best of our knowledge, is the very first report for the synthesis of a degradable ROMP copolymer. After that commercially available **CTA2** was used to produce the copolymer **P28** (Table 1, entry 7) with a 100-fold decrease in the amount of catalyst used.

Furthermore, to show the versatility of this method, other monomers **M1, M3** and **M4** were also polymerized with DHF in the presence of chain transfer agents **CTA1** and **CTA2** for different monomer /**CTA/G2** ratios in a similar manner as described above yielding the copolymers (**P29-P35**) with high monomer conversion, and controlled molecular weights (determined by monomer**/CTA** ratio, Table 1, entry 8-14). All polymers obtained were characterized by SEC (DMF) and ^{1}H NMR spectroscopy.

Next, treatment of these catalytic copolymers (**P26, P31, P33,P35**) with dilute HCl also resulted in the complete degradation within 30 minutes (SEC analyses, see Fig 4c., SI, Fig S46-S48), further suggesting a good degree of alternation throughout the polymer backbone.
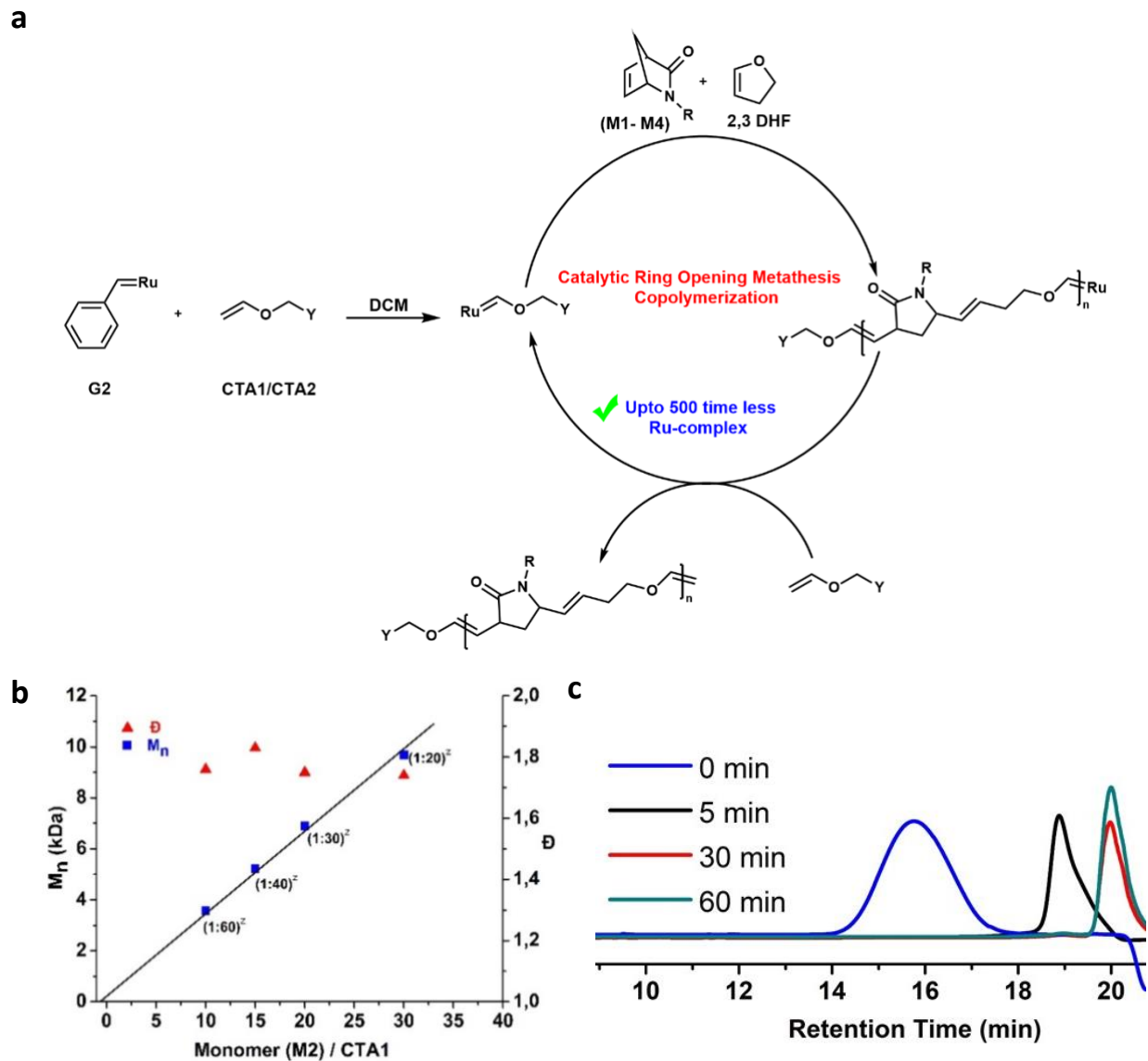
Fig 4: (a) Mechanism for the catalytic syntheses of degradable ROMP polymers using vinyl ethers as chain transfer agents. (b) Plot of the number average molecular weight (M_n, SEC (DMF) and molecular weight dispersity ($Đ$) versus the **[M2]/[CTA1]** ratio showing a linear correlation. The ratios reported in brackets (z) denote the **[G2]/[CTA1]** ratio. (c) SEC (DMF) analyses for the degradation of **P26** under mild acidic condition.

Table 1 : One-pot catalytic copolymerization data of monomers M1-M4 with DHF using chain transfer agents CTA1 and CTA2

Entry	Polymer	CTA	Monomer (M)	G2:CTA:M:DHF	M_n (Non catalytic) (kDa)	M_n (Catalytic, monomer/CTA) (theo; kDa)	M_n (obs.) SEC[a] (DMF; kDa)	Đ
1	**P22**	CTA1	M2	1:20:600:1200	167.4	8.37	9.68	1.74
2	**P23**	CTA1	M2	1:30:600:1200	167.4	5.58	6.89	1.75
3	**P24**	CTA1	M2	1:40:600:1200	167.4	4.18	5.23	1.83
4	**P25**	CTA1	M2	1:60:600:1200	167.4	2.79	3.56	1.77
5	**P26**	CTA1	M2	1:100:1200:2400	334.8	3.34	4.32	1.76
6	**P27**	CTA1	M2	1:500:10000:20000	2790	5.58	7.12	1.93
7	**P28**	CTA2	M2	1:100:4000:8000	1116	2.79	3.28	1.78
8	**P29**	CTA1	M1	1:10:400:800	71.6	7.16	8.78	1.89
9	**P30**	CTA1	M1	1:10:1000:2000	179	17.90	18.72	1.77
10	**P31**	CTA1	M1	1:400:16000:32000	2864	7.16	8.43	1.98
11	**P32**	CTA2	M1	1:100:4000:8000	716	7.16	8.39	1.92
12	**P33**	CTA1	M3	1:50:600:1200	115	2.31	3.69	1.84
13	**P34**	CTA1	M3	1:60:400:800	115	1.93	2.84	1.75
14	**P35**	CTA1	M4	1:50:400:800	219	4.38	5.25	1.83

[a] SEC (DMF) was calibrated with poly(ethylene oxide) standards

Conclusions

In conclusion, we have demonstrated the living copolymerization of commercially available Vince lactam and its derivatives with DHF, yielding easily degradable functional polymers (under mild acidic condition) with controlled molecular weights, narrow dispersities and fair degree of alternation. Also macro-initiated triblock copolymer was synthesized from poly(ethylene glycol) divinyl ether for the very first time. More interestingly, we have successfully developed a versatile approach towards the synthesis of degradable telechelic copolymers catalytically (upto 500 times catalytic) using vinyl ethers

as chain transfer agents. This method provides a more economical and environmentally friendly way to synthesize degradable ROMP polymers from easily available monomers and chain transfer agents quite straightforwardly. We believe that this new strategy with a very high decrease (500-fold) in the costly and toxic catalyst loading will find new applications in material science, biomedicine and technology.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Instruments data, Experimental methods, NMR data, SEC data. (PDF)

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A.M and I.M contributed equally. All authors have given approval to the final version of the manuscript.

Notes

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