A Single Functionalization Agent for Heterotelechelic ROMP Polymers

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ABSTRACT: Heterotelechelic polymers are an important class of materials finding applications in bioconjugation, imaging, sensing and synthesis of organic/inorganic hybrid systems with interesting features. However, the synthesis of such polymers is challenging. Here, we report a mechanistically unique and most efficient method based on a single functionalization agent to prepare heterotelechelic polymers by ring-opening metathesis polymerization. Different functionalization agents can be synthesized in one simple step from inexpensive commercial starting materials. The functionalization agents initially generate a functional initiator from commercial Grubbs' first generation ruthenium benzylidene catalyst. During this process, a functional dihydrofuran derivative is produced. After functional initiation and propagation of a suitable monomer, the dihydrofuran derivative functionally terminates the polymerization yielding a primary alcohol terminated heterotelechelic polymers. Molecular weight control is achieved by varying the ratio between monomer and Grubbs' first generation catalyst. This method may emerge as a popular choice to prepare heterotelechelic polymers due to its simplicity and efficiency.

Ring-opening metathesis polymerization (ROMP) has emerged as one of the most popular polymerization methods due to its ability to produce polymers with controlled molecular weights from monomers with and without functional groups.[1,2,3,4,5,6,7,8,9,10,11,12] Grubbs' first (**G1**) and third generation catalyst (**G3**) are the most common initiators for ROMP owing to their high initiation to propagation rate ratio[13,14]. ROMP has also been employed in the synthesis of telechelic polymers due to its high functional group tolerance. Telechelic polymers can be classified into three classes i.e. monotelechelic, homotelechelic and heterotelechelic. Monotelechelic polymers i.e. those carrying a functional group at only one chain-end are typically synthesized by the termination of the propagating polymer chain using functional chain transfer agents (CTAs) such as substituted vinyl ethers,[15,16] vinyl esters,[17] acrylates,[18] vinyl carbonates and lactones,[19] protected amines,[20] acyclic olefins[21] or cyclic olefins.[22] Homotelechelic polymers carry the same functional group at both chain-ends. Their synthesis is achieved by polymerizing a strained cyclic olefin in the presence of a bifunctional CTA carrying protected alcohols,[23] epoxides and methacrylates,[24] carboxylic acids and amines[25] or trithiocarbonate RAFT initiators.[26] Statistical copolymers from strained cyclic olefins and dioxepines were prepared and the polymeric acetals hydrolyzed to yield homotelechelic polymers.[27]

Heterotelechelic polymers i.e. those carrying a different functional group at either chain-end are an important class of materials finding applications in bioconjugation, imaging, sensing and the synthesis of organic/inorganic hybrid systems with interesting features.[28] However, the synthesis of such polymers is challenging and there are relatively few reports of heterotelechelic polymer syntheses. Heterotelechelic polymers were produced by the sacrificial synthesis strategy. [29] First, 2-methyl-1,3-dioxepine (**MDO**) monomer was polymerized followed by polymerization of norbornene derivatives by ROMP and finally the polymerization was terminated with vinylene carbonate (**VC**) or 3H-furanone (**HF**). **MDO** forms the sacrificial block giving hydroxy end-group upon hydrolysis while the aldehyde or carboxylic acid end-group were given by **VC** or **HF**, respectively to the polymer chains. However, this strategy is not atom-economical, as the whole block is sacrificed to introduce one end-group on the polymer chain. Another route to synthesize heterotelechelic polymers involves the use of a prefunctionalized initiator and termination with a functional CTA.[30,31] However, it involves extensive purification of the initiators and is often low yielding. There are only a few reports for the synthesis of functionalized initiators in good yield without the need of extensive purification using 7-substituted norbornene derivatives,[32] propargyl allyl ethers[33] and enyne sulfonamides.[34] These functional initiators can introduce a functional group at one polymer chain-end. However, these strategies involve the use of another CTA in order to introduce the second functional group at the other chain-end.

Thus, a system based on a single CTA to introduce different functional groups at both polymer chain-ends would be ideal. Our group reported the synthesis of heterotelechelic polymers using a single CTAs by exploiting its regioselectivity during olefin metathesis.[35] However, this approach required the use of a large excess of CTAs (≥35 equiv.). Another approach recently published by us required more synthetic steps in the synthesis of the CTA[36].

Here, we report the synthesis of heterotelechelic polymers in one pot based on a single functionalization agent (FA) exploiting its regioselectivity in olefin metathesis. This mechanistically unique strategy is atom economical (requiring only 6 equiv. of the FA) and produces functional catalysts in very high yields (89-95%). Additionally, the FAs can be synthesized in one step from inexpensive commercially available starting materials.

First, we synthesized three FAs i.e. **FA1** ((E)-2-(4-chlorostyryl)-4,7-dihydro-1,3-dioxepine)), **FA2** ((E)-2-(4-nitrostyryl)-4,7-dihydro-1,3-dioxepine)) and **FA3** ((E)-2-(4-bromostyryl)-4,7-dihydro-1,3-dioxepine) (see Figure 1) in one step from commercially available cinnamaldehyde derivatives and *cis*-2-butene-1,4-diol (see Supporting Information).

We hypothesized that **G1** (Figure 1) would first undergo a ring-opening metathesis (ROM) reaction with the *endo* cyclic double bond of FA (**FA1**/**FA2**/**FA3**), as the endo cyclic double bond is more reactive than the *exo* cyclic double bond due to ring strain (see Figure 1)[10].

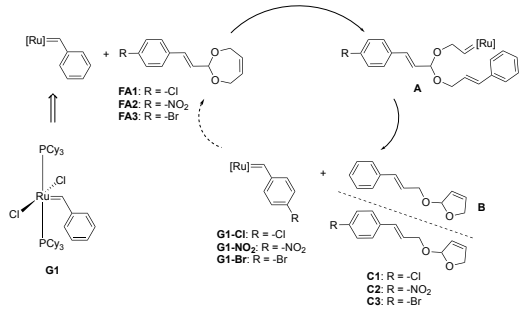

Figure 1. Functional initiator synthesis from reaction between commercially available **G1** and **FA1**-**FA3**.

The newly formed carbene complex (**A**) would ideally undergo an intramolecular ring closing metathesis (RCM) reaction rather than an intermolecular propagation reaction with another *endo* cyclic double bond. This step would yield the new functionalized carbene complex (**G1-Cl**/**G1-NO₂**/**G1-Br**) and a 2,5-dihydrofuran (DHF) derivative (**B**). As the FA is used in excess, the new functionalized carbene complex would react with excess FA in a similar fashion, thereby producing a new DHF derivative (**C1**/**C2**/**C3**) and regenerating itself in the process. In the end, the reaction mixture would contain a new functionalized carbene complex and two DHF derivatives.

To test the RO/RCM hypothesis shown in Figure 1, **G1** (1 equiv.) was reacted with **FA1**-**FA3** (6 equiv.) in CD_2Cl_2 at room temperature and the reaction was followed by ^{1}H NMR spectroscopy. The disappearance of the benzylidene signal of **G1** and formation of the corresponding new carbene signal of functionalized complex (**G1-Cl**/**G1-NO₂**/**G1-Br**) in excellent yields were observed (see Figure 2). Inherently, the formation of **B** (1 equiv.) and **C1** (1.82 equiv.: 47% conversion of **FA1**)/**C2** (1.1 equiv.: 35% conversion of **FA2**)/**C3** (1.58 equiv.: 43% conversion of **FA3**) was also observed. While 3.18 equiv. of **FA1**/3.9 equiv. of **FA2**/3.42 equiv. of **FA3** remained unreacted in the given reaction time. Next, *exo*-*N*-methylnorbornene imide (**MNI**) (20 equiv.) was allowed to react with **G1-Cl** (prepared as mentioned above). The ^{1}H NMR spectrum was recorded after 10

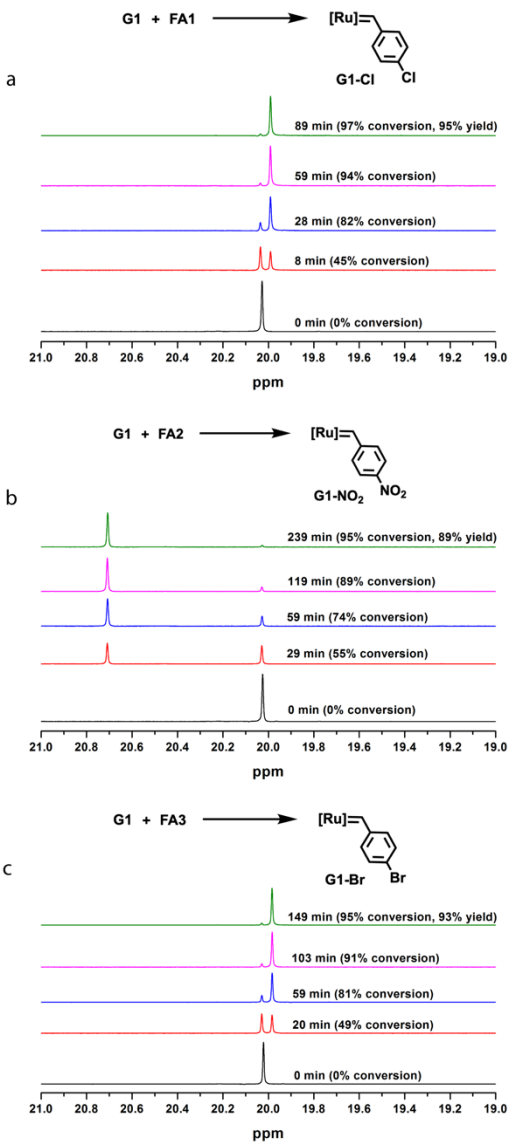

Figure 2. ^{1}HNMR spectra (CD_2Cl_2, 300 MHz) of the reaction of **G1** (1 equiv.) with (a) **FA1** (6 equiv.) forming **G1-Cl** (19.99 ppm) within 89 min (97% conversion, 95% yield), (b) **FA2** (6 equiv.) forming **G1-NO₂** (20.71 ppm) within 239 min (95% conversion, 89% yield) and (c) **FA3** (6 equiv.) forming **G1-Br** (19.98 ppm) within 149 min (95% conversion, 93% yield).

min. The **MNI** was polymerized (as evident by appearance of the olefinic protons belonging to polymer, see Figure S2b, SI) and the propagating carbene complex was converted to **G1-Cl** after reacting with the DHF derivatives (which were present in the reaction mixture along with **G1-Cl**) within this short time (see Figure S2a, SI). The acidic hydrolysis of the polymer produced **P0** ($M_{n,\,theo}$=3.5 kDa, $M_{n,\,found}$=4.8 kDa, Đ=1.54, see Figure S4, SI) carrying a *p*-chloro phenyl and a hydroxyl end-group as confirmed by isotopically resolved matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-ToF MS) (see Figure S8, SI). Thus, we concluded that the propagating carbene complex also reacted regioselectively with the DHF derivatives. The reaction of the propagating carbene complex with remaining amounts of **FA1** can also occur. However, this reaction will lead to the same product which is ob-

tained in the case of reaction with the DHF derivatives. Subsequently, we wanted to explore the minimum amount of **FA1** required to achieve high conversion to **G1-Cl** from **G1**. In order to explore this, 3 equiv. of **FA1** were reacted with **G1** to produce **G1-Cl**.

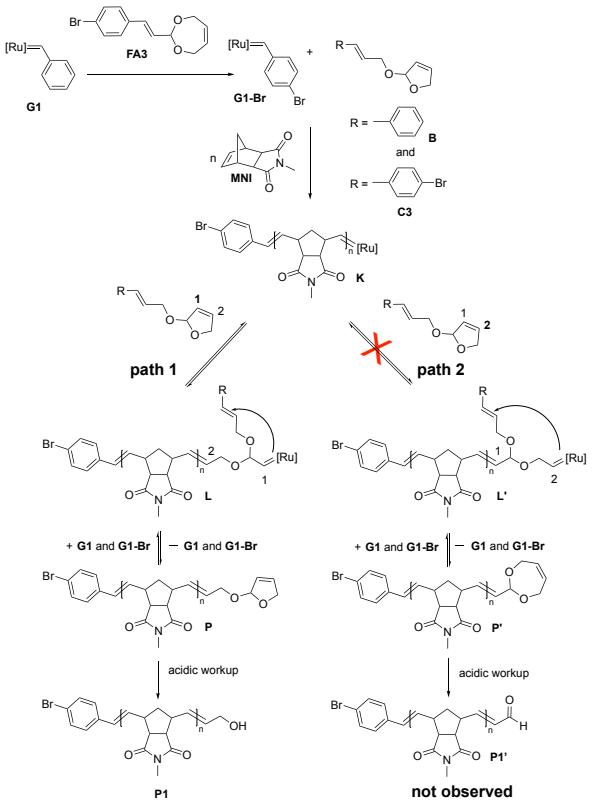

Figure 3. Synthesis of heterotelechelic polymers based on a one-pot reaction containing the monomer (**MNI**) a functionalization agent **FA3** and Grubbs catalyst **G1**. Path1 and 2 are representations of hypothetical reaction pathways of which only the product of path 1 (**P1**) is observed.

It took 8 hours to reach 88% conversion (see Figure S1, SI) while the same reaction with 6 equiv. of **FA1** achieved 97% conversion in 1.5 hours (see Figure 2a). Thus, 6 equiv. is the suitable amount of **FA1** to achieve high conversion of **G1** into **G1-Cl** in reasonably short time. Further, we reacted **FA1** with **G3**. Unfortunately, decomposition of **G3** was observed. In order to synthesize a heterotelechelic polymer, **G1** (1 equiv.) was reacted with **FA3** (6 equiv.) to produce **G1-Br** and DHF derivatives (**B** and **C3**) while leaving 3.42 equiv. of **FA3** unreacted, as mentioned earlier (see Figure 3). Then, monomer **MNI** (32.26 equiv.) was added to this reaction mixture. This leads to the formation of propagating carbene complex (**K**) which can react with either the DHF derivatives or **FA3**. In principle, the DHF derivatives could react via two pathways (Figure 3, path1 and 2). Path 1 involves the ROM reaction of **K** with the *endo* cyclic double bond at **C-1** to form the new carbene complex **L** (Figure 3). Subsequently, **L** can undergo an intramolecular RCM reaction to produce polymer **P** carrying the p-bromo phenyl and a DHF end-group (Figure 3). Acidic workup leads to cleavage of the DHF end-group of **P** and thus yield a polymer **P1** carrying the *p*-bromo phenyl group at one end and a hydroxyl group on the other chain-end (Figure 3). Path 2 involves the ROM reaction of **K** with the *endo* cyclic double bond at **C-2** to produce the new carbene complex **L'** (Figure 3). **L'** could undergo an intramolecular RCM reaction to generate polymer (**P'**) carrying a *p*-bromo phenyl and a dioxepine end-group.

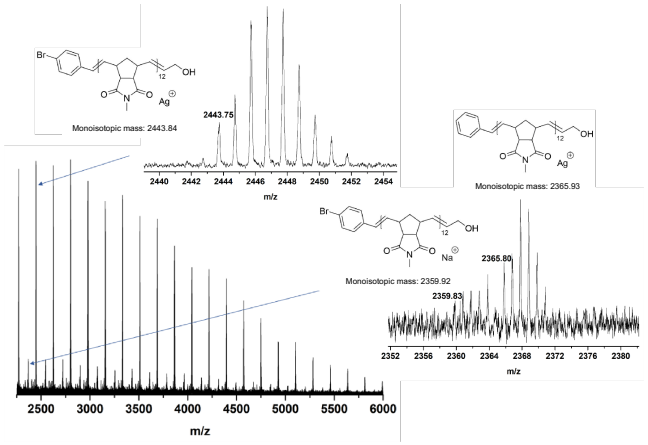

Figure 4. MALDI-ToF mass spectrum of **P1** (with silver cation) showing *p*-bromo phenyl and hydroxy end-groups (major peaks). The minor peaks belong to the same polymer attached to a sodium cation. The other minor peaks belong to a polymer (with silver cation) carrying phenyl and hydroxy end-groups which would have produced by the 5% remaining **G1** catalyst.

A polymer (**P1'**) carrying a *p*-bromo phenyl and an aldehyde end-group would be produced upon acidic workup of **P'**. However, the structural analysis of the polymer by MALDI-ToF MS (see Figure 4) revealed that the polymer carries exclusively the *p*-bromo phenyl and hydroxyl end-groups. The ^{1}H NMR spectrum (see Figure S14, SI) of the polymer also confirmed the absence of aldehyde end-groups. In order to prove the reaction of **K** with the DHF derivatives (**B** and **C3**), a similar reaction was setup and run for 15.75 hours to ensure almost complete conversion of **FA3** to the corresponding DHF derivatives **B** (1 equiv.) and **C3** (4.76 equiv.) in 96% conversion along with the formation of **G1-Br** (see Figure S3, SI). The monomer **MNI** was added to this reaction mixture to form the polymer **P1''**. The MALDI-ToF mass spectrum (see Figure S9, SI) of **P1''** showed the same end-groups as obtained above where a mixture of DHF derivatives and **FA3** were present in the solution. The ^{1}H NMR spectra (see Figure S14 and S15, SI) of both polymers were also similar. From this data we conclude that the one-pot polymerization reaction follows path 1 (Figure 3) producing **P1** exclusively. It is conceivable that path 2 is not observed due to the increased steric demand in the hypothetical metallacyclobutane intermediate. It's worth noting that the allylic branched cyclopentene monomers[37,38] have also shown a propensity for high degrees of regio-regular insertion during ROMP in addition to cyclooctene monomers.[39] The reaction of **K** with remaining amounts of **FA3** can only react via one pathway due to the symmetry of the *endo* cyclic bond. This reaction is not shown in Figure 3 as it will give the same product as shown for path1. The DHF end-group in the MALDI-ToF mass spectrum of polymer **P1** was not observed probability due to cleavage of DHF end-group during the MALDI ToF sample preparation. The molecular weight (M_n) and dispersity (Đ) of **P1** was determined by gel permeation chromatography (GPC). The M_n and Đ of the **P1** were found to be 6.6 kDa and 1.76, respectively. Subsequently, the ratio between **MNI** and **G1** (64.51:1 and 96.77:1) was varied to synthesize different molecular weight polymers **P2** (M_n=11.3 kDa, Đ=1.91) and **P3** (M_n=15.1 kDa, Đ=2.00) (see Table S1 and Figure S5, SI). The structure of **P2** and **P3** was confirmed by MALDI-ToF

MS (see Figure S10 and S11, SI) and ^{1}H NMR spectroscopy (see Figure S16 and S17, SI). The dispersity broadens with increased molecular weight of polymers. This observation is probably due to premature chain termination caused by **C3** when using higher amounts of **MNI** (see Table S1, SI). Next, **G1** (1 equiv.) was reacted with **FA2** (6 equiv.) to produce **G1-NO$_2$** and DHF derivatives while leaving 3.9 equiv. of **FA2** unreacted, as mentioned before (see Figure 3). Then, monomer **MNI** (32.26 equiv.) was polymerized after adding it to the reaction mixture. The MALDI-ToF mass spectrum (see Figure S12, SI) revealed that the obtained polymer **P4** (M_n=6.1 kDa, Đ=1.81: see Figure S6, SI) carries *p*-nitro phenyl and hydroxy end-groups. The characterization of **P4** was also performed by ^{1}H NMR spectroscopy (see Figure S18, SI). Finally, another monomer *exo*-*N*-phenylnorbornene imide (**PNI**) (32.26 equiv.) was used to make heterotelechelic polymer **P5** by this method using **G1-Br** (prepared from **G1** (1 equiv.) and **FA3** (6 equiv.)). The polymer **P5** (M_n=4.8 kDa, Đ=2.15: see Figure S7, SI) was characterized by ^{1}H NMR spectroscopy (see Figure S19, SI). The MALDI-ToF mass spectrum of **P5** did not show the desired end groups. So, **P5** was hydrolyzed with HCl (aq.) overnight to cleave the DHF end-group yielding polymer **P5'**. The MALDI-ToF mass spectrum (see Figure S13, SI) of **P5'** showed that it carries desired *p*-bromo phenyl and hydroxy end-groups.

We developed a mechanistically unique and most efficient polymerization method till date based on single FAs for the synthesis of heterotelechelic polymers by ROMP. Different FAs were explored for this purpose. The FAs reacted with commercial Grubbs initiator **G1** in a RO/RCM fashion to produce the corresponding functional catalysts and DHF derivatives. The functional catalysts initiated the polymerization of **MNI**/**PNI** while the DHF derivatives functionally terminated the polymerization to yield heterotelechelic polymers. The ratio between **MNI** and **G1** was varied in order to synthesize heterotelechelic polymers with different molecular weight. The structures of the polymers were analyzed by MALDI-ToF MS and ^{1}H NMR spectroscopy.

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COMPETING INTERESTS

The authors declare no competing interests.

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ASSOCIATED CONTENT

Supporting Information available: Experimental procedures, GPC data, MALDI-ToF MS data, NMR spectra.

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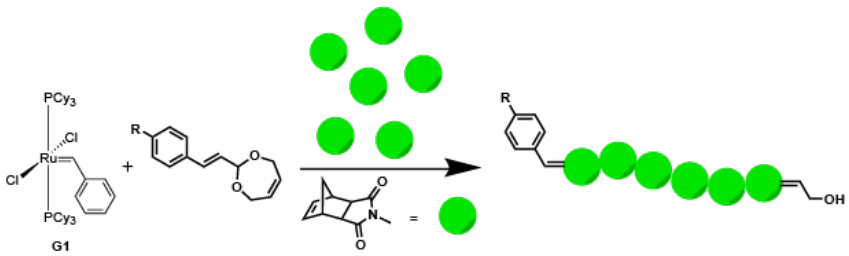
Graphical Abstract



Ring Opening Metathesis Polymerization (ROMP)