One-Pot Heterotelechelic Metathesis Polymers via Regioselective Chain Transfer Agents

Ankita Mandal,[‡] Indradip Mandal,[‡] Andreas F. M. Kilbinger*

Department of chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg (Switzerland)

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ABSTRACT: Single chain transfer agents are used to synthesize narrowly distributed heterotelechelic ROMP polymers in one pot, exploiting a new mechanistic and synthetic approach. The chain transfer agents carrying different functional groups are synthesized in few straightforward steps. Pre-functionalization of commercially available Grubbs' third-generation catalyst is realized in situ using regioselective chain transfer agents within a short reaction period. After monomer consumption, the excess chain transfer agent in the reaction medium automatically end-functionalizes the polymer chain yielding a heterotelechelic polymer via a ring-opening- ring-closing sequence. ^{1}H NMR, MALDI-ToF, and SEC analyses confirmed end group functionalization as well as excellent control over molecular weight and dispersity. This strategy highlights a new way of synthesizing one-pot heterotelechelic ROMP polymers straightforwardly and efficiently.

Introduction

Ring opening metathesis polymerization (ROMP) has emerged as an efficient method for polymer synthesis finding applications in different areas, such as therapeutics, bioconjugation, imaging and materials science both in academic and industrial environments.[1-10] It is a powerful technique for synthesizing different polymer architectures, often with precise control over molecular weight, dispersity, and monomer composition.[11-17] Molybdenum and ruthenium based complexes developed by the Schrock and Grubbs groups are the main well defined metathesis catalysts finding extensive applications in polymer chemistry.[18] Among all these, the third generation Grubbs' catalyst (**G3**) is the most popular in ROMP due to its commercial availability and high initiation to propagation rate ratio, making it suitable for living polymerization.[19-22] The high functional group tolerance of the catalyst has made ROMP highly prevalent for the synthesis of telechelic polymers.[23-29]

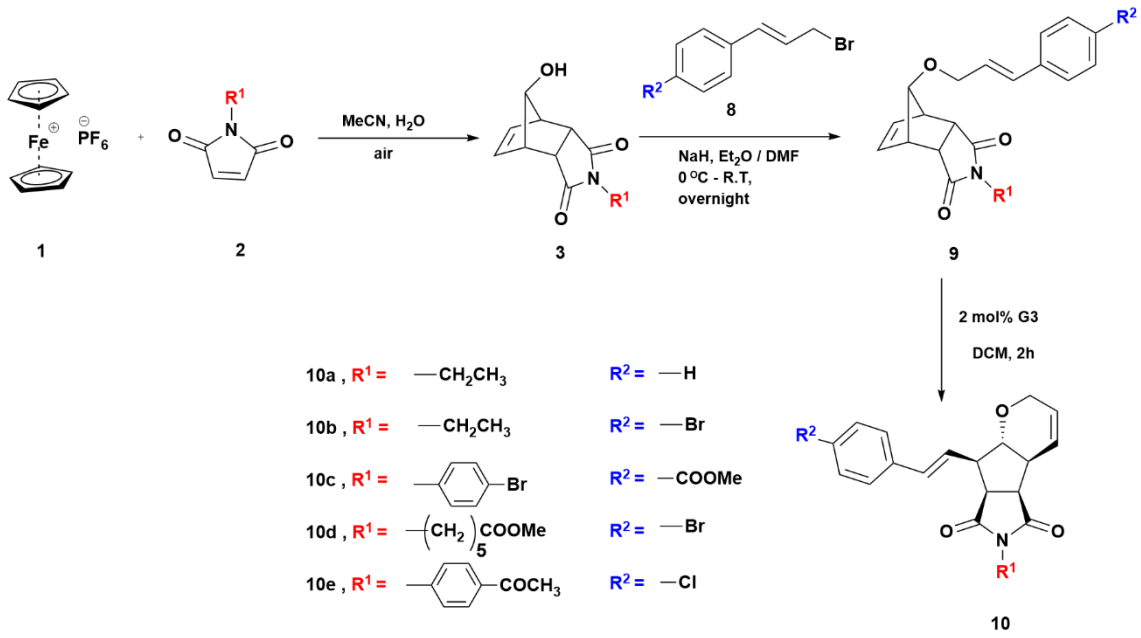
Mono-end functional polymers can be synthesized by terminating the polymer chain with vinyl carbonates, lactones, protected amines, unsaturated acetals, acrylates or substituted vinyl ethers but also via cross metathesis with acyclic and cyclic olefins.[30-33]

Homotelechelic polymers, that is, polymers carrying the same functional group at both the chain ends, can be synthesized from monomers such as cyclooctene or cyclooctadiene by sacrificing the living character of the polymerization. Narrowly dispersed homotelechelic polymer synthesis has been reported by the Grubbs group[34] as well as our group.[35]

Heterotelechelic polymers, that is, polymers carrying different functional groups at either chain end, find widespread application in biomaterials synthesis, protein conjugation, imaging, sensing and many more.[36,37] Synthesis of such polymers via several living polymerization techniques such as RAFT,[38] ATRP,[39] cationic polymerization[40] and others have been reported. However, the synthesis of heterotelechelic polymers with specific control over composition, molecular weight and molecular weight distribution, is significantly more challenging by ROMP and there are only few reports. One way of preparation follows the sacrificial synthesis strategy.[41] However, this method is limited to few functional end groups such as one alcohol and either an aldehyde or a carboxylic acid end group. Another way to synthesize heterotelechelic polymers is by prefunctionalization of the initiator followed by termination with a different functional moiety.[42-45] There are only few reports where pre-functionalized initiators can be synthesized in high yielding reactions that allow their use without additional purification.[46-48] However, all these strategies typically require cross-metathesis after monomer propagation with an excess of a functional symmetrical chain transfer agent (CTA) to introduce the desired end group. A heterotelechelic polymer synthesis using a single regioselective chain transfer agent has recently been reported by our group[49] but the method was limited to Grubbs' 1st generation catalyst (**G1**). Furthermore, heterotelechelic polymers synthesized via this particular strategy show a high dispersity for mechanistic reasons.

The synthesis of narrowly dispersed heterotelechelic polymers using only a single chain transfer agent would therefore be mechanistically interesting and potentially useful in various disciplines bordering synthetic polymer chemistry. Here, we have reported a new mechanistic and synthetic approach for making narrowly dispersed heterotelechelic polymers in one-pot using a single chain transfer agent carrying different functional end groups. This strategy paves the way for synthesizing well-defined heterotelechelic polymers that might be of great interest for material science, biochemistry, or industrial use.

Scheme 1. Synthesis of chain transfer agents (10a -10e)



Results and discussion

Recently, our group reported catalytic living ROMP with reversible chain transfer agents (rCTA) based on a degenerative reversible chain transfer mechanism.[50,51] However, the main drawbacks of the currently available rCTAs are their poor stability, difficult synthetic access and lack of functional groups.

To address the latter, we followed a synthetic procedure that allows the preparation of 7-anti-hydroxy-norborneneimides **3** (**Scheme 1**).[52] Alkylation of the hydroxy group of **3** with cinnamyl bromide derivatives **8** yielded the CTA precursors **9** (**Scheme 1**). Using Grubbs' 3rd generation catalyst (**G3**), a ring-opening-ring closing sequence previously reported[50] allowed us to obtain compounds **10** carrying one type of functional group in para position of the styrene moiety (**Scheme 1**, **10a**-**10e**, blue) and a different functional group on the imide nitrogen atom (**Scheme 1**, **10a**-**10e**, red).

Initial kinetic investigations where **10a** (10 equiv.) was added to a solution of **G3**-initiated (1 equiv.) *N*-methylnorborneneimide (**MNI**, 20 equiv.) in deuterated dichloromethane (DCM-d_2) revealed that **10a** reacted nearly 12 times slower with the propagating ruthenium carbene than the non-functional analogous compound (*E*)-7-styryl-2,4a,5,6,7,7a-hexahydrocyclopenta[b]pyran[50] (see supporting information Fig S1). We hypothesized that coordination of the imide carbonyl oxygen atoms to the ruthenium center might be responsible for the observed low reaction rates. This assumption was further supported by the fact that addition of titanium tetraisopropoxide to an otherwise identical experiment gave a rate of reaction that was at least ten times higher (see supporting information Fig S2).

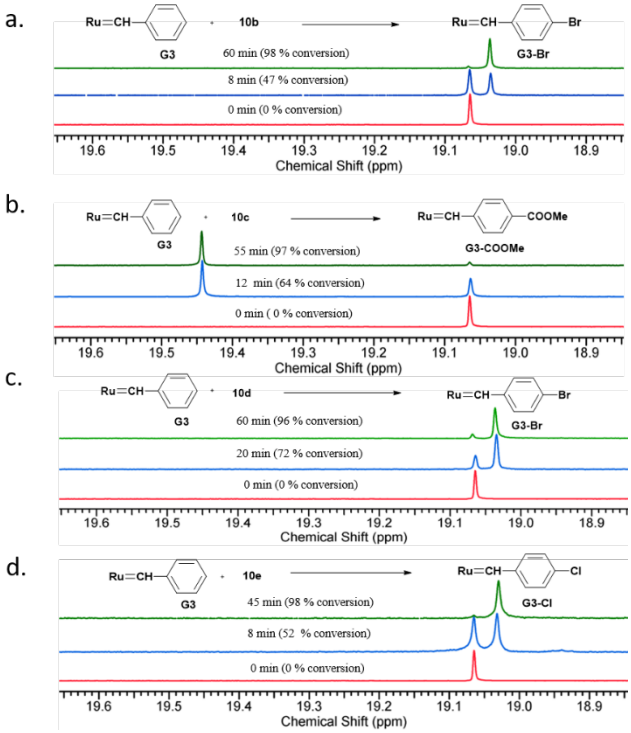


Figure 1. ^{1}H NMR spectra (CD_2Cl_2, 400 MHz) of reactions: (a) **G3** (19.07 ppm) with 20 equiv. of **10b** forming **G3-Br** (19.03 ppm) within 60 minutes (98% conversion), (b) **G3** with 20 equiv. of **10c** forming **G3-COOMe** (19.46ppm) within 55 minutes (97% conversion), (c) **G3** with 20 equiv. of **10d** forming **G3-Br** (19.03 ppm) within 60 minutes (96% conversion) (d) **G3** with 20 equiv. of **10e** forming **G3-Cl** (19.03 ppm) within 45 minutes (98% conversion).

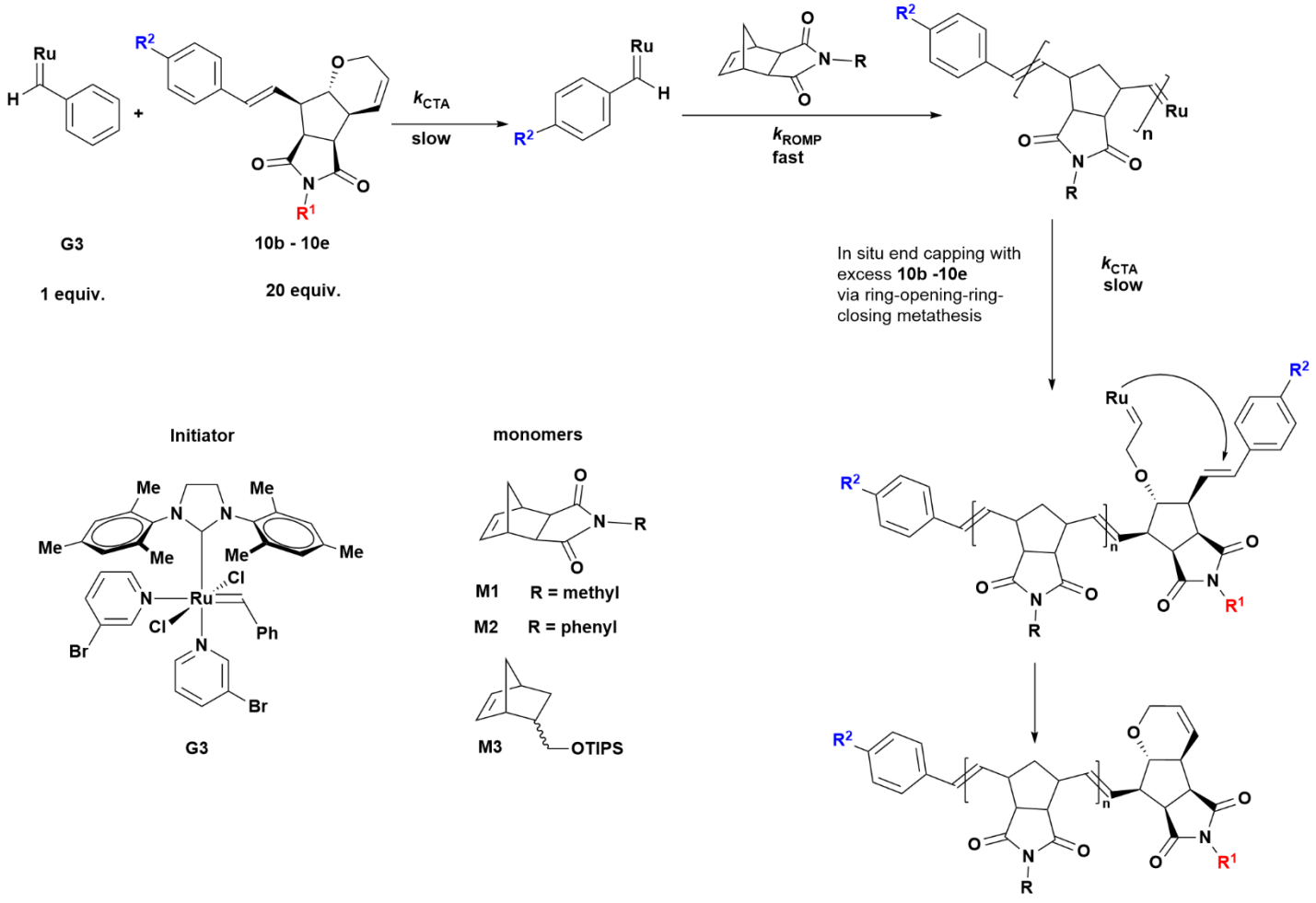
Although these new CTAs (**10**) are not appropriate for use in catalytic living ROMP (see supporting information Table-A), we

assumed that they might be very useful for the preparation of one-pot heterotelechelic polymers.

We have previously reported that the exocyclic double bond of this type of CTA is sterically hindered and remains inert towards secondary metathesis reactions.[50] Therefore, this type of CTA reacts with ruthenium carbene complexes via its endocyclic double bond in a ring-opening-ring-closing sequence. Here, in analogy, the commercial ruthenium benzylidene complex (**G3**) will react with the endocyclic double bond of the CTAs (**10**) via a ring-opening/ ring-closing sequence thereby generating new functional catalysts. These catalysts could subsequently be used for the functional initiation of suitable norbornene derivatives. As the rate of propagation of norbornene derivatives (k_{ROMP}) is much higher than the rate of transfer to the CTA (k_{CTA}) the polymerization of norbornene derivatives could be easily carried out in the presence of the excess CTAs (**10**) without undesired chain transfer events reducing the molecular weight of the polymer. Finally, when all monomers are consumed the end functionalization would occur automatically with the excess of CTAs (**10**) present in the reaction medium via a ring opening/ ring closing sequence. (**Scheme2**). Therefore, when 1 equiv. of **G3** was treated with 20 equiv. of CTA (**10a – 10e**) (shown in **Scheme 2**) **G3** first reacted with the endocyclic double bond of the CTA (**10a – 10e**) rather than the exocyclic double bond which is sterically hindered. Then, via ring-opening-ring-closing metathesis new functional catalysts were generated (shown in **Scheme 2**). Next, on adding monomers (**M1**/**M2**/**M3**) the polymerization was carried out without undesired chain transfer occurring [because the rate of propagation of norbornene derivatives (k_{ROMP}) is much higher than the rate of transfer to the CTAs (k_{CTA})] and upon consumption of all monomer an in-situ end capping with the excess of CTA (**10a – 10e**) (via a similar ring-opening-ring-closing sequence) gave the heterotelechelic polymers (shown in **Scheme 2**).

To prove our hypothesis, CTA **10b** was synthesized as shown in **Scheme 1**. Next, **G3** was reacted with 20 equiv. of **10b** and the reaction followed by ^{1}H NMR spectroscopy until almost complete conversion (98%) of **G3** benzylidene (19.07 ppm) to **G3-Br** benzylidene (19.03 ppm, **Figure 1a**) was observed. After successful pre-functionalization of the ruthenium carbene complex with the functional group R^2 (=Br for **10b**), 12 equiv. of monomer **M1** were added.

Scheme 2. One pot synthesis of heterotelechelic polymers



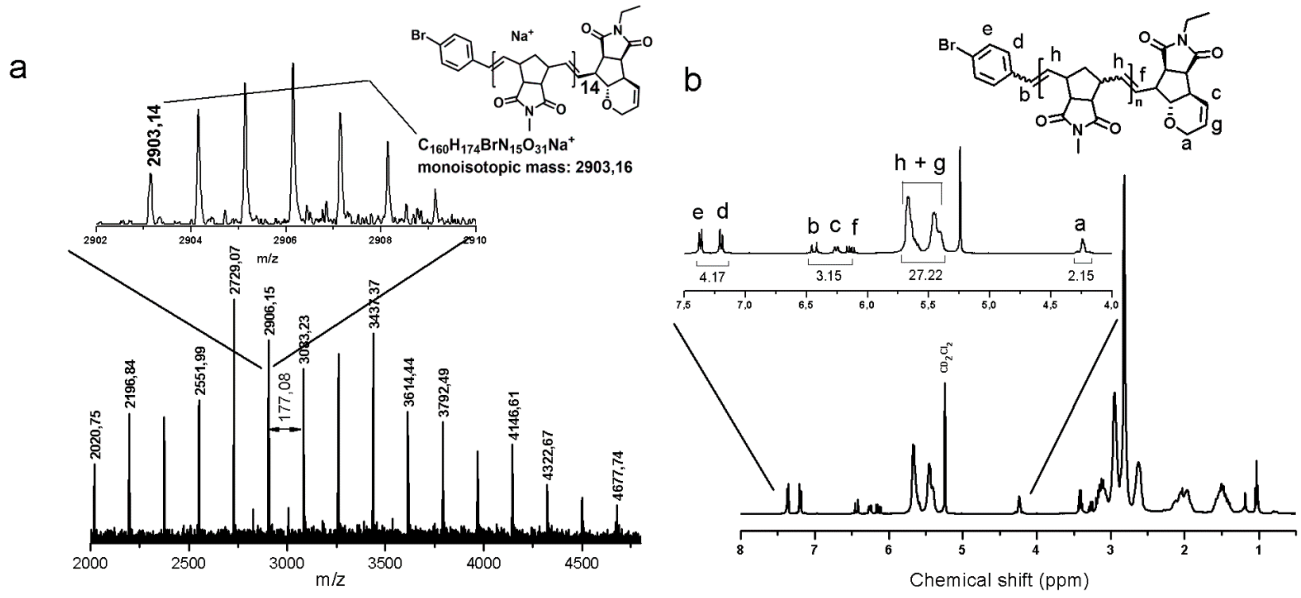


Figure 2. (a) MALDI-ToF mass spectrum (DCTB, NaTFA) of polymer **P1** with the correct repeating unit mass observed . (b)^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of polymer **P1**. Selected signals of both end groups (a-g) with peak integrals are marked in the spectrum. Backbone olefinic protons with integration are also marked as (h).

The reaction with the highly strained monomer **M1** is significantly faster than the chain transfer to CTA **10b** leading to a very fast propagation of **M1**. Once all monomer **M1** was consumed the chain transfer reaction with the CTA **10b** became dominant and the group R^1 (=ethyl for **10b**) was installed at the polymer chain end. This resulted in the synthesis of a narrowly dispersed polymer **P1** ($M_{n,SEC}$ ($CHCl_3$) = 3.1 kDa, Đ =1.12, **Table 1**, entry 1) carrying defined groups R^1 and R^2 at either of its chain ends. Although M_n determined by SEC ($CHCl_3$) was slightly higher than the expected value the M_n calculated from ^{1}H NMR integration (2.7 kDa) was in close accordance with the theoretical molecular weight based on the monomer to **G3** ratio (2.5 kDa). We believe that SEC ($CHCl_3$) calibration with polystyrene standards caused this discrepancy of Mn vaules. The end groups were confirmed by MALDI-ToF mass spectrometric analysis as well as ^{1}H NMR spectroscopy (**Figure 2**). An isotopically resolved MALDI-ToF mass spectrum matching both end groups is shown as an inset to **Figure 2(a).** Furthermore, a repeating structure with an average of 177.08 g mol^{-1} was observed, matching the correct molecular mass of monomer **M1.** Correct matching of both end groups (a-g) and main chain olefinic protons (h) in the ^{1}H NMR spectrum of polymer **P1** is shown in **Figure 2(b)**. Even though R^2 cannot be considered a functional group, mechanistically speaking **P1** represented a heterotelechelic polymer.

Next, to test the efficacy of this process in synthesizing higher molecular weight heterotelechelic polymers, **G3** was pre-functionalized with **CTA 10b** in a similar manner as described above followed by polymerization with 100 equiv. of monomer **M1** leading to the heterotelechelic polymer **P2**. ($M_{n,SEC}$ ($CHCl_3$) =20.5 kDa, Đ =1.26, **Table 1**, entry 2, also see supporting information). Full control over molecular weight as well as dispersity signified that the chain transfer constant of the CTA is low enough not to affect the degree of polymerization. Only towards the end of the propagation reaction, when the monomer concentration has drastically dropped, the chain transfer reaction with the CTA becomes dominant leading to a narrowly dispersed heterotelechelic polymer.

Thereafter, we investigated different monomers (**M2, M3**) to expand the applicability of this method. Heterotelechelic polymers **P3** and **P4** were synthesized using monomers **M2** and **M3** respectively via prefunctionalization with CTA **10b** under the identical reaction conditions as above (**P3**: $M_{n,SEC}$ ($CHCl_3$) = 2.9 kDa, Đ =1.14, **Table 1**, entry 3, **P4**: $M_{n,SEC}$ ($CHCl_3$) = 3.9 kDa, Đ =1.13, **Table 1**, entry 4). In both cases MALDI-ToF mass spectrometric analyses confirmed the presence of the expected end groups. (see supporting information Fig S66,Fig S67).

Furthermore, to show the versatility of this method and to produce truly heterotelechelic polymers, a series of **CTAs** (**10c** to **10e**) carrying different functional end groups were synthesized. Next, prefunctionalization of **G3** using 20 equiv. of CTA **10c** was followed by ^{1}H NMR spectroscopy. Disappearance of the **G3** benzylidene carbene (19.07 ppm) and formation the new carbene **G3-COOMe** (19.46 ppm, **Figure 1b**) was observed within one hour with excellent conversion (97%, **Figure 1b**). Thereupon addition of 15 equiv. of monomer **M1** gave the heterotelechelic polymer **P5** carrying a methyl benzoate group at one end and a bromo phenyl moiety on the other end ($M_{n,SEC}$ ($CHCl_3$) = 3.8 kDa, Đ =1.11, **Table 1**, entry 5). End groups were confirmed by MALDI -ToF mass spectrometry and ^{1}H NMR spectroscopy (see supporting information Fig S68 , Fig S58).

Similarly, **G3** was functionalized with CTA **10d** and CTA **10e** to generate the corresponding new carbene complexes within a short reaction time (**Figure 1c, 1d**). Heterotelechelic polymers **P6** and **P7** were synthesized by prefunctionalization of **G3** with 20 equiv. of CTA **10d** followed by addition of 10 equiv. and 50 equiv. of monomer **M1** respectively. In both the cases SEC analyses showed excellent molecular weight control as well as narrow molecular weight distributions (**P6**: $M_{n,SEC}$ ($CHCl_3$) = 3.9 kDa, Đ =1.13, **Table 1**, entry 6, **P7**: $M_{n,SEC}$ ($CHCl_3$) = 9.9 kDa, Đ=1.19, **Table 1**, entry 7).

In a similar fashion, the prefunctionalization of **G3** with CTA **10e** followed by addition of monomer **M1** gave a chlorophenyl initiated

polymer **P8** with an acetophenone moiety on the imide nitrogen atom at the other chain end ($M_{n,SEC}$ ($CHCl_3$) = 3.1 kDa, Đ =1.09, **Table 1**, entry 8). End groups were confirmed by MALDI-ToF mass spectrometric analyses (**P6**: see supporting information Fig S69, **P8**: see supporting information Fig S70).

Table 1. Summary of all heterotelechelic polymers synthesized

Entry	Polymer	CTA	Monomer	G3:Monomer ratio	M_n (theo) (kDa)	M_n(calc. from ^{1}H NMR spectroscopy) (kDa)	M_n(obs.) SEC ($CHCl_3$)[a] (kDa)	Đ
1	P1	10b	M1	12	2.5	2.7	3.1	1.12
2	P2	10b	M1	100	18.1	19.5	20.5	1.26
3	P3	10b	M2	10	2.8	3.2	2.9	1.14
4	P4	10b	M3	10	3.2	3.3	3.9	1.13
5	P5	10c	M1	15	3.2	3.2	3.8	1.11
6	P6	10d	M1	15	3.2	3.4	3.9	1.13
7	P7	10d	M1	50	9.4	9.5	9.9	1.19
8	P8	10e	M1	12	2.6	2.7	3.1	1.09

[a] SEC ($CHCl_3$) was calibrated with polystyrene standards.

Conclusions

In conclusion, commercially available Grubbs' benzylidene complex (**G3**) was readily functionalized in-situ using an excess of the functional CTAs (**10**). Subsequent polymerization and automatic end functionalization towards the end of the propagation reaction led to the synthesis of heterotelechelic polymers (**P1 to P8**) using different monomers (**M1**-**M3**) and varying molecular weights (monomer to initiator ratio **10 to 100**) (**Table 1**). In all cases SEC analyses showed narrow molecular weight distributions. For polymers **P1**, **P3**-**P6** and **P8** MALDI -ToF mass spectrometry confirmed the presence of both functional end groups (**Figure 2** and see supporting information). This method represents a facile new approach for the one-pot synthesis of narrow dispersity hetero-telechelic ROMP polymers. We believe that this method could be most useful for the conjugation of biomolecules or the attachment of end-functional polymers onto surfaces or nanoparticles**.**

Experimental Section

A General Procedure for the Synthesis of Heterotelechelic Polymers

G3 (1 equiv., 0.0045 mmol) was dissolved in dry degassed dichloromethane (0.2 mL). Separately CTA **10** (20 equiv.,0.09 mmol) was dissolved in dry degassed dichloromethane (0.6 mL). The **G3** solution was then added to the CTA solution. The reaction mixture was stirred at room temperature for 1 h in order to ensure almost complete conversion of **G3** to respective functional catalyst. After that monomer (**M1**/**M2**/**M3**) dissolved in dry degassed dichloromethane (0.2 M) was added quickly to the above solution. After complete polymerization followed by end functionalization (10 min), the reaction is quenched by adding excess ethyl vinyl ether (0.5 mL). The solvent was removed under reduced pressure. The concentrated solution obtained was precipitated 3 times into cold methanol to give the respective heterotelechelic polymer**.**

ASSOCIATED CONTENT

Supporting Information

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

Instruments data, Experimental methods, NMR data, MALDI-ToF data, SEC data and HRMS data. (PDF)

AUTHOR INFORMATION

Corresponding Author

Andreas F. M. Kilbinger - Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland.
orcid.org/0000-0002-2929-7499.
Email: andreas.kilbinger@unifr.ch

Author

Ankita Mandal - Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland.
orcid.org/0000-0002-2743-3258

Indradip Mandal - Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland.
orcid.org/0000-0003-4552-7415

Author Contributions

‡These authors contributed equally. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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