Catalytic Living Ring Opening Metathesis Polymerisation: The Importance of Ring Strain in Chain Transfer Agents

Peng Liu+, Mohammad Yasir+, and Andreas F. M. Kilbinger

Abstract: A recently developed catalytic living ring opening metathesis polymerisation (ROMP) was investigated using a series of reversible chain transfer agents (CTA) carrying either cyclopentene or cyclohexene rings, differing only in ring strain. All cyclopentene derivatives examined showed significantly faster reaction rates than the corresponding cyclohexene derivatives. This resulted in lower molecular weight dispersities and better control of the molecular weight for the cyclopentene compared to the cyclohexene CTAs. Both Grubbs' second and third generation catalysts could be employed in catalytic living ROMP using cyclopentene CTA derivatives. The kinetics of different CTAs were studied, block copolymers were synthesised and residual ruthenium quantified by ICP-OES. All polymers were fully characterised by NMR, GPC and MALDI-ToF mass spectrometry. The new cyclopentene CTAs are readily synthesised in a few straightforward steps and provide faster reaction kinetics than all previously reported reversible CTAs.

Ring opening metathesis polymerisation (ROMP), which uses the metathesis of cyclic olefins to synthesise linear polymers, has become a very important method for polymer synthesis in biomedical, material, academic and industrial applications.[1–8] Living ROMP, wherein irreversible chain-transfer events and termination reactions are absent, is an important polymerisation technique, due to its excellent control of molecular weight and the narrow molecular weight distribution of the resulting polymers.[9,10] For polymerisations, ruthenium carbene complexes developed by Grubbs et al. (**G2**: (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro (phenylmethylene)(tricyclohexylphosphine)-ruthenium and **G3**: dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] (benzylidene)bis(3-bromopyridine)-ruthenium(II)) are frequently used mainly due to their easy handling and high functional group tolerance. However, in a typical living ROMP polymerisation, the ruthenium catalyst will always be covalently bound to the end of the growing polymer chain. It is, therefore, mechanistically determined that each catalyst can only form one polymer chain, which means stoichiometric amounts of the transition metal complex are required with respect to the number of polymer chains formed in a living ROMP. This can result in high catalyst loadings, especially during the synthesis of low molecular weight polymers, which is expensive and leads to potentially toxic ruthenium residues in these polymers.

Numerous methods have been developed to reduce the level of catalyst in the final metathesis products.[11–26] However, these methods mostly rely on easy removal of the transition metal complex or improved product separation. To date, only few reports exist on catalytic metathesis polymerisations producing multiple polymer chains per ruthenium complex. Acyclic diene metathesis polymerisation (ADMET), pioneered by Wagener et al. uses catalytic amounts of metal complex[27–29] in a step-growth process. Homotelechelic polymers prepared by ruthenium complexes were first described by Grubbs and co-authors using an irreversible chain transfer agent (CTA) in the presence of sub-stoichiometric quantities of ruthenium complex.[30–35] Fewer examples have been reported on the synthesis of heterotelechelic polymers using only catalytic quantities of transition metal complex.[36–39] However, none of the examples given above can be considered as living, as molecular weight distributions are typically broad, and block copolymers cannot be made.

We recently described a mechanism for catalytic living ROMP that relies on a degenerative reversible chain-transfer polymerisation that required only a catalytic amount of ruthenium carbene complex.[40] Here, we report new CTAs (Figure 1) based on either cyclopentene or cyclohexene derivatives and provide a kinetic analysis that shows the importance of ring strain in CTAs for degenerative chain transfer metathesis polymerizations.

Catalytic living ROMP[40] is based on a degenerative chain transfer mechanism in which a sub-stoichiometric quantity of
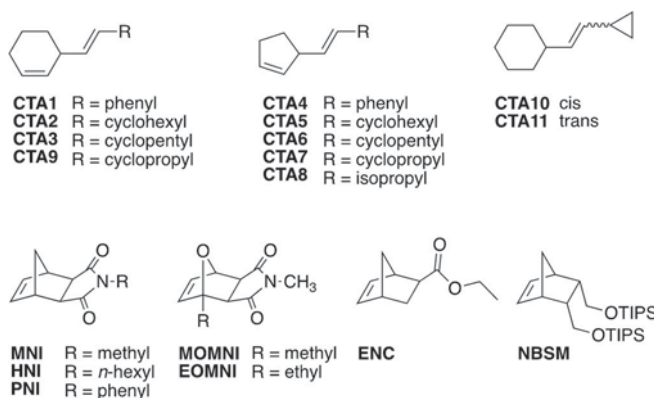
[*] P. Liu,[+] M. Yasir,[+] A. F. M. Kilbinger
Department of Chemistry, University of Fribourg
Chemin du Musée 9, 1700 Fribourg (Switzerland)
E-mail: andreas.kilbinger@unifr.ch

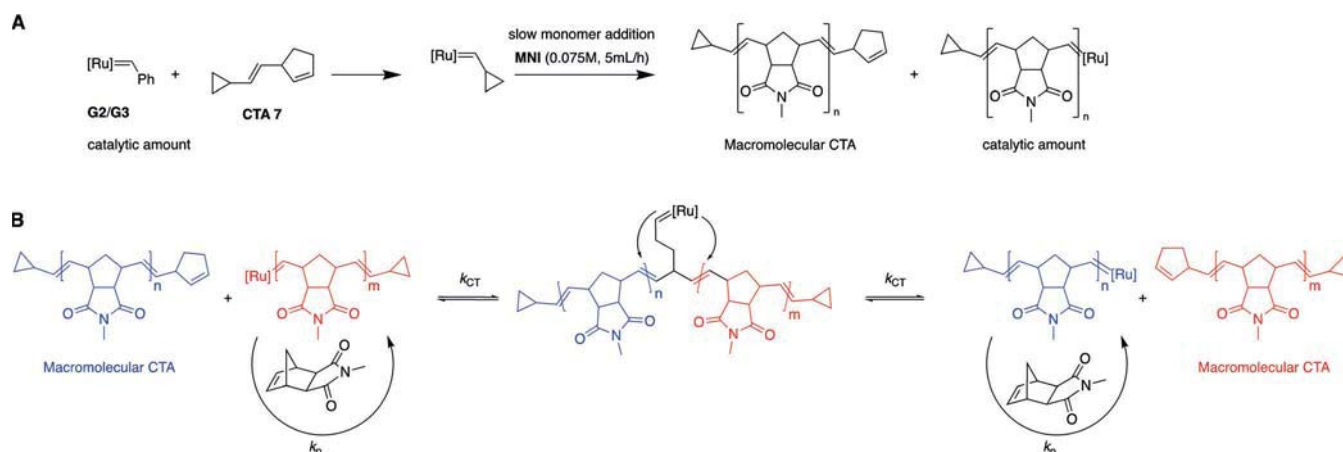[+] These authors contributed equally to this work.

Figure 1. Top: Chain transfer agents (**CTA1**–**CTA9**) and model compounds **CTA10**–**11**. Bottom: Monomers (**MNI**, **HNI**, **PNI**, **MOMNI**, **EOMNI**, **ENC**, **NBSM**) investigated in this study.

Figure 2. A) Polymerization of **MNI** in the presence of **CTA7** under slow monomer addition conditions yields mainly polymer chains being end-functionalized with the cyclopentenyl unit and a small number (catalytic amount) of propagating chains. B) The degenerative chain transfer mechanism[41] exploited in this investigation shown as an example using **CTA7** and **MNI**. The polymer end group of the macromolecular **CTA** (shown in blue) exchanges with the propagating carbene end group (polymer shown in red) via an intermediate (right) in a degenerate equilibrium. k_p: propagation rate constant, k_{CT}: chain transfer rate constant. [Ru] = **G2** or **G3** based propagating carbene complexes.

a propagating ruthenium carbene chain end of a polymer exchanges rapidly with other chain ends. This results in quasi-simultaneous growth of all polymer chains leading to narrow molecular weight distributions and control of molecular weight (see Figure 2 B as an example with **CTA7** and **MNI**).

As previously reported, **CTA1**[40] (Figure 1) reacts only very slowly with propagating ruthenium alkylidene complexes. It is for this reason that it cannot be employed as a chain transfer agent in catalytic living ROMP. In order to assign the low reactivity of **CTA1** to the cyclohexenyl group, **CTA2–3** were synthesized both of which carried the same endocyclic double bond as **CTA1** but different substituents (cyclohexyl and cyclopentyl groups) attached to the exocyclic double bond.[41] However, neither **CTA2** nor **CTA3** show a higher reactivity than **CTA1** in time-resolved ^{1}H-NMR spectroscopic experiments (see Supporting Information). As the low reactivity of **CTA1–3** is caused by the endocyclic double bond, common to all three CTAs, we decided to synthesize a series of new CTAs carrying endocyclic double bonds within five-membered rings (**CTA4–8**) in which the ring strain was assumed to be higher. In addition to the common cyclopentenyl group, **CTA4–8** differ in the substituent attached to the exocyclic double bond. **CTA4** carries a phenyl group attached to the exocyclic double bond and is therefore similar in structure to **CTA1**, whereas **CTA5** represents the saturated version of **CTA4**, carrying a cyclohexyl substituent attached to the exocyclic double bond.

In a catalytic living ROMP a commercial ruthenium benzylidene complex first reacts with a reversible chain transfer agent (for example **CTA4–8**) yielding a new ruthenium carbene complex (carrying the group R, Figure 1 **CTA4–8**). A strained cyclic monomer is then added slowly to this mixture of CTA and newly formed ruthenium carbene complex (Figure 2 A). Due to the low monomer concentration, the propagation reaction and reaction with the CTA become equally likely, leading to a reversible chain transfer equilibrium (Figure 2 B) in which the polymer end groups of two chains exchange as described previously.[40]

To investigate the reactivity of **CTA4–5** we followed the reaction of propagating **MNI** and **CTA4–5** by ^{1}H-NMR spectroscopy (addition of 10 equiv of **CTA4** or **CTA5** to a **G3** initiated **MNI** (34 equiv) solution). We observed a fast and complete conversion of the signal corresponding to the propagating **MNI** alkylidene (18.50 ppm) to the new carbene (a benzylidene (19.06 ppm) for **CTA4** and cyclohexylmethylidene (18.97 ppm) for **CTA5**). We furthermore observed that over time the **G3**-benzylidene (from **CTA4**) decomposed less rapidly than the **G3**-cyclohexylmethylidene (from **CTA5**). This initial investigation showed clearly that **CTA4–5** carrying the more strained cyclopentenyl groups were dramatically more reactive than the cyclohexenyl carrying **CTA1–3**. Despite the greater tendency to open the five-membered ring, no ruthenium-alkylidene signal could so far be recorded that would correspond to the ring-opened intermediate indicating that such alkylidenes represent transient structures that immediately undergo ring closing reactions.

Next, three further CTAs (**CTA6–8**) were investigated, all carrying the ring strained cyclopentenyl group but yielding different ruthenium alkylidenes upon reaction with the propagating **G3** complex (addition of 10 equiv of either **CTA6,7** or **8** to a **G3** initiated **MNI** (34 equiv) solution). It could be shown that **CTA6–8** all gave rapid and complete conversions to the new alkylidene signals when followed by ^{1}H-NMR spectroscopy. The stability of the newly formed ruthenium alkylidenes also varied significantly and decreased in the following order: Ru-cyclopropylmethylidene (17.20 ppm, from **CTA7**) > Ru-benzylidene (19.04 ppm, from **CTA4**) > Ru-cyclopentylmethylidene (18.58 ppm, from **CTA6**) > Ru-cyclohexylmethylidene (18.97 ppm, from **CTA5**) = Ru-isopropylidene (18.66 ppm, from **CTA8**). However, in any catalytic living ROMP reaction these stability differences are not important as these ruthenium carbene complexes only exist for a very short time at the pre-equilibrium stage (Figure 2 A).

In our previous investigation[40] we could show that our CTA reacted exclusively via the "endocyclic double bond

first" pathway. **CTA7** carries a cyclopropyl group attached to the exocyclic double bond that is sterically less demanding than the residues of all other CTAs investigated here or previously. To investigate whether **CTA7** reacts via the edocyclic or exocyclic double bond first, we synthesized model compounds **CTA10** (*cis*) and **CTA11** (*trans*) differing in their exocyclic double bond configuration but lacking the endocyclic double bond altogether.

Time-resolved ^{1}H-NMR spectroscopic experiments revealed (Supporting Information), however, that when a propagating (**MNI**) **G3** catalyst (1 equiv) was exposed to **CTA9–11** (10 equiv) **CTA10** formed the new cyclopropylmethylidene carbene with 90% conversion after 24 min. whereas **CTA11** only formed 64% (24 min.) and **CTA9** 62% (24 min.) of the new carbene. The cyclohexene carrying **CTA9** therefore shows reaction rates on the same order of magnitude as the cross metathesis with the *trans* configured **CTA11. CTA7**, however, forms the new cyclopropylmethylidene under identical reaction conditions with a conversion of 100% in 8 min. As the steric demand of cyclopentyl or cyclohexyl groups is very similar,[42] we estimated that the steric hindrance of the exocyclic double bond in **CTAs7,9** and **11** was also similar. This would suggest that a very different mechanism, most likely the ring opening–ring closing sequence is responsible for this massively increased reaction rate.

Encouraged by these results, we next carried out the polymerisation of **MNI** under catalytic living ROMP conditions (see Supporting Information). Since the rate of propagation of ring-strained monomers, such as norbornenes, is significantly faster than the olefin metathesis reaction with the CTA ($k_{CT} \ll k_p$, see Figure 2B),[43] the monomer concentration was kept low at all times, which was realised by slow addition via a syringe pump. Reaction conditions were optimised using **CTA5**.

When **MNI** (0.075 mol L^{-1}) was added slowly (5 mL h^{-1}) to the solution of Grubbs' third-generation catalyst (**G3**) and **CTA5**, the desired polymer was formed (**polymer 1**, $M_{n\,GPC}$ (CHCl$_3$) = 7100 g mol^{-1}, Đ = 1.18, M$_{peak}$ (MALDI-ToF) = 4001.71 g mol^{-1}). An isotopically resolved MALDI-ToF mass spectrum matching the polymer structure with both **CTA5** end-groups (cyclohexyl and cyclopentenyl) is shown in Figure 3.

As expected, the molecular weight of the produced polymer was much lower than that calculated from the monomer:**G3** ratio (M_n = 53 100 g mol^{-1}) indicating that successful reversible chain transfer had taken place. In case of a non-catalytic polymerisation, the molecular weight of the polymer would have been significantly higher (see Table 1). All of the optimisation results can be found in the Supporting Information. Similar results were obtained when Grubbs' second-generation catalysts (**G2**) was used under the optimised reaction conditions (Supporting Information).

In order to compare the efficiency of **CTA1–8** we carried out eight different catalytic living ROMP polymerizations using monomer **MNI** (see Table 1 and Supporting Information). As expected, **CTA1–3** (entries 1–3, Table 1) did not yield polymers (**polymer 3–5**) with controlled molecular weights (see above). Instead, the molecular weights obtained
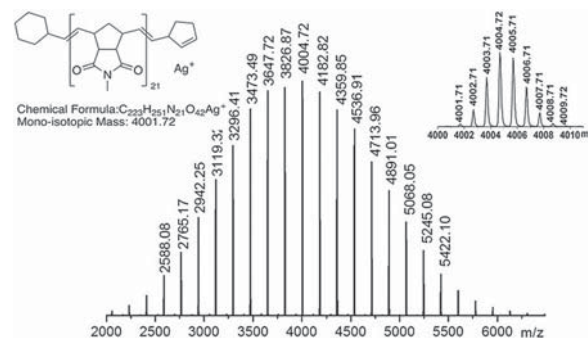

Figure 3. MALDI-ToF mass spectrum (DCTB, AgTFA) of **polymer 1**. Left: Chemical structure of **polymer 1** with calculated mono-isotopic mass. Center: Mass distribution. Right: Most intense peak of the distribution, isotopically resolved.

Table 1: Catalytic Living ROMP using **CTA1–8**.[a]

#	Polymer	CTA	$M_{n\,calc.}$[b]	$M_{n\,calc.}$[c]	$M_{n\,obs.}$[d]	Đ[d]	Yield [%]
1	**polymer 3**	**CTA1**	53 100	5310	41 000	1.29	99
2	**polymer 4**	**CTA2**	53 100	5310	38 000	1.35	99
3	**polymer 5**	**CTA3**	53 100	5310	34 000	1.25	99
4	**polymer 6**	**CTA4**	53 100	5310	9900	1.18	99
5	**polymer 1**	**CTA5**	53 100	5310	7100	1.18	98
6	**polymer 7**	**CTA6**	53 100	5310	7800	1.16	99
7	**polymer 8**	**CTA7**	53 100	5310	8900	1.17	99
8	**polymer 9**	**CTA8**	53 100	5310	9000	1.17	99

[a] All of the reactions were carried out with 4.45 mg **G3** (0.005 mmol) and 10 equiv of CTA in 1.5 mL degassed DCM, followed by 300 equiv of **MNI** (266 mg. 1.5 mmol), which was dissolved in 20 mL degassed DCM (0.075 mol L^{-1}) added by a syringe pump at 5 mL h^{-1} under Ar. [b] M_n under non-catalytic conditions was calculated with a degree of polymerization X_n = [monomer]:[**G3**] = 300:1. [c] M_n under catalytic living ROMP conditions was calculated using a degree of polymerization X_n = [monomer]:[CTA] = 30:1. [d] Determined by GPC (chloroform). Note that entries 1–3 employing cyclohexenyl carrying **CTA1–3** did not result in any molecular weight control.

for these CTAs resembled those of classical living ROMP emphasizing once more that the chain transfer to **CTA1–3** is too slow to control the molecular weight in a catalytic fashion. **CTA4–8**, on the other hand, gave excellent molecular weight control of the resulting polymers (**polymer1**, **polymer 6–9**) and narrow molecular weight dispersities. Isotopically resolved MALDI-ToF mass spectra matched the masses for polymers with end groups corresponding to the CTA employed (see Supporting Information).

To expand the applicability of catalytic living ROMP, different monomers such as *exo-N*-hexyl norbornene imide (**HNI**, Figure 1), *exo-N*-phenyl norbornene imide (**PNI**, Figure 1), *endo*-5-norbornene-2,3-bis(triisopropyl)silylmethanol (**NBSM**, Figure 1) and *exo*-ethyl-5-norbornene carboxylate (**ENC**, Figure 1) were polymerised under catalytic living ROMP conditions using **CTA5** or **CTA7**. The isotopically resolved MALDI-ToF MS spectra of all polymers matched the two expected end groups of **CTA5** or **CTA7** (see Supporting Information, **polymer 10–13**).

It is furthermore worth noting that when we used *exo-N*-methyl-7-oxabicyclo[2.2.1]hept-4-methyl-5-ene-2,3-dicarboximide (**MOMNI**, Figure 1) and *exo-N*-methyl-7-oxabicyclo-

[2.2.1]hept-4-ethyl-5-ene-2,3-dicarboximide (**EOMNI**, Figure 1), carrying sterically demanding groups on the bridge head carbon that slow down propagation, polymerisations could be run in one pot (see Supporting Information, **polymer 14–15**) without the need of a slow monomer addition via a syringe pump. This feature will be further investigated in the near future.

To prove that the monomer:CTA ratio determines the polymer molecular weight and that the polymerisation fulfils living characteristics, different molecular weight polymers were synthesised by changing the **MNI**:**CTA5** ratio (Figure 4). A linear correlation between the molecular weight (Mn, GPC) and the **MNI**:**CTA5** ratio was obtained as expected for a living polymerization under reversible chain transfer conditions.
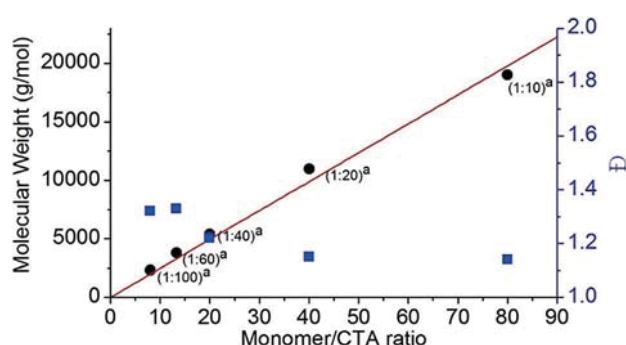

Figure 4. Plot of the molecular weight (Mn, GPC(CHCl$_3$), black circles) and molecular weight dispersity (Đ, blue squares) versus the [**MNI**]/[**CTA5**] ratio. [a] The ratios reported in brackets denote the [**G3**]/[**CTA5**] ratio.

The molecular weight dispersities of the resulting polymers was low (Đ = 1.2–1.3) and the masses of the polymers matched the assumed structures with **CTA5** end groups (see above) which provides a strong indication that the polymerisation process is indeed living (Figure 4, see also Supporting Information **polymer 16–20**).

Furthermore, the **G3**:**CTA5** ratio was also varied during the experiment described above (see ratios in brackets in Figure 4). For low molecular weight polymers a ratio of **CTA5**:**G3** = 100 was used, in other words, one molecule of 3rd generation Grubbs catalyst was responsible for the synthesis of 100 living polymer chains. This once more emphasises the significant reduction of the amount of transition metal possible with this catalytic method.

One important feature of a living polymerisation is the ability to prepare block copolymers. To further prove that our newly developed chain transfer agents produced living polymers, monomers **MNI** (300 equiv, 0.075 mol L^{-1}) and **HNI** (300 equiv, 0.075 mol L^{-1}) were added (5 mL h^{-1}) to the **G3**/**CTA5** (1:10) mixture sequentially. GPC (chloroform) analysis performed after addition of both monomers showed a monomodal molecular weight distribution and a molecular weight of 17 900 g mol^{-1} (**polymer 21**, Supporting Information) supporting a block copolymer formation. A more rigorous proof for the proposed degenerate chain transfer mechanism and block copolymer formation was obtained

when the polymer taken from the catalytic living ROMP of **MNI**, **CTA5** and **G3** was precipitated, dried and analysed and subsequently redissolved and exposed to **HNI** (300 equiv, 0.075 mol L^{-1}, 5 mL h^{-1}) and **G3** (0.005 mmol) for the growth of a second polymer block (Figure 5). GPC characterisation after polymerizing the first (M_{nGPC} (CHCl$_3$) = 7100 g mol^{-1}, Đ = 1.18) and second monomer (M_{nGPC} (CHCl$_3$) = 22 500 g mol^{-1}, Đ = 1.36) revealed the formation of a diblock copolymer (Figure 5).

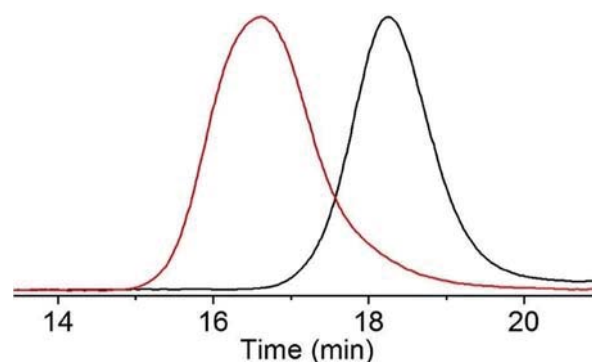**Figure 5.** GPC trace of **polymer 1** (black, M_{nGPC} (CHCl$_3$) = 7100 g mol^{-1}, Đ = 1.18) and block copolymer **polymer 22** (red, M_{nGPC} (CHCl$_3$) = 22 500 g mol^{-1}, Đ = 1.36). Catalyst **G3** and **CTA5** were employed for this reaction.

Polymers obtained by catalytic living ROMP are noticeably less coloured than those obtained by classical living ROMP (Supporting Information). To quantify the residual ruthenium in our catalytic living ROMP polymer, two similar molecular weight and dispersity polymers were synthesised by catalytic and classical living ROMP (Supporting Information). To emphasise the efficiency of our method: only 33 mg of polymer (M_{nGPC} (CHCl$_3$) = 6900 g mol^{-1}, Đ = 1.15) could be synthesised non-catalytically using 4.45 mg of **G3**, while 266 mg of polymer (M_{nGPC} (CHCl$_3$) = 7200 g mol^{-1}, Đ = 1.20) was synthesised via catalytic living ROMP using the same amount of **G3**. Furthermore, inductively coupled plasma optical emission spectroscopy (ICP-OES) showed that 1.38 ppm of ruthenium remained in 3.5 mg of the polymer prepared non-catalytically after two precipitations in cold methanol whereas only 0.21 ppm ruthenium was left in 3.5 mg of the catalytically prepared polymer sample (Supporting Information). This result sums up several advantages of the catalytic living ROMP method, as with the same amount of **G3** complex, more polymer at lower cost and with lower residual transition metal contamination can be prepared.

In conclusion, we have developed a series of new chain transfer agents which can be prepared in good yields and few straightforward steps for a recently developed catalytic living ring opening metathesis polymerisation method. Kinetic investigations of the chain transfer agents clearly showed that their efficiency during the degenerate chain transfer process depends highly on their ring strain. While the cyclopentenyl carrying chain transfer agents yielded well-controlled polymers with low molecular weight dispersities, cyclohexenyl carrying chain transfer agents exhibited only

low reactivity. Grubbs' second and third generation catalysts were examined in catalytic living ROMP and produce polymers with the expected end groups which are mechanistically defined by the chain transfer agent employed. Block copolymers could be synthesised either via continuous slow addition of two different monomers or via chain extension of a separately prepared macromolecular chain transfer agent. The lowest ruthenium catalyst-to-CTA ratio examined in this report was 1:100. This equates to a 100-fold saving of ruthenium carbene complex compared to a classical living ROMP. The residual ruthenium in the final polymer was also analysed by ICP-EOS and found to be significantly reduced compared to non-catalytically prepared metathesis polymers. Catalytic living ROMP combined with the simplified chain transfer agent synthesis reported here offers a huge potential especially for the synthesis of functional polymers for biomedical, materials, industrial and academic use where very low ruthenium contamination is crucial.

Conflict of interest

The authors declare no conflict of interest.

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