Narrowly distributed homotelechelic polymers in 30 minutes: Using fast *in-situ* pre-functionalised ROMP initiators.

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ABSTRACT

Today's olefin metathesis catalysts show high reactivity, selectivity and functional group tolerance and allow the design of new syntheses of precisely functionalised polymers. Here we describe a general "one-pot" synthesis for narrow polydispersity bis-end-functional (=homotelechelic) ROMP polymers exploiting the propagating ruthenium complex' inherent selectivity for strained norbornenes over acyclic internal olefins. This approach represents a straightforward general method of homotelechelic polymers carrying almost any functional end group (within the limitations of the catalyst's functionality tolerance). Complete pre-functionalisation of the initiator is realised *in-situ* within minutes and without the need of further purification steps. The excess acyclic olefin re-enters the catalytic cycle after monomer consumption is complete giving a homotelechelic polymer. ^{1}H-NMR spectroscopic and MALDI-ToF-MS analysis show highly efficient end group functionalisation.)

KEYWORDS: Ring-opening metathesis polymerisation, ruthenium initiators, pre-functionalisation, homotelechelic polymers, kinetic control.

INTRODUCTION

Highly efficient ruthenium(II) olefin metathesis catalysts were described by Grubbs et al. in the early 1990s.[1] Shortly after, a range of derivatives thereof became commercially available, all offering a specific character in their reaction with olefins. High functional group tolerance, low oxophilicity and well-defined kinetics are some of their manifold advantages, when applied to the olefin metathesis reaction. These catalysts polymerise monomers in living ring-opening metathesis polymerisations (ROMP) with little catalyst degradation and side reactions that would lead to ill-defined materials.

Ruthenium(II)-complexes carrying tricyclohexylphosphine ligands, as well as a benzylidene residue represent initiators with a long shelf life and good initiation kinetics.[2] However, this ease of use came with a disadvantage as far as polymer end group modification was concerned. Initiating ring opening polymerisation reactions using these complexes necessarily leads to a non-functional styrenyl residue at the focal unit of the polymer. For syntheses where the end groups of the commonly linear polymer are irrelevant to the performance of the resulting material (i.e. where functionality is for example placed onto the repeat unit rather than at the chain end[3,4]), this limitation to styrenyl end-groups is negligible. However, in syntheses where functional polymer end group (=telechelic polymer) is vital, few straightforward synthetic strategies exist to vary the focal unit. Specially pre-functionalised metathesis initiators often suffer from reduced stability and must be prepared anew for every functional focal group to be introduced.

Early functional metathesis initiators used alkylidene transfer between the catalyst and diazoalkenes as a carbene source.[5] More recently, functional initiators

were prepared from commercial catalyst sources via alkylidene exchange with substituted styrenes.[6-9] This method allows a variety of functional groups to be introduced and ensures that the functional focal group is placed on every polymer chain. Nonetheless, a new initiator species has to be synthesised for every functional focal group that is introduced.

ROMP polymer backbones with low steric demand allow secondary metathesis reactions to occur. This effect has been exploited to synthesise telechelic polymers involving chain transfer agents (CTAs) for ROMP. In these so-called ROMP/CT systems, acyclic symmetrical internal olefins act as the source for the functional end group. Homotelechelic polymers can be achieved via chain transfer reactions to the transfer agents and to the polymer. In these cases, however, the polymerisation will inevitably loose its living character and the resulting molecular weight distribution will broaden to a statistically expected polydispersity index (PDI) of 2. The theoretical molecular weight of the polymers synthesised in a ROMP/CT approach typically correlates with the monomer to CTA ratio (as long as c(CTA) >> c(Initiator)).[10]

A second approach to telechelic ROMP polymers is achieved synthesising statistical copolymers incorporating small amounts of cleavable monomer units.[11] Arranging these cleavable units in an ABA block copolymer structure, telechelic polymers with alcohol or thiol end groups can be generated by post-polymerisation cleavage of the outer (A) polymer blocks (e.g. hydrogenation or acidic hydrolysis).[12]

Here we describe a general one-pot synthesis for narrow polydispersity bis-end-functional (homotelechelic) ROMP polymers exploiting the inherent selectivity of the propagating ruthenium complex for strained norbornenes over acyclic internal olefins. This approach represents a straightforward general method to homotelechelic polymers carrying almost any functional end group (within the limitations of the catalyst functionality tolerance).

EXPERIMENTAL

Materials

Benzylidene-bis(tricyclohexylphosphine) dichlororuthenium, Bis(tricyclohexyl-phosphine) benzylidine ruthenium dichloride, (1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro (phenylmethylene)(tricyclohexylphosphine)ru-thenium, Dichloro[1,3-bis(2,4,6-trimethylphen-yl)-2-imidazolidinylidene](benzylidene) bis(3-bromopyridine)ruthenium, 4-(dimethylamino) pyridine (DMAP), di-tertbutyl dicarbonate, 5-bromo-1-pentene, 4-pentene-1-ol, thionyl- chloride, ethyl vinylether, Meldrum's acid and benzylamine were purchased from Sigma-Aldrich and used without further purification. c*is*-4-Octene was purchased from Alfa Aesar. Triethylamine was purchased from Acros Chemicals, distilled from calcium hydride, and stored over potassium hydroxide.

Instrumentation

ESI-MS analyses for synthesised compounds was carried out on a Bruker 4.7T BioAPEX II. MALDI-ToF-MS analyses of the polymers was carried out on a Bruker ultrafleXtreme™ using 2-[(2E)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix and silver trifluoroacetate as the added salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) with a Viscotek GPCmax VE2001 GPC Solvent/Sample Module, a Viscotek UV detector 2600, a Viscotek VE3580 RI detector, and two Viscotek T6000 M columns (7.8 Å, 300 mm, 10^3–10^7 Da) at a flow rate of 1mL/min for samples measured in THF and with a system consisting of a Duratec vacuum degasser, a JASCO PU-2087plus pump, an Applied Biosystems UV absorbance detector 759A (set to 254 nm wavelength), a Knauer Smartline RI detector 2300 and two MZ-Gel SD plus linear columns (300 x 8 mm, 5 µm) at a flow rate of 1mL/min for samples measured in chloroform. Calibrations were carried out using Malvern Polycal™ UCS-PS polystyrene standards. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (^{1}H-NMR 300 MHz, ^{13}C-NMR 75 MHz). Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer and thermo gravimetric

analysis was carried out on a Mettler Toledo TGA/SDTA851[e] equipped with sample robot TSO801RO.

Methods

Exemplary synthesis of symmetrical olefin bis(N-hydroxysuccinimidyl)-4-octendioate (5) by cross metathesis

N-hydroxysuccinimidyl-4-pentenoate (1.0 g, 5.1 mmol, 1 eq) and [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro-(phenylmethylene)-(tricyclohexylphosphine)ruthenium (216 mg, 0.26 mmol, 0.05 eq) were dissolved in degassed methylenechloride (10 mL) and the solution was stirred over night at ambient temperature under static vacuum to remove ethylene from the solution. The mixture was concentrated under vacuum and purified by column chromatography (ethyl acetate:hexane gradient) to give 0.87 g of the product **5** (2.4 mmol, 93% yield) as a grey coloured solid.

^{1}H-NMR (300 MHz, CDCl3), ppm: δ 5.60 (m, 2H), 2.84 (s, 8H), 2.70 (t, J=7.3 Hz, 4H), 2.46 (m, 4H), 2.72 (t, J=7.7 Hz, 2H), 2,5 (m, 2H); 13C-NMR (75 MHz, CDCl3), ppm: δ 169.08, 168.00, 129.14, 30.75, 27.31, 25.58; HRMS (ESI *m/z*) $[M+Na]^+$ calculated for $[C_{16}H_{18}N_2O_8+Na]^+$, 389.0955; found, 389.0953.

Exemplary synthesis of homotelechelic polymer PNHSMNI (PM5)

A glass vial was charged with olefin **5** (33 mg, 0.28 mmol, 8 eq), purged with argon and sealed with a septum. Initiator **C2** in degassed methylenechloride (4.0 mL, 2.8 mM, 1 eq) was added via a syringe and the resulting solution was stirred for 10 minutes. After this period of pre-functionalisation a solution of *N*-methyl-5-norbornene-2,3-dicarboximide (MNI) **8** in methylenechloride (1.0 mL, 56.4 mM, 15 eq) was added and the reaction was stirred for further 30 minutes followed by the addition of ethyl vinylether (0.05 mL, 0.5 mmol, 46 eq) to transfer the catalyst into the less reactive Fischer-type carbene species. The polymer was precipitated in methanol, stirred for 30 minutes and filtered. Redissolving in methylenechloride and precipitating gave the polymer **PM5** (31 mg, 91 % yield, $M_{n(GPC,\ Chloroform)}$= 6400 g/mol, PDI: 1.3).

^{1}H-NMR (300 MHz, $CDCl_3$), ppm: δ 5.60 (m, 2H), 2.84 (s, 8H), 2.70 (t, *J* = 7.3 Hz, 4H), 2.46 (m, 4H), 2.72 (t, *J* = 7.7 Hz, 2H), 2,5 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$), ppm: δ 169.08, 168.00, 129.14, 30.75, 27.31, 25.58; HRMS (ESI *m/z*) $[M+Na]^+$ calculated for $[C_{16}H_{18}N_2O_8+Na]^+$, 389.0955; found, 389.0953.

RESULTS AND DISCUSSION

Proof of concept

First evidence of the exceptional inherent selectivity of catalyst **C2** for the polymerisation of highly strained norbornene derivatives over less strained cycloalkenes was obtained from sacrificial syntheses of hetero-telechelic polymers.[13] In these syntheses methyldioxepine is polymerised in a ring-opening fashion to give a cleavable first polymer block, followed by polymerisation of a norbornene derivative and subsequent functional chain termination. In these experiments, incomplete polymerisation of methyldioxepine at the time of norbornene monomer addition resulted in the formation of dihydroxy homotelechelic polymers after sacrificial cleavage of the poly-dioxepine block. As the homotelechelic polymer had the aimed-for molecular weight, a statistical incorporation of excess dioxepine into the norbornene polymer block could be excluded. We therefore assumed that the propagation of dioxepine was "interrupted" by the fast propagation of norbornene and only continued to polymerise after all norbornene had been consumed.

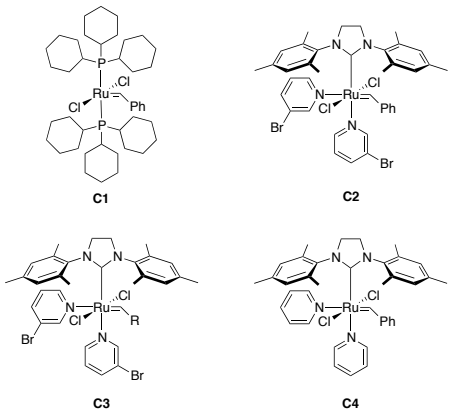
To verify this hypothesis we synthesised a homotelechelic dihydroxy functional polynorbornene via the sacrificial synthesis route.[12] The assumption that the very reactive ruthenium catalysts **C2** and **C4**[14] exhibited very high selectivity for norbornenes over dioxepines would allow the sequential polymerisation of dioxepine (in the absence of norbornene), then norbornene (with the catalyst selecting norbornene over dioxepine) and finally dioxepine (once all norbornene had been consumed). This would allow staying within a kinetically controlled regime of polymer growth to achieve not only control over molecular weight but also the molecular weight distribution. In fact, it has been described that the mechanism of functional group

introduction with chain transfer agents (CTAs) in ROMP/CT initially follows a kinetically controlled polymer growth to very high molecular weights. Only subsequent backbiting and chain-transfer events lead to a reduction of the molecular weight when approaching the thermodynamic equilibrium (defined by the initial monomer to CTA ratio).[15]

To verify whether kinetic differences of the involved substrates lead to selectivity towards homo-propagation over cross-propagation we conducted the following competition experiment: Methyldioxepine **7** a cyclic olefin with moderate ring strain and slow propagation constant[16] was added in an 8-fold excess to a solution of the initiator **C2**. After 30 minutes, another 25 equivalents *exo*-*N*-methyl-5-norbornene-2,3-dicarboximide (MNI) **8** and an additional 9 equivalents of **7** (to assure the presence of **7** during the polymerisation step) were added. The resulting polymer **PM1a** (PDOMNI) showed a narrow molecular weight distribution with only minor broadening upon acidic hydrolysis (hydrolysed polymer = **PM1b**) (Figure S1).

Statistical incorporation of **7** into the polymer would have lead to its random degradation and a significant broadening of the molecular weight distribution upon hydrolysis. Assuming the formation of oligo-methyldioxepine blocks at both chain ends of the polyMNI block explains the shift towards slightly lower molecular weight after hydrolysis (see supplementary information).[16] This polymerisation reaction is finished within minutes after addition of monomer **8**. This differs significantly from the reported ROMP/CT systems where thermodynamic equilibrium is reached typically after 12 to 72 hours.[17-20]

CHART 1



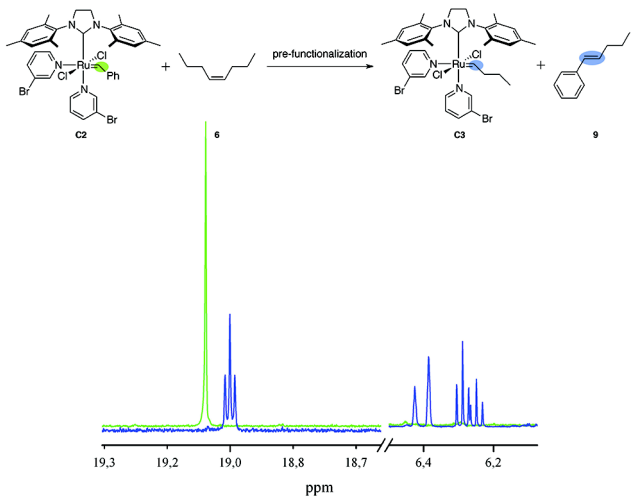


FIGURE 1 The conversion of initiator **C2** into pre-functionalised catalyst **C3** can be monitored by ^{1}H-NMR. The singlet at 19.06 ppm (green) originating from **C2** disappears and **C3** is formed, indicated by a new triplet signal at 19.00 ppm (blue).

The substituted norbornene monomer **8** reduces backbiting during the reaction, which narrows the molecular weight distribution and conserves the control over molecular weight given by the initiator to monomer ratio. A ROMP/CT approach using the same monomers would take several days - if not completely fail - to produce well-defined homotelechelic polymers.[21]

To generalise this method we applied the above-mentioned protocol to functional acyclic symmetrical olefins. Meldrum's acid functionalised olefin **1** was synthesised and reacted in an 8-fold excess with the initiator **C2**. In less than 15 minutes the new pre-functionalised ruthenium initiator **C3** was formed (verified by the disappearance of the **C2**-specific carbene signal at 19.06 ppm and the appearance of a new triplet at 18.92 ppm in the ^{1}H-NMR spectrum, Figure 1 shows the analogous NMR study on the reaction between **C2** and **6**). During the reaction of the **C2** benzylidene catalyst with **1** a beta-substituted styrene species is formed in equimolar amounts to the catalyst.

Excess of symmetrical aliphatic olefin **1** and the decreased metathesis reactivity of the newly formed beta-substituted styrene derivative render the back

reaction to the initial ruthenium benzylidene complex unfavourable.

After 15 minutes of pre-functionalisation, 25 equivalents of norbornene monomer **8** were added. The reaction with the highly strained norbornene **8** is significantly faster than with the symmetrical acyclic olefin **1** leading to a fast and selective polymerisation of **8**. Once the concentration of **8** has dropped sufficiently, the chain transfer reaction with **1** becomes dominant again and the polymer chain is functionally terminated. In this way, a homotelechelic polymer **PM2** (PMAMNI) carrying Meldrum's acid at both chain ends is formed as could be shown by its isotopically resolved MALDI-ToF mass spectrum. Neither benzylidene residues at the focal unit from incomplete pre-functionalisation nor methylidene residues at the terminal unit from the quenching reaction of ethyl vinylether with unfunctionalised polymer chains could be found in the ^{1}H-NMR spectrum or the MALDI-ToF mass spectrum (Figure 2 and Figure S2).

The terminal Meldrum's acids are thermo labile and undergo a pericyclic reaction producing highly reactive ketenes upon heating[22-24] as verified by IR-spectroscopy (Figure S3) and thermo gravimetric analysis (Figures S4-S6).

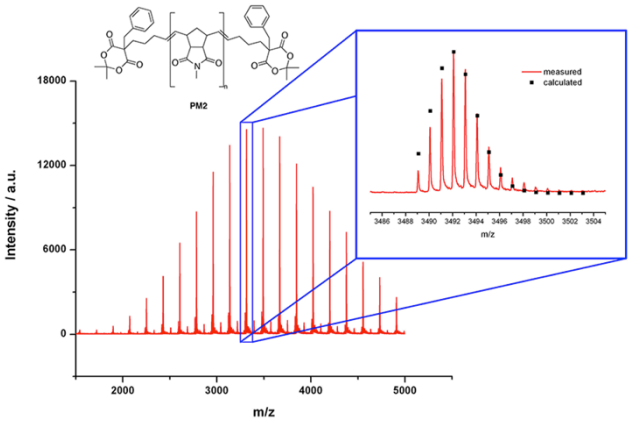


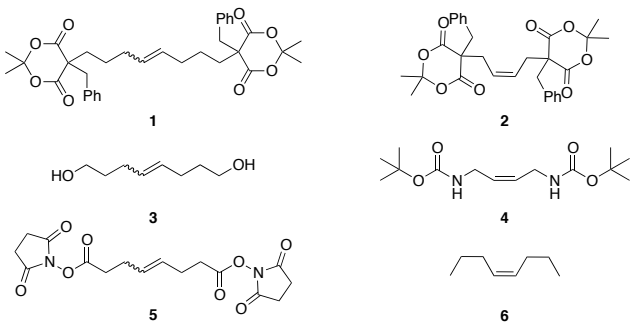
FIGURE 2 MALDI-ToF mass spectrum of homotelechelic poly(*N*-methyl-5-norbornene-2,3-dicarboximide) carrying Meldrum's acid end groups **PM2.** The detected masses correspond to the diketene species, produced by cycloreversion of the Meldrum's acid during laser desorption. No benzylidene end group from the initial ruthenium benzylidene catalyst was found. *Inset*: Isotope pattern measured (red line) and calculated (black squares) for the 17mer *(m/z)* $[C_{196}H_{215}N_{17}O_{36}+Ag]^{+}$, monoisotopic mass: 3489.46.

In contrast to the aforementioned methods to synthesise homotelechelic ROMP polymers, this method achieves narrow polydispersity polymers within a desirable range of PDIs between 1.1 and 1.4, depending on the structure of the functional end group. The control over molecular weight is only determined by the monomer to initiator ratio.

The polymerisation reactions are typically finished within a few minutes. Detection of the propagating carbene signal using ^{1}H-NMR spectroscopy experiments is therefore difficult because in most cases the incorporation of monomer is too fast to be recorded on the timescale of an NMR-experiment. Only the carbene triplet signal of the reformed functionalised initiator species can be observed.

To show the versatility of this method we used a set of functional symmetric olefins **1**-**6**, which all give access to telechelic ROMP polymers with defined end groups. It should be noted that in many reports on functionalisation reagents *cis*-olefin substrates[19,25-28] are used which often require additional synthetic steps to prepare. In our approach, however, it is advantageous to use the thermodynamically more stable *trans*-olefin substrate since this configuration promises a higher value for k_{ROMP}/k_{CM} (k_{ROMP} = rate of polymerisation, k_{CM} = rate of cross metathesis, see Figure 3). We therefore chose the olefin metathesis homodimerisation of terminal olefins using Grubbs-type catalysts to prepare olefins **1**, **3** and **5**. This strategy leads to a high amount of *trans*-olefin and also screens compatibility with the involved ruthenium catalysts.[29,30]

CHART 2



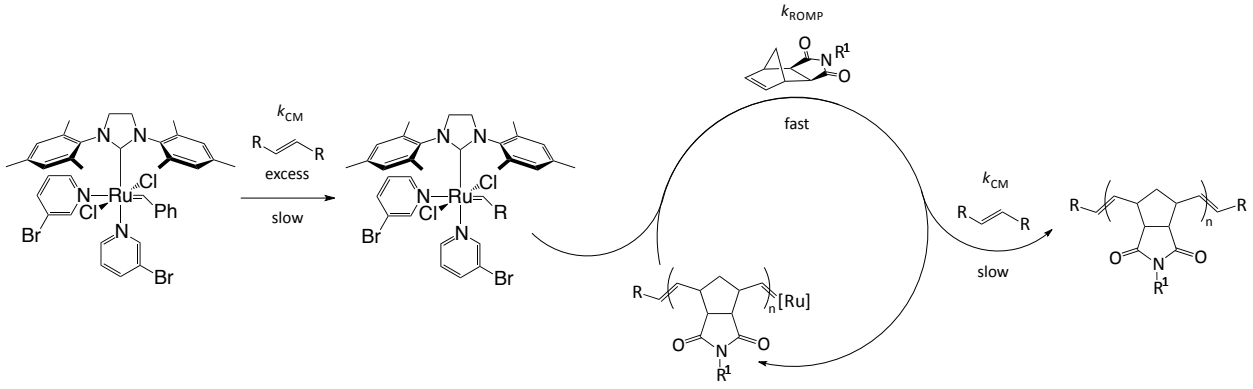


FIGURE 3 *In-situ* pre-functionalisation of Ru(II)-catalyst and synthesis of homotelechelic polymer.

Within this set of symmetric olefins, we included two (**2** and **4**), which carry their functional group at the allylic position whereas the others carried at least one additional methylene spacer between the olefin and the functional group. This criterion was found essential for efficient metathesis reactions with the given catalyst systems.[31-33] Olefin **1** carries the same functional group as **2** only placed two carbon-carbon bonds further away from the olefin. The shorter Meldrum's acid functionalised olefin **2** shows no metathesis activity at all, with Grubbs 1st and 3rd generation catalyst **C1** and **C2.** Its higher homologue **1** reacts surprisingly fast and efficiently forms homotelechelic polymer **PM2** (PDI=1.2) when monomer **8** is added. This strongly indicates that steric rather than chelating effects of the Meldrum's acid moiety are the limiting factor.[34] The BOC-protected amino functionalised olefin **4** reacts readily with catalyst **C2** but leads to a broad molecular weight distribution of the resulting polymer **PM3** (PNHBOCMNI, from monomer **8,** PDI=1.6) indicating a slow initiation caused by steric effects of the pre-functionalised initiator **C3**.

When olefin **3** was used to form bishydroxy homotelechelic polymer **PM4** (POHMNI, from monomer **8,** PDI=1.2), the MALDI-ToF mass spectrometric analysis revealed the characteristic mass pattern of a migrated olefin (see supplementary information Figure S7). Ruthenium catalysed olefin migration[35] in **3** creates different asymmetric dihydroxy olefins which eventually lead to homotelechelic polymers. They differ only in the length (number of methylene units) of the aliphatic primary alcohol at the polymer chain end. β-Substituted styrene groups from incomplete pre-functionalisation as well as terminal olefinic end groups from subsequent termination with ethyl vinylether could not be observed. Olefin migration in primary alkene-ols has previously been observed in reactions involving Ru(II)-catalyst species.[36,37] In olefins lacking the presence of primary alcohols, no migration was observed.[19,29,30]

Using olefin **5** as the functionalising agent, we successfully synthesised polymer **PM5** (PNHSMNI, from monomer **8**, PDI = 1.3) which carries *N*-hydroxysuccinimidyl ester (NHS ester) groups at both chain ends (for MALDI-ToF-MS analysis see supplementary information Figure S9). Post-polymerisation functionalisation of these reactive chain ends was demonstrated by complete derivatisation with benzylamine. MALDI-ToF mass spectrometric analysis showed no activated ester or carboxylic acid end groups. Homotelechelic polymer **PM6** (PBAMNI) with benzylamide end groups was observed exclusively (Figure S10).

CHART 3

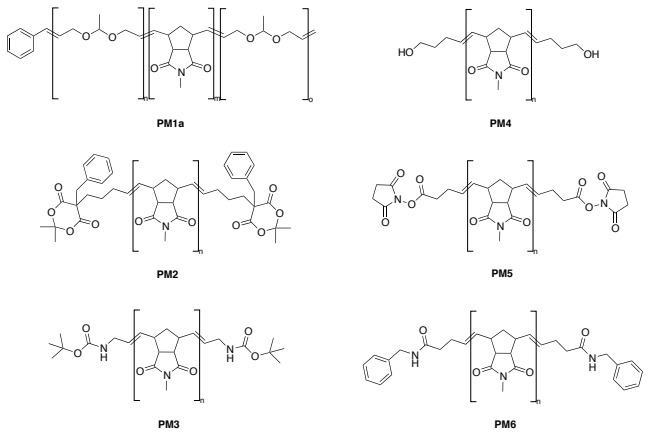


TABLE 1 Homotelechelic polymers synthesised.

Sample	Mn (theor.) ($gmol^{-1}$)	Mn (GPC) ($gmol^{-1}$)	PDI
PM1b	4500	7400 [a]	1.2
PM2	3200	7900 [b]	1.2
PM3	3100	14100 [b]	1.6
PM4	1900	8200 [a]	1.2
PM5	3000	6400 [b]	1.3

[a] measured in THF, [b] measured in chloroform

Chain transfer agents have also been used extensively with other types of polymerisation. In radical polymerisations in particular, the chain transfer agent is chosen such that the molecular weight of the polymer chains can be lowered. In the living radical polymerisation RAFT (=reversible addition fragmentation chain transfer), a reversible chain transfer agent with a fairly high chain transfer constant is employed keeping the physical polymer chain length increment between transfer events small. This effect is exploited in achieving the overall control over the molecular weight distribution.

The approach described above for the living ROMP is conceptually very different in that a chain transfer agent with a particularly low chain transfer constant ($C = k_{transfer}/k_{propagation}$) is present during a living chain growth polymerisation. In fact, the chain transfer constants of the internal olefins **1**, **3**-**6** described above are so low that the degree of polymerisation is virtually not affected by their presence. The reaction with the CTA only becomes relevant when the monomer concentration has dropped below a critical concentration, i.e. towards the end of the propagation reaction. This results in the "automatic" end-functionalisation at the end of the propagation reaction. ROMP behaves like a living polymerisation for many monomers and short reaction times. Long reaction times can lead to catalyst decomposition and a deviation from true living behaviour. A method such as the one described here ensures that the end-functionalisation reaction occurs immediately after propagation, thereby reducing the extent of potential catalyst decomposition and ensuring high degrees of end-functionalisation.

Molecular weight limits of the method

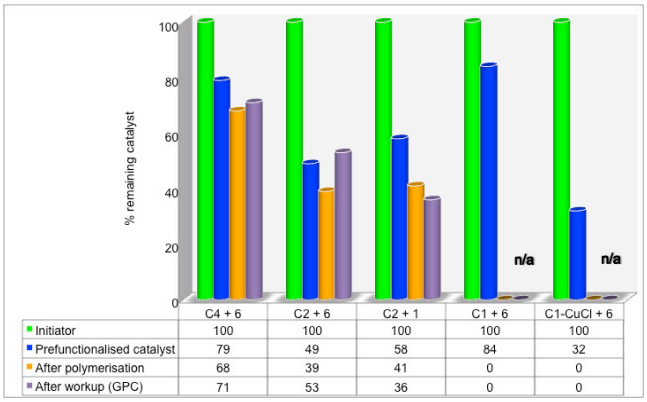
The explanation for the successful synthesis of homotelechelic polymers was based purely on the assumption that the kinetics of the metathesis reaction of strained cyclic olefins and acyclic internal olefins with the ruthenium catalyst differ significantly. The average degree of polymerisation is defined by the ratio of the rate of polymerisation and the rate of cross metathesis (R_{ROMP}/R_{CM}). As the concentration of monomer decreases during polymerisation so does R_{ROMP}. As a consequence, a molecular weight broadening should be observed when aiming for higher molecular weight telechelic polymers using otherwise identical cyclic monomers and acyclic internal olefins.

In our experiment, catalyst **C2** was pre-functionalised with olefin **6** as described above and added to solutions of monomer **8** with different concentrations, keeping the total volume constant. A significant broadening of the molecular weight distribution can be observed for higher molecular weights (see table 2) as expected theoretically. For polymerisations below a molecular weight of ca. 10000 g mol^{-1} narrow polydispersity polymers can be obtained with this general method.

TABLE 2 Monotelechelic poly(MNI) terminated with *cis*-octene 6.

DP (theor.)	Mn (theor.) ($gmol^{-1}$)	Mn (GPC) ($gmol^{-1}$) [a]	PDI
9	1800	3600	1.1
19	3400	6300	1.3
36	6500	10900	1.3
47	8500	14500	1.7
93	16700	25700	1.8

[a] GPC measurements were carried out on chloroform.



	C4 + 6	C2 + 6	C2 + 1	C1 + 6	C1-CuCl + 6
Initiator	100	100	100	100	100
Prefunctionalised catalyst	79	49	58	84	32
After polymerisation	68	39	41	0	0
After workup (GPC)	71	53	36	0	0

FIGURE 4 Comparison of the carbene concentration at various stages of the polymerisation: initial carbene concentration (green), during the reaction with symmetrical olefin (blue), after polymerisation (yellow) and calculated from GPC analysis of the resulting polymers (violet).

Stability of the pre-functionalised initiator

In kinetically controlled homotelechelic polymer syntheses the molecular weight of the polymer should be largely defined by the monomer/initiator ratio. However, in our experiments we observed systematically higher molecular weights than aimed for.

When further analysing the correlation between resulting molecular weight and initial monomer to catalyst ratios, we found a complex behaviour regarding the different ruthenium catalysts **C1**, **C2** and **C4** (Figure 4). A side reaction that does not follow the expected propagation or transfer reaction reduces the amount of catalyst available for polymerisation. This phenomenon was also observed by Matson et al. and referred to as catalyst death during cycles of pulsed-addition ring-opening metathesis polymerisation.[38] Matson et al. attribute the catalyst death rate to an unknown decomposition reaction during the polymerisation step. However, examining the metathesis reaction of different catalysts with the internal olefin *cis*-octene **6** by ^{1}H-NMR spectroscopy we observed most of the catalyst degradation during the initial pre-functionalisation step. 1-Phenyl-1-pentene **9** formed during the olefin metathesis reaction between benzylidene catalysts and *cis*-octene **6** served as an internal ^{1}H-NMR-spectroscopic integration standard (Figure 1). 21% of catalyst loss was assigned to the reaction between initiator **C4** and *cis*-octene **6**, 51% to the reaction between initiator **C2** and **6** and 42% loss of catalyst for the reaction between **C2** and olefin **1**.

84% of carbene signals remained after the reaction of **C1** with **6**. However, not all initiator **C1** had reacted with **6** leading to a mixture of end-groups in the subsequent attempt to synthesise homotelechelic polymers.[39] We attributed the inefficient initiation of Grubbs 1st generation catalyst **C1** to inhibiting effects by free phosphine ligands from the propagating catalyst species. We therefore added Cu(I)Cl to scavenge the free phosphine ligands.[40,41] A complete conversion of the initial α-carbene ^{1}H-NMR signal at 20.02 ppm into the new triplet signal (19.27 ppm) of the pre-functionalised initiator was observed. Unfortunately, the addition of Cu(I)Cl lead to a rapid decay of the catalyst species and was therefore not suitable to give reproducible results.

For the experiments with catalysts **C2** and **C4**, the decay of ruthenium carbene signals as observed in the ^{1}H-NMR spectra continued during the following polymerisation reaction. A further 14%, 20% and 29% loss of active catalyst species was observed during the reaction between pre-functionalised initiator species and olefin (**C4**+**6**, **C2**+**6** and **C2**+**1** respectively). However, we have no evidence of whether the side reactions during the different stages of the experiment are in fact identical. The catalyst decomposition observed by ^{1}H-NMR spectroscopy is in good agreement with the resulting higher molecular weights determined by GPC analysis (yellow and violet bars, Figure 4).

CONCLUSIONS

We report a fast "one-pot" procedure to narrow polydispersity homotelechelic ROMP polymers exploiting the Ru-catalysts' inherent substrate selectivity. The commercially available third generation Grubbs catalyst is pre-functionalised *in-situ* using an excess of a functional symmetrical *trans*-olefin. Subsequent polymerisation of a norbornene derivative proceeds in the presence of excess acyclic olefin without chain transfer. Polymer end-functionalisation occurs "automatically" with the excess of acyclic olefin after the monomer has been

consumed. The molecular weight control of the homotelechelic polymers is determined by the monomer to catalyst ratio only. The acyclic functional olefins examined in this study allow the synthesis of narrow polydispersity telechelic polymers up to 10000 g mol^{-1}, a valuable range for most industrial and academic applications.

This method represents one of the fastest and most versatile end-functionalisation methods for ROMP to date, limited only by the catalysts' tolerance of the functional end-groups.

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GRAPHICAL ABSTRACT

NILS HANIK AND ANDREAS F. M. KILBINGER

NARROWLY DISTRIBUTED HOMOTELECHELIC POLYMERS IN 30 MINUTES: USING FAST *IN-SITU* PRE-FUNCTIONALISED ROMP INITIATORS.