

# Efficient Amine End Functionalization of Living Ring Opening Metathesis Polymers

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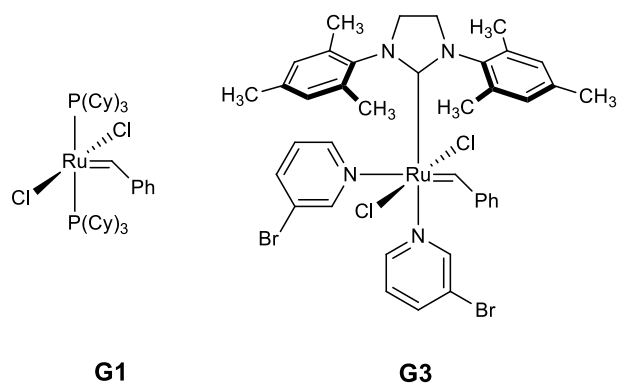
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**ABSTRACT.** An efficient strategy for the synthesis of mono amine end functionalized living polymers using ring opening metathesis polymerization with ruthenium initiators is reported. A new end capping agent for this purpose was synthesized and its efficiency for end functionalization was evaluated using two common ruthenium based initiators. Finally, terminal cross metathesis was also explored as another alternative towards the synthesis of amine end functionalized polymers and the comparison between the two techniques is presented.

**KEYWORDS** ring opening metathesis polymerization, end-functional polymer, terminal cross metathesis, living polymerization

## Introduction

Ring opening metathesis polymerization (ROMP) has very quickly become one of the methods of choice of chemists to synthesize highly functional low dispersity polymers with control over molecular weight and architecture.<sup>1</sup> The air and moisture sensitive molybdenum carbene catalysts typically used for olefin metathesis are sensitive to many protic and polar functional groups such as for example aldehydes.<sup>2</sup> Polymers prepared with molybdenum and tungsten carbene initiators can therefore be end-functionalized in a relatively straightforward manner using suitably substituted aldehydes.<sup>3,4,5,6,7</sup> However, due to the restricted functional group tolerance of these initiators, many functional groups cannot be present in the polymer structure. In contrast, the Grubbs type ruthenium carbene catalysts (Figure 1) are stable towards many functional groups. Polymers prepared with these ruthenium initiators can thus tolerate the presence of many functional groups but at the same time methods for a functional termination are scarce for the same reason.<sup>8</sup> Ethyl vinyl ether termination is one of the most widely used non-functional termination methods for ROMP transferring a methylene unit onto the polymer chain end.

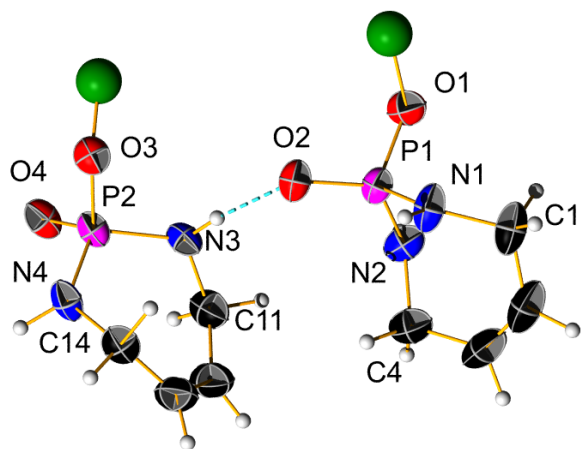
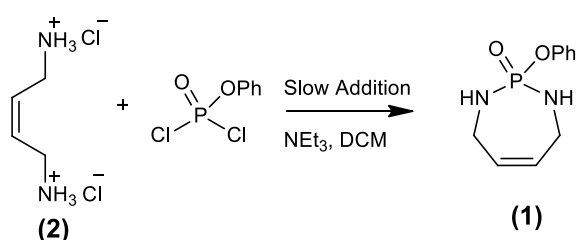


**Figure 1:** Ruthenium initiators used for ring opening metathesis polymerization.

Many strategies have been developed for the synthesis of mono telechelic functional polymers by ROMP. Prefunctionalized initiators have been used to synthesize such polymers<sup>9</sup> but the synthesis of a new catalyst for every new functionality is difficult and the yields are often low. End capping agents based on custom terminating agents,<sup>9d,10</sup> acrylates,<sup>11</sup> vinyl carbonates and lactones<sup>12</sup> have also been used

to synthesize mono end functionalized polymers from ring opening metathesis polymerization. Recently, Hilf et al. reported the “Sacrificial Synthesis” strategy for the synthesis of mono end functionalized living ring opening metathesis polymers.<sup>13</sup> The strategy involves the polymerization of a new monomer onto the end of a first polymer block, thus leading to a diblock copolymer. This new second block is then chemically cleaved to yield the desired functionality at the end of the polymer chain. Via this method a variety of mono end functional polymers carrying alcohol, thiol or carboxylic acid end groups are readily accessible. End functionalization strategies for a number of different functional groups for living ROMP were recently reviewed.<sup>14,15</sup>

Amine end functionalization is more difficult due to the ability of the free amino groups to coordinate to the ruthenium catalyst.<sup>16</sup> Protected amine chain transfer agents have been used to overcome this difficulty.<sup>17</sup> However, very long reaction times are sometimes required which could potentially give rise to chain transfer to the growing polymer chain itself depending on the monomer structure polymerized.



**Figure 2:** Synthesis (*top*) and single crystal x-ray structure (*bottom*) of **1**. The phenyl rings are shown as single atoms (green) for clarity. The hydrogen-bond is represented as a blue dashed line.

A new cyclic olefin, 2-phenoxy-2,3,4,7-tetrahydro-1*H*-1,3,2-diazaphosphepine 2-oxide (**1**) was synthesized to overcome this difficulty. In this compound, the phosphorous bridge plays two roles – it forms a closed ring, which allows its use as a sacrificial monomer in ROMP and simultaneously acts as a protecting agent for the amino groups.<sup>18</sup> Single crystal x-ray diffraction confirmed the synthesis of the new compound (Figure 2, bottom).

## Experimental Section

**Materials:** Grubbs initiators **G1** and **G3**, phenyl phosphodichloridate, ethyl vinyl ether, 4-dimethylaminopyridine (DMAP), di-*t*-butyl dicarbonate and trifluoroacetic acid were purchased from Sigma-Aldrich and used without further purification. (*Z*)-but-2-ene-1,4-diammonium chloride<sup>19</sup> (**3**) and *exo-N*-methyl norbornene imide<sup>20</sup> (**MNI**) were synthesized as reported previously. Triethyl amine was purchased from Acros chemicals, distilled from calcium hydride and stored over potassium hydroxide.

## Instrumentation:

Mass analysis of the polymers was carried out on a Bruker FTMS 4.7T BioAPEX II using 2-[(2*E*)-3-(4-*tert*-butylphenyl)-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) equipped with a Viscotek GPCmax VE2001 GPC Solvent/Sample Module, a Viscotek UV-Detector 2600, a Viscotek VE3580 RI-Detector and two Viscotek T6000M columns (7.8 x 300 mm, 10<sup>3</sup> - 10<sup>7</sup> Da). All measurements were carried out at room temperature using THF as the eluent with a flow rate of 1 mL/min. The system was calibrated with polystyrene standards in a range from 10<sup>3</sup> - 3×10<sup>6</sup> Da. NMR spectra were recorded on a Bruker Avance III 300MHz NMR Spectrometer (<sup>1</sup>H NMR 300MHz; <sup>13</sup>C NMR 75 MHz). J-resolved <sup>1</sup>H-NMR spectroscopy was done on a Bruker Avance III 500MHz instrument (<sup>1</sup>H NMR 500 MHz).

**Single crystal x-ray diffraction:** A crystal was mounted on a loop and all geometric and intensity data were taken from this crystal. Data collection using Cu-K $\alpha$  radiation ( $\lambda = 1.54186 \text{ \AA}$ ) was performed at 200 K on a STOE IPDS-IIT diffractometer equipped with an Oxford Cryosystem open flow cryostat.<sup>21</sup> Absorption correction was partially integrated in the data reduction procedure.<sup>22</sup> The structure was solved and refined using full-matrix least-squares on F<sup>2</sup> with the SHELX-97 package.<sup>23</sup> All heavy atoms could be refined anisotropically. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depositing numbers CCDC- 856639

(**1**) C<sub>20</sub> H<sub>26</sub> N<sub>4</sub> O<sub>4</sub> P<sub>2</sub>, M= 448.39 g.mol<sup>-1</sup>, monoclinic, *P*2<sub>1</sub>/*c* (Nr. 14), *a* = 11.0494(6); *b* = 9.2838(5); *c* = 23.0031(12)  $\text{\AA}$ ;  $\beta$  = 101.655(4) ; *V* = 2311.0(2)  $\text{\AA}^3$ , *Z* = 4,  $\rho_{\text{calcd.}}$  = 1.300 Mg m<sup>-3</sup>, F(000) = 944, *T* = 200 K,  $\lambda = 1.54186 \text{ \AA}$ ,  $\mu(\text{Cu-K}\alpha)$ , 4.09° <  $\theta$  < 64.98°, 12335 reflections of which 3544 unique and 3544 observed, 275 parameters refined, GOOF (on *F*<sup>2</sup>) = 1.084, *R*<sub>1</sub> =  $\sum|F_o - F_c| / \sum F_o = 0.0489$ , *wR*<sub>2</sub> = 0.1301 for *I* > 2 $\sigma$ (*I*).

### **Typical polymerization procedure in an NMR tube:**

The ruthenium initiator (either **G1** or **G3**) was taken in an NMR tube and purged by continuous flow of argon for 15 minutes. Degassed dichloromethane-d<sub>2</sub> was added to the tube under argon and shaken until all the initiator was dissolved. The monomer **MNI** was purged under argon in a separate vial. Degassed dichloromethane-d<sub>2</sub> was added to the monomer under a flow of argon via a syringe. This solution was immediately transferred to the NMR tube containing the initiator. The NMR tube was capped and inverted once to ensure efficient mixing. The tube was kept standing for some time (typically 45 minutes) to ensure complete monomer consumption. Compound **1** was purged with argon for 30 minutes, dissolved in degassed dichloromethane-d<sub>2</sub> and added to the NMR tube for end

functionalization. The NMR tube was inverted to ensure complete mixing and immediately transferred into the NMR spectrometer for subsequent recording of NMR spectra.

#### **Typical procedure for Ring Opening Metathesis Polymerization:**

The catalyst (**G1** or **G3**), monomer (**MNI**) and sacrificial monomer **1** were taken in separate Schlenk flasks and purged free of oxygen by three cycles of alternating high vacuum and argon atmosphere. Dry dichloromethane was taken in a separate Schlenk flask and degassed by three consecutive freeze-vacuum-thaw cycles. This degassed dichloromethane was added to each Schlenk flask. The catalyst solution was added quickly to the **MNI** solution using a syringe and the resulting solution was kept stirring at room temperature for 45 minutes. An aliquot of this solution was quenched with ethyl vinyl ether and analyzed as a reference sample. The sacrificial monomer **1** was quickly added to the remaining solution via a syringe and the solution was kept stirring for 30 minutes. Ethyl vinyl ether was subsequently added to quench the reaction and the polymer was precipitated in cold methanol. The polymer was redissolved in dichloromethane and reprecipitated twice into methanol, filtered and dried under high vacuum.

#### **Typical procedure for terminal cross metathesis:**

**G1** was purged under argon, dissolved in dry degassed dichloromethane and a degassed solution of **MNI** in dichloromethane was quickly added. The solution was kept stirring for 45 minutes at rt. The chain transfer agent **7** was separately purged under argon, dissolved in dry degassed dichloromethane and added to the **G1-MNI**-solution. Aliquots of this solution were taken every 30 minutes, quenched with 2 drops of ethyl vinyl ether, precipitated in cold methanol and analyzed by  $^1\text{H}$  NMR to monitor the completion of the reaction.

$^1\text{H}$  NMR of **3** from **G1**: (DCM-  $d_2$ , 300MHz):  $\delta$  = 7.12 - 7.45 (m, 5 H), 6.49 – 6.61 (m, 1H), 6.25 – 6.38 (m, 0.75 H), 5.86 – 6.04 (m, 1.4H), 5.85 – 6.04 (m, 28H), 5.45 – 5.62 (m, 5H), 5.05 – 5.25 (m, 2H),

2.95 – 3.40 (m, 36H), 2.81 – 2.95 (m, 46H), 2.59 – 2.81 (m, 25H), 2.00 – 2.26 (m, 19H), 1.44 – 1.79 (m, 28H)

<sup>1</sup>H NMR of **6** from **G1**: (DCM- d<sub>2</sub>, 300MHz): δ = 7.11 - 7.45 (m, 5 H), 6.48 – 6.61 (m, 0.9H), 6.25 – 6.38 (m, 0.71 H), 5.61 – 6.07 (m, 26H), 5.42 – 5.61 (m, 4H), 5.06 – 5.27 (m, 0.28H), 3.49 – 3.76 (m, 1.6H), 2.95 – 3.49 (m, 34H), 2.81 – 2.95 (m, 42H), 2.60 – 2.80 (br s, 24H), 1.42 – 2.29 (m, 49H)

<sup>1</sup>H NMR of **3** from **G3**: (DCM-d<sub>2</sub>, 300MHz): δ = 7.15 - 7.47 (m, 5 H), 6.45 – 6.60 (m, 1H), 6.21 – 6.40 (m, 0.53 H), 5.60 – 5.88 (br s, 12H), 5.38 – 5.62 (br s, 11H), 5.02 – 5.25 (m, 2H), 2.88 – 3.35 (m, 68H), 2.50 – 2.76 (br s, 13H), 1.84 – 2.28 (m, 13H), 1.39 – 1.80 (m, 14H)

<sup>1</sup>H NMR of **6** from **G3**: (DCM- d<sub>2</sub>, 300MHz): δ = 7.14 - 7.47 (m, 5 H), 6.47 – 6.62 (m, 1H), 6.23 – 6.40 (m, 0.5 H), 5.62 – 5.87 (br s, 13H), 5.35 – 5.62 (br s, 11H), 5.06 – 5.27 (m, 0.5H), 3.30 – 3.6 (br s, 2,2H), 2.85 – 3.35 (m, 70H), 2.55 – 2.79 (br s, 14H), 1.88 – 2.32 (m, 14H), 1.38 – 1.77 (m, 13H)

**2-phenoxy-2,3,4,7-tetrahydro-1H-1,3,2-diazaphosphepine 2-oxide (1)**: Phenyl phosphodichloridate (1.20g, 5.7mmol, 1eq) and dry dichloromethane (400mL) were kept stirring in an ice bath. DMAP (0.07g, 0.57mmol, 0.1eq) and triethylamine (4.34g, 42.9mmol, 7.7eq) were slowly added. The mixture was kept stirring for 15 minutes until the solution turned yellow. (Z)-but-2-ene-1,4-diaminium chloride (1.00g, 6.3mmol, 1.1eq) was separately dissolved in dry dichloromethane (30mL) and triethylamine (2.17g, 21.4mmol, 3.8eq). This mixture was added to the phenyl phosphodichloridate solution over 4 hours. The resulting mixture was stirred at rt for 30 minutes and refluxed under argon for three hours. Water was added and the mixture was extracted thrice with dichloromethane, dried over MgSO<sub>4</sub> and concentrated in vacuum. Column chromatography (1:4 ethyl acetate:hexane) of the yellow waxy solid over silica gave the colourless product (0.78g, 61.35% yield). The compound was crystallized from DCM/n-hexane for single crystal x-ray structure determination.

<sup>1</sup>H NMR (chloroform-d, 300MHz): δ = 7.12 - 7.39 (m, 5 H), 5.65 (t, J=2.3 Hz, 2 H), 3.59 - 3.85 (m, 4 H), 3.17 - 3.49 (m, 2 H).

$^{13}\text{C}$  NMR (chloroform-d ,75MHz):  $\delta = 150.82, 129.59, 128.76, 124.55, 120.56, 39.02$ .

**(Z)-di-tert-butyl but-2-ene-1,4-diyl dicarbamate (7)** (Z)-But-2-ene-1,4-diaminium chloride **3** (0.20g, 1.25mmol, 1eq) was added slowly to an ice cold solution of di-t-butyl dicarbonate (0.65mg, 3mmol, 2.4eq) and triethylamine (1.00g, 9.9mmol, 7.9eq) in 20mL dry dichloromethane. The solution was allowed to warm up to room temperature and stirred for 6 hours. Water was added and the dichloromethane layer was washed 3 times with water, concentrated, dried over  $\text{MgSO}_4$  and evaporated under vacuum to give 0.35g of **7** in 98% yield. The compound was pure by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR analysis and was used without further purification.

$^1\text{H}$ -NMR (chloroform-d, 300MHz):  $\delta = 5.56$  (t,  $J=4.5$  Hz, 2 H), 4.85 (br. s., 1.7 H), 3.70 - 3.88 (m, 4 H), 1.45 ppm (s, 18 H).

$^{13}\text{C}$  NMR (chloroform-d ,75MHz):  $\delta = 155.84, 128.73, 79.24, 36.99, 28.29$ .

### Results and Discussion:

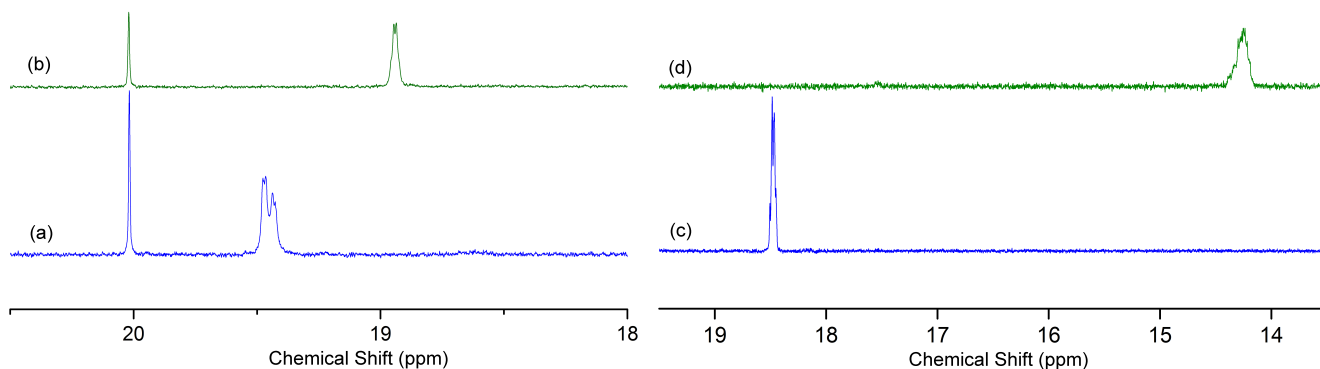
In order to examine the polymerization capability of the new sacrificial monomer **1**, five equivalents of **1** were added to the ruthenium initiators **G1** and **G3** in dichloromethane- $d_2$  in separate NMR tubes. In the NMR tube containing catalyst **G1**, the initiator successfully reacted with **1** but failed to propagate. The ruthenium carbene peak in the  $^1\text{H}$ -NMR spectrum shifted partially from 20.01 ppm to 18.93 ppm. The unreacted initiator peak (20.01 ppm) is typically observed due to the slow initiation profile of the less reactive **G1** initiator. However, with **G3**, compound **1** did propagate, but yielded only very short oligomers consisting of 2-3 repeat units, as analyzed by  $^1\text{H}$ -NMR spectroscopy. In this case, the ruthenium carbene peak shifted completely from 19.04 ppm to 14.28 ppm. Compound **1** was designed as a sacrificial monomer and should ideally initiate fast and propagate slowly. The initial experiments with initiators **G1** and **G3** showed that these prerequisites were fulfilled, which is important for an efficient and atom economical polymer end functionalization with a sacrificial monomer.



In a second experiment, the norbornene monomer **MNI** was added to the NMR tubes containing **G1** and **G3** initiated compound **1**. In both cases no initiation or propagation of **MNI** could be observed. In both cases, the ruthenium catalysts when reacted with **1** formed a very unreactive carbene. Unfortunately, we did not succeed at isolating the new carbene complex as it decomposed too rapidly in air.

To investigate whether **1** could deactivate the **MNI**-initiated ruthenium catalysts **G1** and **G3** to give end functionalized polymers, 20 equivalents of **MNI** were added to the above mentioned initiators in two separate NMR tubes. The solutions were kept at room temperature for 40 minutes, giving them enough time to polymerize to completion. An aliquot of each solution was quenched with ethyl vinyl ether as reference samples. A large excess (10 equivalents) of **1** was subsequently added to both remaining solutions in order to end-functionalize the polymers. After 3 minutes the <sup>1</sup>H-NMR-spectrum of both samples showed no traces of the propagating **MNI** carbene and only the signals for the carbene complex with **1**, as observed in Figure 3.

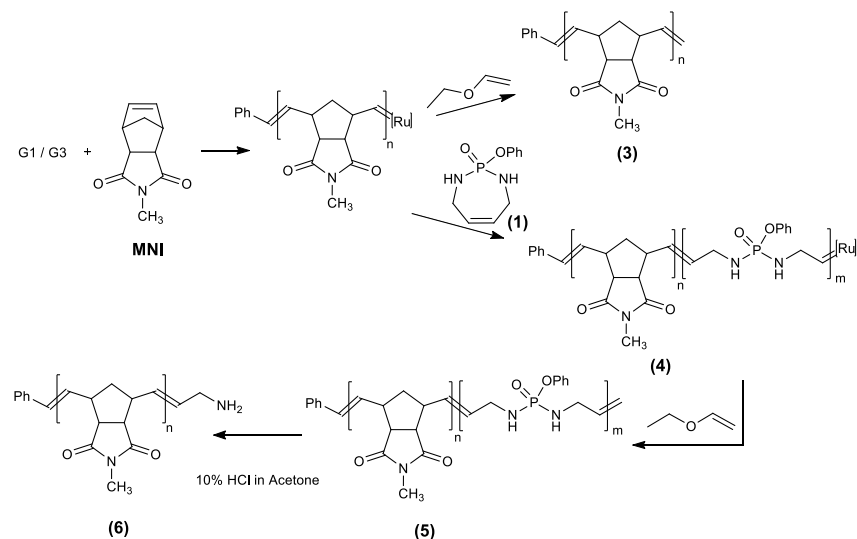
To test the end functionalization efficiency of **1**, the NMR experiments were repeated with progressively reduced amounts of the sacrificial monomer. It was found that 1.2 equivalents of **1** (with respect to the propagating carbene) added to an **MNI** polymerization was the minimum amount necessary to completely shift the peak of the initiated ruthenium carbene of **G1** from 19.46 ppm to 18.93 ppm within 3 minutes. However, at least 5 equivalents of **1** were necessary to completely shift the initiated ruthenium carbene peak of **G3** from 18.49 ppm to 14.28 ppm within 3 minutes. This is in very good agreement with our previous observation that **G3** slowly polymerizes **1** to small oligomers and that the catalyst **G1** does not propagate **1** at all.



**Figure 3:**  $^1\text{H}$  NMR spectra of a) **G1** and **MNI** reacted for 45 minutes. b) After the addition of 1.2 equivalents of **1** to a. c) **G3** and **MNI** reacted for 45 minutes. d) After addition of 5 equivalents of **1** to c.

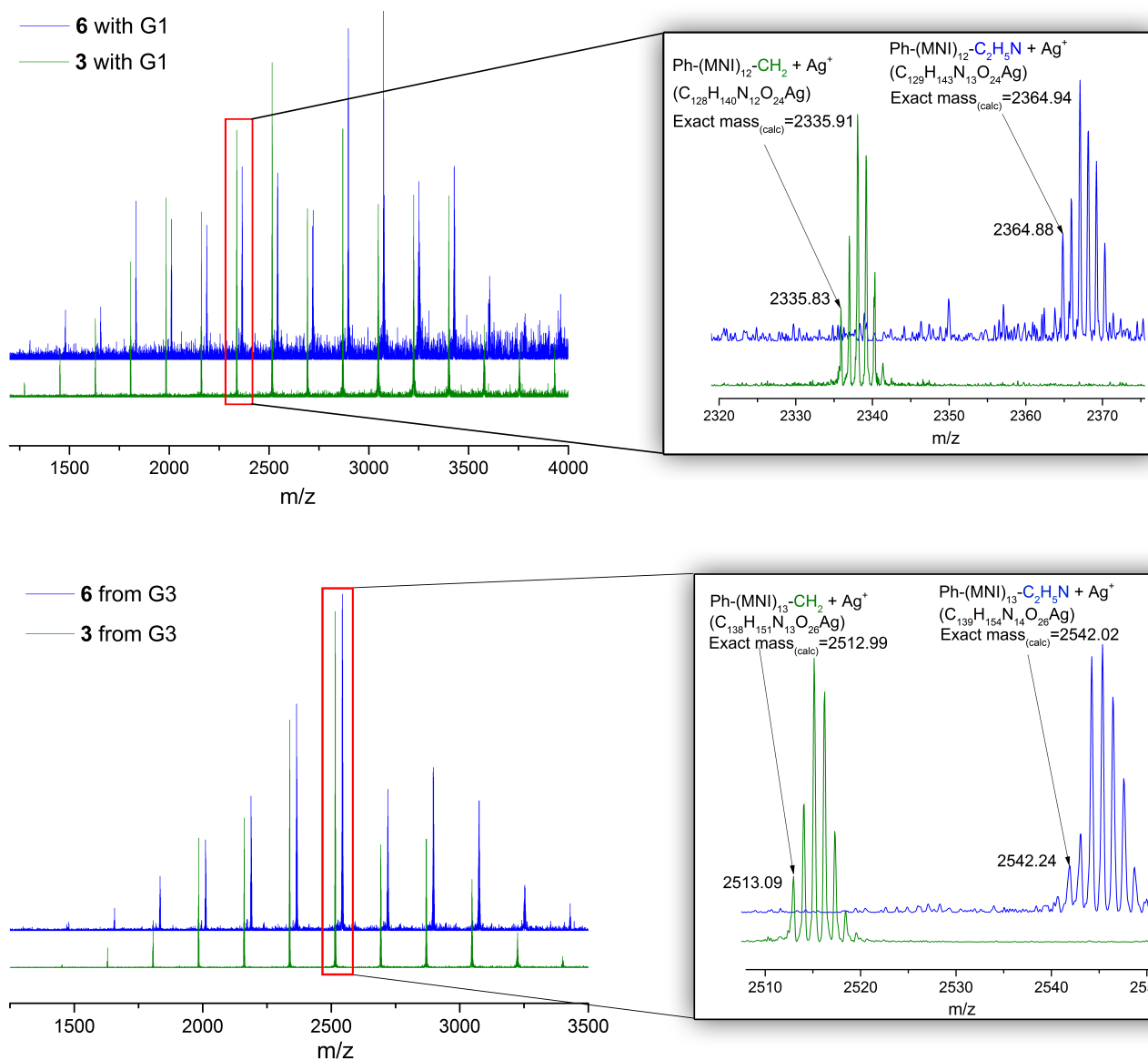
Figure 3b shows an unexpected coupling pattern observed for the carbene signal resulting from the reaction of **G1** and **1**. A 2D  $J$ -resolved  $^1\text{H}$ -NMR spectrum was therefore recorded to investigate the coupling pattern in more detail. The signal at 18.93 ppm involves at least two different nuclei, each giving a triplet coupling pattern (see supporting information). This complex  $^1\text{H}$ -NMR pattern for the ruthenium carbene peak can currently not be explained. Addition of ethyl vinyl ether, however, resulted in the formation of the Fischer carbene signal at 14.51 ppm. Similarly, addition of ethyl vinyl ether to the **G3** initiated polymer **4** resulted in the complete shift of the carbene signal at 14.28 ppm to a Fischer carbene signal at 13.63 ppm (see supporting information). Thus, in both cases, the ruthenium alkylidene is not very reactive towards norbornene derivatives but still forms a Fischer carbene with ethyl vinyl ether.

In order to investigate whether amine end-functional polymers could be obtained using sacrificial monomer **1**, polymerizations on a slightly larger scale (100 mg) were carried out. Amine end functionalized polymers were easily obtained from the polymers quenched with **1** by simple acidic hydrolysis using 10% HCl in acetone (Scheme 1).



**Scheme 1:** Schematic synthesis of amine end functionalized living ring opening metathesis polymers

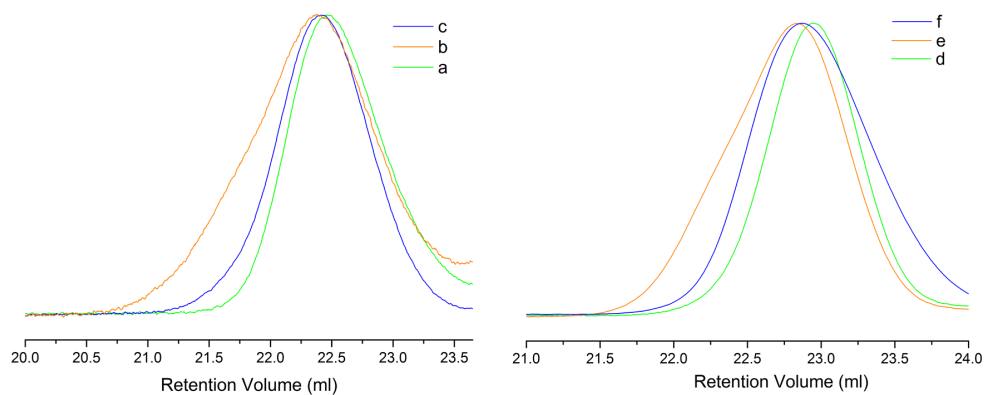
The amine end functionalization of the polymers was confirmed by FT-ICR mass spectrometry (Figure 4), GPC (Figure 5) and  $^1\text{H}$  NMR-spectroscopy. A complete shift of the molecular weight distribution was observed in the FTICR mass spectra of the amine end functionalized polymers compared to the reference polymer samples quenched with ethyl vinyl ether (Figure 4). Comparison of the mass spectra of the ethyl vinyl ether terminated polymer and the amine end functionalized polymer showed a difference of exactly 29 mass units, corresponding exactly to a terminal  $-\text{CH}_2\text{-NH}_2$  unit. It should be noted that incomplete end functionalization with lesser equivalents of **1** could easily be detected in the mass spectrum (See supporting information).



**Figure 4:** (top) FT-ICR mass spectra of polymer **3** synthesized from **G1** (reference sample), polymer **6** synthesized from **G1** (bottom) FT-ICR mass spectra of polymer **3** synthesized from **G3** (reference sample) and polymer **6** synthesized from **G3**. Insets show the isotopically resolved peaks which are in good agreement with the calculated exact mass of the polymers.

Figure 5 shows the GPC traces of the ethyl vinyl ether terminated reference samples (**3**), the polymers reacted with **1** (**5**) and the amine end-functionalized polymers after hydrolysis of the sacrificial block (**6**). The shifts in hydrodynamic volume between the individual samples are relatively small as expected for a slowly or non-propagating sacrificial monomer **1**. While only very small changes in GPC retention time can be observed for the polymers initiated with **G1**, larger shifts in retention time are observed for

the polymerizations initiated with **G3**. This further supports the assumption that initiator **G1** only reacts once with the sacrificial monomer **1** whereas **G3** slowly propagates monomer **1**.

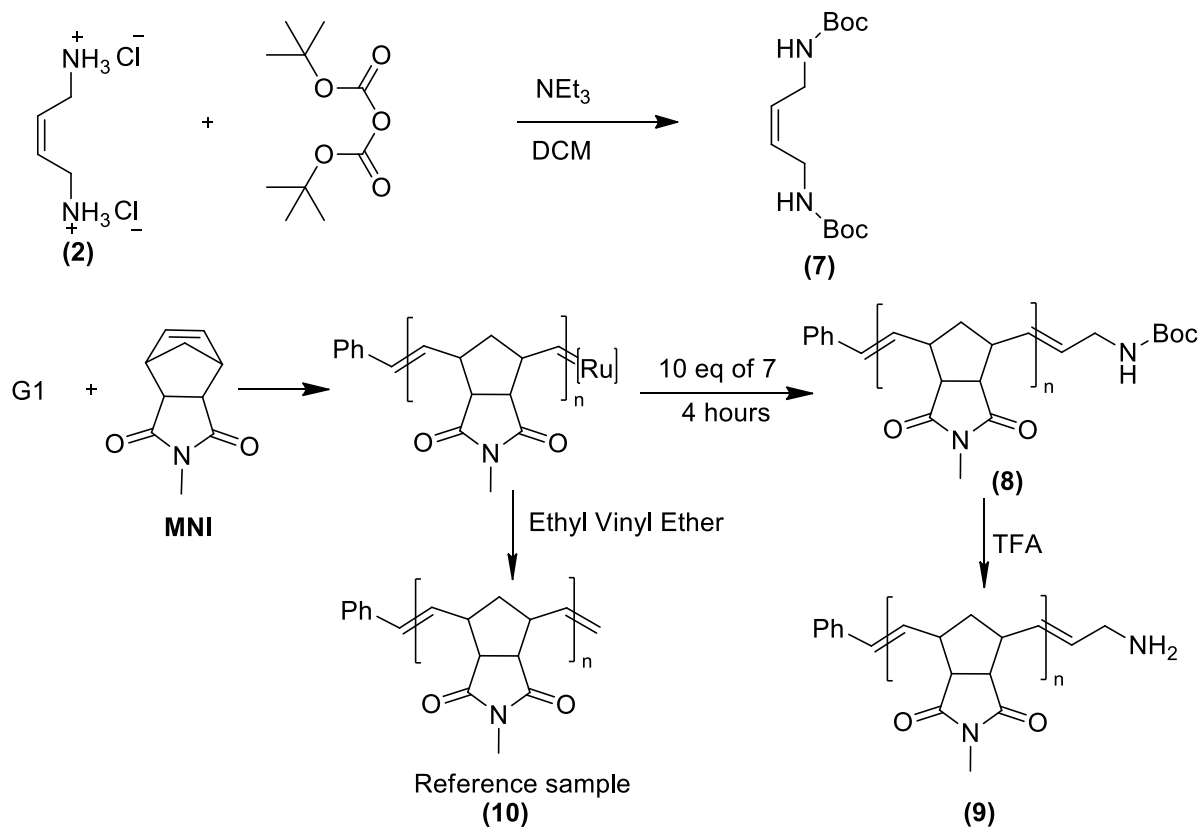


| Polymer          | GPC trace | $M_w$ | $M_n$ | PDI |
|------------------|-----------|-------|-------|-----|
| <b>3</b> from G1 | a         | 4788  | 3827  | 1.3 |
| <b>5</b> from G1 | b         | 5763  | 3848  | 1.5 |
| <b>6</b> from G1 | c         | 5004  | 3903  | 1.3 |

| Polymer          | GPC trace | $M_w$ | $M_n$ | PDI |
|------------------|-----------|-------|-------|-----|
| <b>3</b> from G3 | d         | 4302  | 3538  | 1.2 |
| <b>5</b> from G3 | e         | 5891  | 3870  | 1.5 |
| <b>6</b> from G3 | f         | 5086  | 4098  | 1.2 |

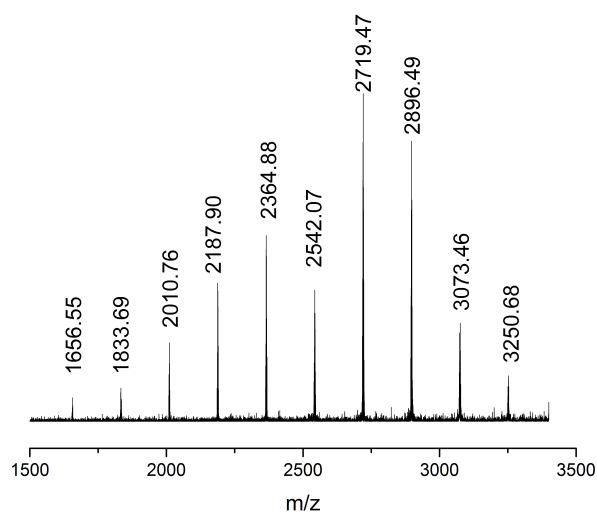
**Figure 5:** GPC studies of reference polymer sample versus intermediate polymer and amine end functionalized polymer (see Scheme 1).

In all the polymerization experiments, the degree of polymerization was kept very low ( $DP_n$  ca. 10) due to the mass limitation of the MALDI FT-ICR mass spectrometer, which is only sensitive up to a molecular weight of ca.  $4000 \text{ g mol}^{-1}$  and in order to be able to detect the end group in  $^1\text{H}$  NMR studies.  $^1\text{H}$ -NMR studies did, however, allow us to observe successful end functionalization of even larger polymers having a molecular weight of up to 20kDa. For these larger polymers the ruthenium carbene peak was found to undergo similar deactivation upon the addition of **1** proving that **1** can be effective for the end capping of much larger polymers as well.



**Scheme 2:** Synthesis and terminal cross metathesis of symmetrical protected diamine

In order to compare this new sacrificial synthesis method to the terminal cross metathesis end-functionalization method, a new chain transfer agent **7** was synthesized (Scheme 2, top). **MNI** was reacted with **G1** for 45 minutes, allowing complete consumption of the monomer and then 10 equivalents of **7** were added. The terminal cross metathesis required ca. 4 hours for the complete conversion to the protected amine end functionalized polymer which was monitored by the change in integration value of the boc protons as compared to the terminal phenyl group in  $^1\text{H-NMR}$  spectroscopy of the precipitated polymers. The amine functionality at the polymer end was confirmed by FT-ICR MS and the mass of each peak was 29 units greater than that of the reference sample polymer **10** terminated by ethyl vinyl ether. The potential disadvantage of this method is that the ruthenium alkylidene is active even after the addition of the transfer agent which could give rise to unwanted metathesis between different olefinic bonds depending on the monomer structure.



**Figure 8:** Mass spectrum of amine mono end functionalized polymer **9** resulting from terminal cross metathesis with transfer agent **7**.

## Conclusion

A fast and efficient way for the synthesis of amine end functionalized ROMP polymers has been developed. The newly synthesized cyclic phosphoramidate sacrificial monomer reacts extremely fast with the Grubbs 1st and 3rd generation initiators but propagates very slowly. This kinetic behavior is the ideal case for a sacrificial monomer which almost resembles the kinetics of a terminating agent. Mass spectrometry analysis of the amine end-functional polymers only showed functional polymer and no traces of non-functionalized material. We compared this new sacrificial monomer to a Boc protected amine chain transfer agent which was used in a terminal cross metathesis. The terminal cross metathesis reaction was not as fast as the phosphoramidate sacrificial monomer but end-functionality efficiency determined by mass spectrometry also showed the amine functional polymer only. The amine end functionalized polymers were derivatized further with excellent degree of functionalization (> 95%, see supporting information).

Both end-functionalization agents can be synthesized in a straightforward manner. In cases where secondary metathesis reactions need to be minimized after the polymer end-functionalization, the new sacrificial phosphoramidate monomer has the advantage of a fast macroinitiation forming a relatively unreactive stable carbene.

The polymers obtained have narrow polydispersities typical of the Grubbs type ruthenium initiators of the first and third generation. The new amine end group functionalization method reported here opens a synthetic path to many possible complex macromolecular architectures and polymer conjugates.

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**Supporting Information Available.** Details of the crystal structure, 2D J-resolved  $^1\text{H}$  NMR spectrum,  $^1\text{H}$  NMR spectra of the Fischer carbenes, MALDI FT-ICR spectrum of the incomplete end functionalized polymer and  $^1\text{H}$  NMR spectrum of further functionalization of the amino end functionalized polymer. This information is available free of charge via the Internet at <http://pubs.acs.org/>.



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