# One-Step Ring Opening Metathesis Block-Like Copolymers and their Compositional Analysis by a Novel Retardation Technique

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***Abstract:*** *Using a one-step synthetic route for block copolymers avoids the repeated addition of monomers to the polymerization mixture, which can easily lead to contamination and, therefore, to the unwanted termination of chain growth. For this purpose, monomers (**M1–M5**) with different steric hindrances and different propagation rates are explored. Copolymerization of **M1** (propagating rapidly) with **M2** (propagating slowly), **M1** with **M3** (propagating extremely slowly) and **M4** (propagating rapidly) with **M5** (propagating slowly) yielded diblock-like copolymers using Grubbs' first (**G1**) or third generation catalyst (**G3**). The monomer consumption was followed by $^1H$ NMR spectroscopy, which revealed vastly different reactivity ratios for **M1** and **M2**. In the case of **M1** and **M3**, we observed the highest difference in reactivity ratios ($r_1 = 324$ and $r_2 = 0.003$) ever reported for a copolymerization method. A triblock-like copolymer was also synthesized using **G3** by first allowing the consumption of the mixture of **M1** and **M2** and then adding **M1** again. In addition, in order to measure the fast reaction rates of the **G3** catalyst with **M1**, we report a novel retardation technique based on an unusual reversible **G3** Fischer-carbene to **G3** benzylidene/alkylidene transformation.*

$C$ontrolling the monomer sequence remains one of the key challenges in polymer synthesis.[1] It can allow the synthesis of block copolymers in just one step using a mixture of monomers. A one-step block copolymer synthesis is very attractive because it not only saves time but also avoids the repeated addition of monomers to the polymerization mixture that can easily lead to contamination and, therefore, to the unwanted termination of chain growth. However, the limitation in controlling the sequence is often the result of low differences in reactivity ratios of the monomers. The reactivity ratios can be tuned by the steric hindrance[2] or electronics[3] of the monomers.

Block copolymers have attracted the attention of researchers due to their ability to form ordered structures by self-assembly which cannot be achieved by either of the block components alone.[4–6] The most common current methods of block copolymer synthesis are based on multistep strategies, such as the repeated monomer addition, polymerization from macroinitiators and the chain-end coupling of polymers.[7–14]

Recently, several reports of one-step block-like copolymer syntheses by anionic ring opening polymerization have been described. Williams and co-workers have developed a dinuclear zinc catalyst which can be switched from copolymerization to homopolymerization, thereby yielding block-like copolymers from mixtures of different monomers such as anhydrides, epoxides, lactones and carbon dioxide.[15–17] Wurm's group reported the synthesis of block-like copolymers from the mixture of epoxides and aziridines with different reactivities depending upon the electron-withdrawing effect of a sulfonamide substituent on the aziridines.[3,18] An alternative way to prepare block copolymers in one pot is the simultaneous polymerization from bifunctional initiators using different propagation mechanisms.[19–25]

An interesting "fire and forget" approach based on anionic polymerization for one-shot block-like terpolymer synthesis from the mixture of butadiene, styrene, and diphenylethylene has recently been reported by Hutchings and co-workers.[26]

A well-known one-step method for block-like copolymer synthesis from styrene and maleic anhydride is based on nitroxide-mediated polymerization.[27] The gradient compositional profile is moderately sharp, as almost 27 % of styrene is consumed at approximately 93 % consumption of maleic anhydride.

The synthesis of block copolymers in one-step via ring opening metathesis polymerization (ROMP) is of great importance because this polymerization technique has a high tolerance towards many functional groups and $O_2$.[28] Other very important features of this method are the ability to form living polymers under mild reaction conditions and high polymerization rates especially with strained cyclic olefins. Grubbs' first (**G1,** dichloro(benzylidene)bis(tricyclohexylphosphine) ruthenium(II)) and third (**G3,** dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine) ruthenium(II)) generation metathesis catalysts are most frequently employed in polymer synthesis due to their high initiation to propagation rate ratios which ensure narrow molecular weight dispersities.[29,30] There are numerous reports of ROMP-based block copolymer syntheses by sequential monomer addition using ruthenium-[31–33] and molybdenum-based metathesis catalysts.[34–38] However, reports on one-step block-like copolymer syntheses

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by ROMP are scarce. The copolymerization of monomers of different reactivities, that is, an *exo*-norbornene capped polystyrene macromonomer (*exo*-PS) and an *endo*-norbornene capped polylactide macromonomer (*endo*-PLA) by ROMP has been reported.[2] However, the reported polymer did not show a sharp gradient compositional profile (with the reactivity ratios: $r_1 = 5$ and $r_2 = 0.19$ for *exo*-PS/*endo*-PLA), which is important if block copolymer microphase separation is aimed for. Choi's group reported the synthesis of ROMP block-like copolymers from the mixture of different reactivity monomers, such as *exo*-norbornene derivatives/*endo*-tricyclo-[4.2.2.0]deca-3,9-diene derivatives and cyclooctatetraene (COT)/[2.2]paracyclophane-1,9-diene.[39–42] Although this is an elegant approach, the synthesis of paracyclophanedienes is very challenging. Moreover, block-like copolymers obtained from COT as a comonomer are unstable in air due to the susceptibility of the polyacetylene block towards oxidation.

Subsequently, there is a critical need for the development of monomers with highly different reactivity and easy synthetic accessibility, which yield stable block copolymers. Herein, we present monomers, **M1** (*N*-methyl-*exo*-norbornene carboximide), **M2** (*N*-methyl-1-methyl-7-oxa-*exo*-norbornene carboximide), **M3** (*N*-methyl-1-ethyl-7-oxa-*exo*-norbornene carboximide), **M4** (*N*-methyl-7-oxa-*exo*-norbornene carboxamide) and **M5** (*N*-methyl-1-hydroxymethyl-7-oxa-*exo*-norbornene carboxamide) with different steric demands (Scheme 1) exhibiting vastly different propagation kinetics. These sterically tunable monomers are easily synthesized in just one-step using commercially available starting materials.
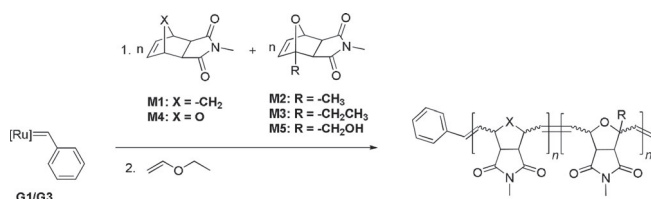
**Scheme 1.** One-step diblock like copolymer synthesis from monomers of different reactivity with metathesis catalyst **G1** or **G3**.

At first, **G1** (1 equiv) was reacted with a [D₂]dichloromethane solution of both monomers **M1** (15 equiv) and **M2** (15 equiv) and the reaction was followed by ¹H NMR spectroscopy. Within the first 50 min of the reaction, monomer **M1** was consumed almost completely (97%), while monomer **M2** had reacted only slightly (17%). The reaction was followed by ¹H NMR spectroscopy until monomer **M2** was 92% consumed (within 3200 min, Figure 1 a, top) to give a diblock-like copolymer **P1–G1** (M$_n$ (GPC, CHCl₃) = 6.5 kDa, Đ = 1.22, Figure S2, Supporting Information).

The high reactivity difference between the two monomers during copolymerization was also confirmed by the reactivity ratios ($r_1 = 19$ and $r_2 = 0.052$ for **M1/M2**, Table S1) calculated by ideal integrated equation.[43] The microstructure of the block-like copolymer of **M1** and **M2** was visualized by using the reactivity ratios (Figure 1a, bottom). The observed reactivity difference between monomers **M1** and **M2** is
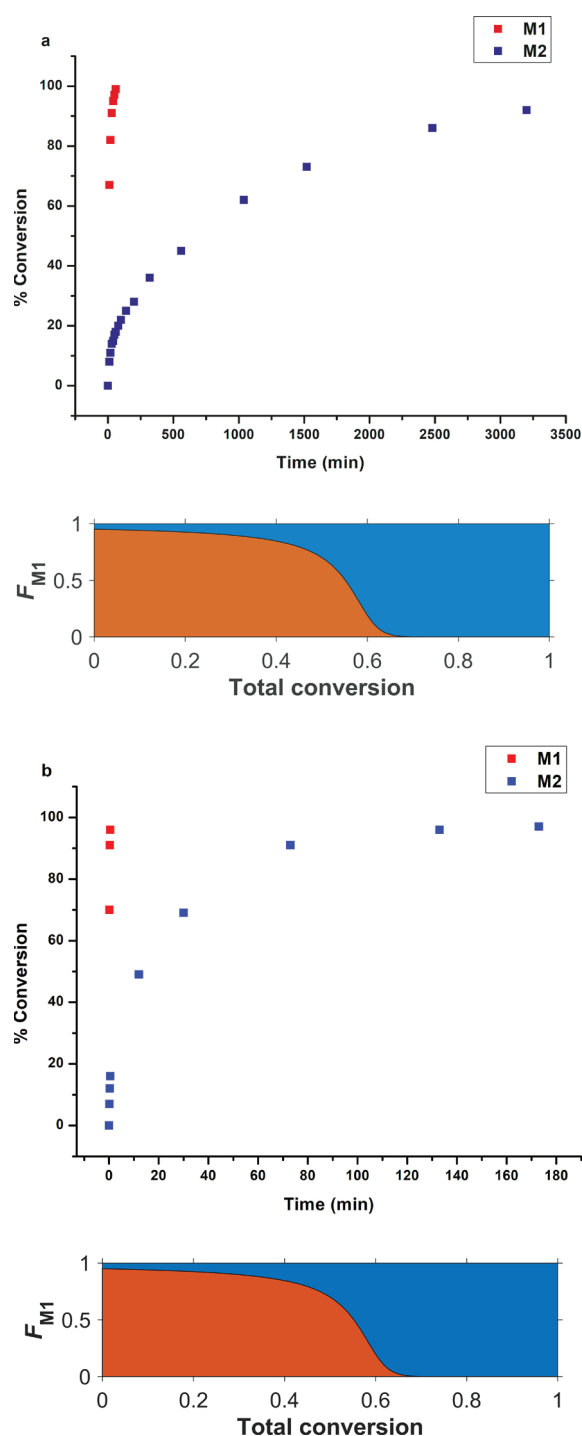
**Figure 1.** Conversion of a mixture of monomers **M1** (15 equiv) and **M2** (15 equiv) when reacted in one step with: (a, top) **G1** (9 mg, 1 equiv) (Figure S1, Supporting Information) and (b, top) **G3** (9 mg, 1 equiv), both in CD₂Cl₂ at rt, observed by ¹H NMR spectroscopy (Figure S3, Supporting Information). Mean composition of the polymer chains (F) versus total conversion determined by ideal integrated fit showing monomer distribution of a diblock-like copolymer based on the reactivity ratios of **M1** (red) and **M2** (blue) with: (a, bottom) **G1** and (b, bottom) **G3**.

attributed to the different steric demand of the two monomers when coordinated to the propagating ruthenium carbene complex of **G1**. As shown before,[44,45] small substituents on

the bridge head position of norbornene derivatives can have a large effect as far as their propagation rate in ROMP is concerned. However, these types of norbornene derivatives have never been investigated for the synthesis of one-step block-like copolymers.

To further shorten the polymerization time, we employed initiator **G3** in an otherwise identical copolymerization setup (see above) followed by $^1$H NMR spectroscopy. When **G3** (1 equiv) was reacted with a [D$_2$]dichloromethane solution of **M1** (15 equiv) and **M2** (15 equiv), very similar reactivity ratios ($r_1 = 19$ and $r_2 = 0.052$ for **M1**/**M2**, Table S1) to **G1** (see above) were observed. These reactivity ratios were used to visualize the microstructure of the block-like copolymer of **M1** and **M2** (Figure 1 b, bottom). However, the diblock-like copolymer **P1–G3** (M$_n$ (GPC, CHCl$_3$) = 5.4 kDa, Đ = 1.12, Figure S4, Supporting Information) was formed in a much shorter reaction time (173 min, Figure 1 b, top). Due to the high reactivity of the **G3** complex, the reaction of **M1** with **G3** was too fast to be time-resolved by $^1$H NMR spectroscopy. Therefore, in order to quantify the incorporation of **M1** into the polymer chain, four identical copolymerization reactions were run (see above) and each terminated with 0.1 mL (103 equiv) of ethyl vinyl ether (EVE) after 10 s (**M1**: 70 %, **M2**: 7 % consumed), 20 s, (**M1**: 91 %, **M2**: 12 % consumed) 30 s (**M1**: 96 %, **M2**: 16 % consumed) and 173 min (**M1**: 100 %, **M2**: 97 % consumed). Nonetheless, due to the extremely rapid consumption of the monomer **M1,** the data points obtained by this method could be erroneous because of the very short time gaps during sampling, on the order of seconds.

An alternative to rapidly terminating samples taken from the reaction is the slowing down of the reaction without affecting the relative rates of propagation. One such method for olefin metathesis reactions employing the **G3** complex is the addition of excess pyridine.[46,47]

We recently showed that a cross metathesis reaction, typically not observed intermolecularly, can proceed rapidly when an intramolecular pathway is available.[45,48] These results prompted us to investigate whether the cross-metathesis reaction between electronically very different olefins, that is, the conversion of a Fischer-carbene to a benzylidene/ alkylidene, could be similarly accelerated via an intramolecular process. Indeed, this reaction was achieved and found to be reversible in nature (Figure S5–S8, Supporting Information). Inspired by this result, **G3** (1 equiv) was reacted with commercially available **C1** (1 equiv), a 1:44 (**G3** benzylidene (19.07 ppm):**G3** Fischer carbene (13.54 ppm)) ratio was observed after 600 min (Figure S8, Supporting Information). This reaction system can slow down the reaction of **G3** with sterically unhindered monomers such as **M1** by liberating very small amounts of active **G3** benzylidene catalyst via an intramolecular equilibrium reaction of the **G3** Fischer carbene with the styrenic double bond (equilibrium of 1:44 alkylidene:Fischer carbene).

In order to prove the above hypothesis, we reacted **G3** (1 equiv) with **C1** (2 equiv) in CD$_2$Cl$_2$ for 180 min and then added a solution of **M1** (15 equiv) and **M2** (15 equiv) in CD$_2$Cl$_2$ to this reaction mixture (Scheme 2). This reaction was followed by $^1$H NMR spectroscopy for almost 2068 min
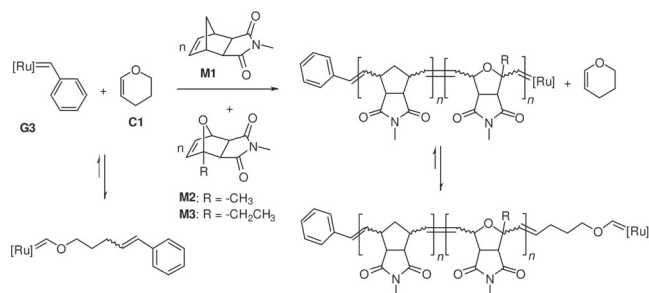


**Scheme 2.** Slowing down the reaction of **G3** with monomers **M1** and **M2** or **M3** using **C1**.
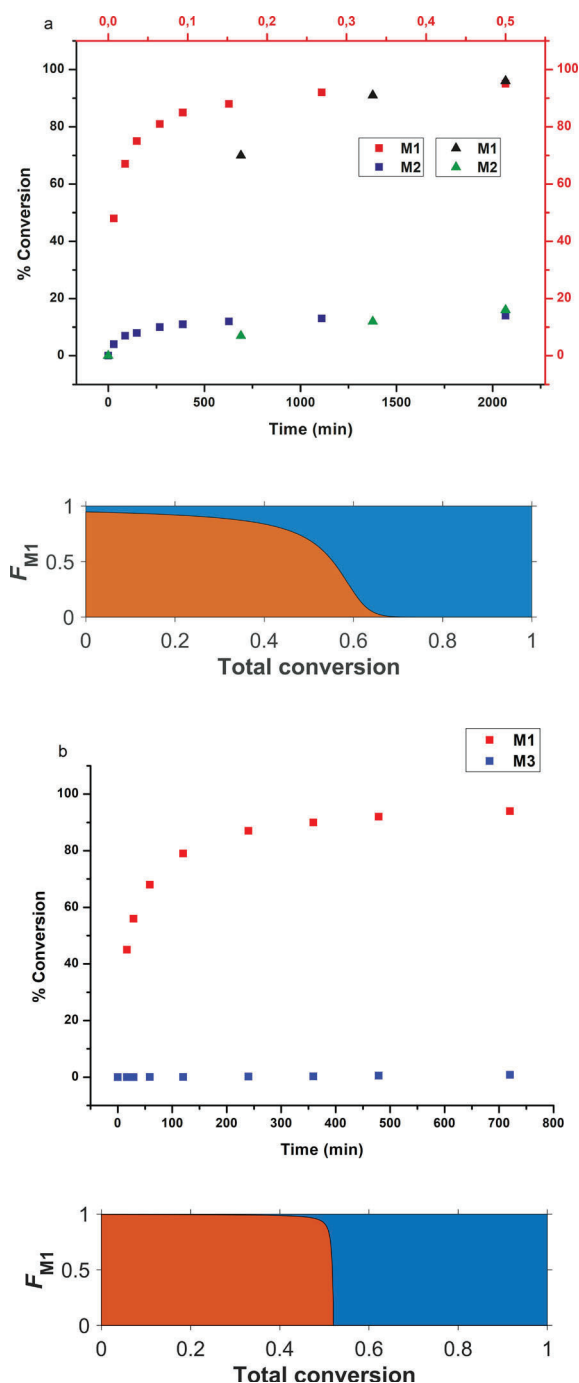
(Figure S10, Supporting Information). The reaction of **G3** with **M1** was slowed down considerably. The time taken to consume **M1** by **G3** when pyran (**C1**) is absent was 30 s. This was increased to 2068 min upon the addition of pyran (**C1**) (Figure 2 a, top). The reaction of **M2** with **G3** was slowed down in the same manner, as the selectivity of monomers (**M1** and **M2**) incorporated is not altered by the addition of **C1**. Additionally, very similar reactivity ratios ($r_1 = 18$ and $r_2 = 0.056$ for **M1**/**M2**, Table S1) were observed as in the case without the addition of **C1**. The microstructure of the block-like copolymer of **M1** and **M2** was visualized by using these reactivity ratios (Figure 2 a, bottom).

Subsequently, different molecular weight diblock-like copolymers **P2-G3** (M$_n$ (GPC, CHCl$_3$) = 12.9 kDa, Đ = 1.09, Figure S4, Supporting Information) and **P3-G3** (M$_n$ (GPC, CHCl$_3$) = 24.7 kDa, Đ = 1.08, Figure S4, Supporting Information) were synthesized by fixing the amount of **G3** as 1 equiv while varying the amount of both monomers **M1** and **M2** from 30 equiv to 60 equiv in 360 and 720 min, respectively. Next, **G3** (1 equiv) was reacted with a dichloromethane solution of **M1** (15 equiv) and **M2** (15 equiv) for 180 min in order to ensure the complete consumption of both monomers. Then, a solution of **M1** (15 equiv) in dichloromethane was added to this reaction mixture and the polymerization was continued for the next 10 min. to give a triblock-like copolymer **P4-G3** (M$_n$ (GPC, CHCl$_3$) = 10.1 kDa, Đ = 1.11, Figure S4, Supporting Information).

In order to synthesize a copolymer with an even sharper gradient compositional profile, a more sterically hindered monomer **M3** was synthesized. **G3** (1 equiv) was allowed to react with **C1** (2 equiv) in CD$_2$Cl$_2$ for 180 min. An equimolar (15 equiv) solution of **M1** and **M3** in CD$_2$Cl$_2$ was added to this reaction mixture (Scheme 2) and the reaction was followed by $^1$H NMR spectroscopy (Figure S11, Supporting Information). After 720 min, monomer **M1** was consumed almost completely (94 %) while monomer **M3** had reacted negligibly (0.86 %) (Figure 2 b, top).

We observed the highest difference in reactivity ratios ($r_1 = 324$ and $r_2 = 0.003$ for **M1**/**M3**, Table S1) reported to date for a copolymerization method. These reactivity ratios were used to visualize the microstructure of the block like copolymer of **M1** and **M3** (Figure 2 b, bottom).

In order to ensure the complete consumption of both the monomers **M1** and **M3**, a separate reaction was run without the addition of retardant **C1**. The reaction was followed by

**Figure 2.** Conversion of monomers: (a, top) **M1** (15 equiv) and **M2** (15 equiv) (Figure S10, Supporting Information) and (b, top) **M1** (15 equiv) and **M3** (15 equiv) (Figure S11, Supporting Information) when reacted in one step with the mixture of **G3** (9 mg, 1 equiv) and **C1** (2 equiv) (square) or **G3** (9 mg, 1 equiv) (triangle), zoomed in view of Figure 1 b, top, both in CD$_2$Cl$_2$ at rt, observed by $^1$H NMR spectroscopy. Mean composition of the polymer chains (F) versus total conversion determined by ideal integrated fit showing monomer distribution of a diblock like copolymer based on the reactivity ratios of: (a, bottom) **M1** (red) and **M2** (blue) and (b, bottom) **M1** (red) and **M3** (blue) with the mixture of **G3** and **C1**.

$^1$H NMR spectroscopy until monomer **M3** was 88 % consumed (within 420 min, Figure S12, Supporting Information)

to give a diblock-like copolymer **P5-G3** (M$_n$ (GPC, CHCl$_3$) = 7.1 kDa, Đ = 1.09, Figure S13, Supporting Information).

To further broaden the scope of this synthetic strategy, a solution of monomers **M4** (15 equiv) and **M5** (15 equiv) in dichloromethane was mixed with **G3** (1 equiv) and the reaction was followed by $^1$H NMR spectroscopy (Figure S14, Supporting Information). This reaction yielded a diblock-like copolymer **P6-G3** (M$_n$ (GPC, CHCl$_3$) = 1.6 kDa, Đ = 1.88, Figure S15, Supporting Information) due to the high difference in reactivity ratios of the monomers ($r_1 = 14$ and $r_2 = 0.069$ for **M4**/**M5**, Table S1).

Our next target was to see the phase separation in the synthesized block-like copolymers. Unfortunately, **P1-G3** and **P5-G3** did not micro phase separate probably due to the similar structural features of both blocks. Thus, a structurally very different monomer **M6** (*N*-ferrocenylcarbonyloxyethyl-*exo*-norbornene carboxamide, Supporting Information) with similarly low steric hindrance as **M1** was synthesized. A dichloromethane solution of **M6** (30 equiv) and either **M2** (30 equiv) or **M3** (30 equiv) was reacted with **G3** (1 equiv) to give diblock-like copolymers **P7-G3** (from **M2**: M$_n$ (GPC, CHCl$_3$) = 16.4 kDa, Đ = 1.10, Figure S16a, Supporting Information) and **P8-G3** (from **M3**: M$_n$ (GPC, CHCl$_3$) = 16 kDa, Đ = 1.11, Figure S16b, Supporting Information) in 360 min (**M2**) or 840 min (**M3**). TEM images of **P7-G3** and **P8-G3** showed sphere like structures (Figure S17a and S17b, Supporting Information).

To conclude, we have developed a convenient method for one-step block copolymer synthesis by ROMP using sterically tunable monomers. The reaction of **G1** with monomers **M1** and **M2** exhibiting different reactivity due to different steric demand, yielded a diblock-like copolymer with narrow dispersity. The reaction time was very long (3200 min) due to the low reactivity of **G1**. To overcome the long reaction times, we used the highly active initiator **G3** in an otherwise identical copolymerization setup. While the polymerization was faster using **G3** (173 min), the copolymerization parameters were similar to those obtained for **G1**. A more sterically hindered monomer **M3** in combination with **M1** was reacted with **G3** to give a copolymer showing the sharpest gradient compositional profile reported for a one-pot copolymerization method to date. The scope of this synthetic strategy was further broadened by synthesizing a diblock-like copolymer from the mixture of monomers **M4** and **M5** where one of the polymer blocks carried a functional hydroxy group in each repeat unit. Using a monomer carrying a ferrocene substituent (**M6**) in combination with either monomer **M2** or **M3** yielded diblock-like copolymers that could be imaged using transmission electron microscopy. Addition of **M1** after the copolymerization of a **M1**/**M2** mixture yielded a triblock-like copolymer, thereby illustrating the simplicity of the procedure. A new retardation method for ROMP, based on an unusual reversible carbene transformation, allowed the kinetic evaluation of even the fastest propagating monomers by $^1$H NMR spectroscopy. This novel technique is mechanistically unique and provides a general platform to analyze the kinetics of substrates reacting rapidly with Grubbs' initiators.

### Conflict of interest

The authors declare no conflict of interest.

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