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Communication

Branched polymers via ROMP of termimers[1]

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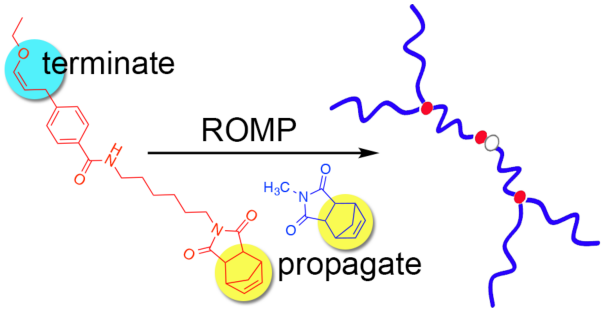
Today's olefin metathesis catalysts show high reactivity, selectivity and functional group tolerance and allow the design of new syntheses of precisely functionalised polymers. Here we investigate the synthesis of a new end-capping reagent allowing the introduction of a highly reactive activated ester end-group at the polymer chain end as well as its prefunctionalization to directly introduce functional moieties. The versatility of this new end-capping reagent is demonstrated by utilizing it to synthesize a so-called termimer (a monomer with termination capabilities). Copolymerization of a norbornene derivative with the termimer lead to hyperbranched ROMP polymers as proven by GPC and MALDI-ToF mass spectrometry.

FIGURE FOR ToC_ABSTRACT



1. Introduction

Over the past two decades many new methods have been developed to introduce functionality during ruthenium catalyzed living ring-opening metathesis polymerization (ROMP). [2,3,4,5] The ruthenium carbene complexes developed by Grubbs et al. show a high tolerance towards polar functional groups. The preparation of functional polymers can therefore easily be achieved polymerizing functional monomers. Another approach is the synthesis of linear end functional polymers carrying exactly one functional group at the end of the chain. The most common method to achieve this aim uses substituted vinyl ethers that already carry the desired end group functionality.[6,7,8,9] Reaction with the propagating ruthenium carbene complex yields a Fischer carbene complex and an end functionalized polymer. Nonetheless, the observed degrees of end-functionality vary substantially depending on the organic moiety transferred and the E/Z ratio of the vinyl ether substrate. To place exactly one functional group onto the chain end of a polymer, a reactive site has to be transformed into the desired chemical moiety. In the living ring-opening metathesis polymerization employing Grubbs' ruthenium carbene complexes the reactive site is the propagating catalyst species, i.e. the ruthenium alkylidene complex. However, when utilizing ruthenium carbene complexes, their high tolerance towards oxygen, water and many polar functional groups impede the desired transformation into a functional end group since the number of potential reactants other than olefins is limited. Thus, what is generally considered one of the great advantages of ruthenium catalyzed olefin metathesis is a slight disadvantage in this particular case.

Nonetheless, several methods have been recently reported by our group that allow the mono end-functionalization of ROMP polymers with specific functional groups such as alcohols,[10,11] aldehydes and carboxylic acids,[12] thiols[13] and amines.[14] By end-functionalizing living ROMP polymers using a cyclohexene derivative, a catalytic living ring opening metathesis process could even be achieved.[15] Synthesizing these end-functional polymers becomes especially useful when using them as macroinitiators for multiblock copolymer

syntheses, building blocks for model networks or as macromonomers or pre-polymers to reach very high molecular weights in subsequent polymerizations.

Here, we describe the synthesis of a functionalizable *cis*-vinyl ether end-capping reagent that allows the introduction of a highly reactive activated ester end-group onto the polymer chain end. Activated ester groups in polymers were previously shown to be excellent functionalities for post-polymerization functionalization.[16] To exemplify the versatility of such an end-capping reagent, we used it to build a so-called termimer, a reagent that can propagate (like a monomer) and at the same time terminate a polymerization reaction. Using such a reagent in the presence of a regular (linear) monomer opens a convergent synthetic route to branched ROMP polymers in which the olefin metathesis reaction is used for propagation and branching. To the best of our knowledge this is the first report of branched ROMP polymers exclusively prepared by olefin metathesis.

2. Experimental Section

2.1. Materials

p-Bromomethyl benzoic acid, *N*-hydroxysuccinimide, *N,N'*-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, palladium-tetrakis(triphenylphosphine), tetraethylammonium chloride, *cis*-tributyl-(2-ethoxyethenyl)stannane, ethyl vinyl ether, vinylacetate, hexamethylenediamine, potassium carbonate, benzylidene-bis(tricyclohexylphosphine)dichlororuthenium **C1** and dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene) bis(3-bromopyridine)ruthenium **C3** were purchased from Sigma-Aldrich and used without further purification. Triethylamine was purchased from Acros Chemicals, distilled from calcium hydride and stored over potassium hydroxide. Succinimidyl 4-(bromomethyl)benzoate **3**,[17] exo-*N*-cyclohexylnorbornene imide **5**

(CyNI) [18] and exo-*N*-methylnorbornene imide **6** (MNI)[19] were synthesized as reported previously. Chemical structures of compounds **5**,**6** and **C3** are shown in the supporting information section. *cis*-Tributyl-(2-ethoxyethenyl)stannane was also synthesized according to a published procedure.[20] This gave a crude material with a 75% *cis* and 25% *trans* content before chromatographic purification. The cis/trans mixture was used for kinetic measurements (see Figure 2).

2.2. Instrumentation

ESI-MS analysis for synthesised compounds was carried out on a Bruker 4.7T BioAPEX II. MALDI-ToF-MS analysis 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 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).

2.3. Syntheses

Succinimidyl 4-(bromomethyl)benzoate 1:

1.00 g *p*-bromomethyl benzoic acid (4.7 mmol, 1 eq) and 0.54 g *N*-hydroxysuccinimide (4.7 mmol, 1 eq) were dissolved in 15 mL DMF. A solution of 0.96 g *N,N'*-dicyclohexylcarbodiimide (4.7 mmol, 1 eq) and 0.06 g 4-dimethylaminopyridine (0.49 mmol, 0.1 eq) in 5 mL DMF was added and the reaction mixture was stirred for 2 hours at room temperature. The colorless precipitate was filtered off and the filtrate was concentrated under

vacuum. Ethyl acetate was added to the residue and filtered hot. The organic layer was washed with sodium bicarbonate (saturated solution) and brine (saturated solution), dried over magnesium sulfate and concentrated under vacuum to give 1.24 g succinimidyl 4-(bromomethyl)benzoate **1** (3.7 mmol, 78 % yield).

^{1}H NMR (300 MHz, $CDCl_3$), ppm: δ 8.12 (d, J=8.7 Hz, 2H), 7.54 (d, J=8.7 Hz, 2H), 4.52 (s, 2H), 2.92 (s, 4H).

cis-Succinimidyl 4-(3-ethoxyallyl)benzoate 2:

Under an argon atmosphere, 350 mg succinimidyl 4-(bromomethyl)benzoate **1** (1.12 mmol, 1 eq), 134 mg palladium-tetrakis(triphenylphosphine) (0.12 mmol, 0.1 eq) and 191 mg tetraethylammonium chloride (1.15 mmol, 1 eq) were dissolved in 10 mL degassed DMF and heated to 110°C. 0.5 g *cis*-tributyl-(2-ethoxyethenyl)stannane (1.38 mmol, 1.2 eq) was added and the solution was stirred for 8 hours before cooling to room temperature. The reaction mixture was poured onto ice and extracted with methylene chloride. The combined organic layer was washed with water and dried over magnesium sulfate. Solvent was evaporated under vacuum and the crude product was purified by column chromatography (6:4 / hexane:ethyl acetate) to obtain 217 mg of *cis*-succinimidyl 4-(3-ethoxyallyl)benzoate **2** (0.72 mmol, 64 %).

^{1}H NMR (300 MHz, $CDCl_3$), ppm: δ 8.03 (d, J=8.3 Hz, 2H), 7.40(d, J=8.3 Hz, 2H), 6.15 (dt, J=6.1, 1.5 Hz, 1H), 4.56 (td, J=7.6, 6.1 Hz, 1H), 3.85 (q, J=7.1 Hz, 2H), 3.51 (d, 7.8 Hz, 2H), 2.87 (s, 4H), 1.26 (t, J=7.1 Hz, 3H).

Amino-functionalized norbornene monomer 3:

A mixture of exo-norbornene-2,3-dicarboxanhydride (2.0 g, 12.2 mmol) and hexamethylenediamine (7.0 g, 60.2 mmol) was heated to 190°C for 2h. The mixture was allowed to cool to room temperature. Further water was removed in a Dean-Stark apparatus

using toluene (50 mL) until a clear solution was obtained. The Toluene was removed by distillation and the crude product was redissolved in methylene chloride. The organic layer was extracted with water and brine. The organic layer was dried over magnesium sulfate and concentrated under vacuum to give 2.85 g (yield 91%) of the amino-functionalized norbornene monomer **3** as a colourless wax.

^{1}H NMR (300 MHz, $CDCl_3$), ppm: δ 6.27 (t, J=1.7, 2H), 3.45 (t, J=7.5, 2H), 3.26 (m, 2H), 2.85-2.50 (m, 4H), 2.02 (s, 2H), 1.63-1.16 (m, 10H).

This product was used without further purification in the synthesis of termimer **4**.

Termimer 4:

To a solution of aminofunctionalized norbornene monomer **3** (207 mg, 0.79 mmol) in anhydrous methylene chloride (5.0 mL), triethylamine (0.05 mL, 0.36 mmol) and subsequently *cis*-succinimidyl 4-(3-ethoxyallyl)benzoate **2** (239 mg, 0.79 mmol) were added. The reaction was stirred for 2 hours before concentrating it under vacuum. The crude product was purified by column chromatography (hexane : ethyl acetate, gradient from 9:1 to 1:1) to obtain 290 mg of termimer **4** (yield 82%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$), ppm: δ 7.68 (d, J=8.5 Hz, 2H), 7.26 (d, J=7.9 Hz, 2H), 6.35 (t, J=5.5, 1H), 6.27 (t, J=1.7 Hz, 2H), 6.07 (dt, J= 6.0, 1.5 Hz, 1H), 4.52 (td, J=7.5, 6.2 Hz, 1H), 3.83 (q, J=7.0 Hz, 2H), 3.50-3.35 (m, 6H), 3.25 (m, 2H), 2.65 (d, J=1.1 Hz, 2H), 1.65-1.30 (m, 9H), 1.26 (t, J=7.0 Hz, 3H), 1.21 (d, J=10.0 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$), ppm: δ 178.06, 167.36, 145.62, 145.52, 137.72, 132.10, 128.30, 126.85, 104.40, 67.68, 61.11, 47.72, 45.07, 42.65, 38.30, 27.79, 27.52, 26.30, 26.12, 15.27.

ESI-MS analysis *(m/z)* calculated for $[C_{32}H_{28}O_4+Na]^+$, 473.24; found, 473.27.

Synthesis of singly branched poly(MNI):

A Schlenk flask equipped with a magnetic stirring bar was charged with initiator **C3** (15.0 mg, 1 eq) evacuated and refilled with argon. Stock solution[21] of monomer **6** in methylene chloride (45 μL, 1.88 M, 5 eq) was added via Hamilton syringe and the resulting solution was stirred for 15 minutes. A second Stock solution containing termimer **4** in methylene chloride (38 μL, 0.22 M, 0.5 eq) was added and the reaction was quenched with an excess of ethyl vinyl ether (0.05 mL) after an additional 45 minutes.

Synthesis of active ester (2) end-capped poly(CyNI):

G1 catalyst (84 mg, 0.1 mmol) was dissolved in dry degassed dichloromethane (0.5 mL) and injected into a solution of **CyNI** (500 mg, 2.0 mmol) in dry degassed dichloromethane (10 mL) via a syringe. After stirring the solution at r.t. for 1h, an excess of **2** (309 mg, 1.0 mmol) was added to the solution via syringe. The solution was stirred for an additional 2h before being precipitated into methanol. The polymer was removed by filtration and dried under high vacuum. For characterization, see supporting information Figures SI-3 and SI-4.

Stepwise convergent synthesis of dendritic poly(MNI):

A Schlenck flask equipped with a magnetic stirring bar was charged with of initiator **C3** (15.0 mg, 1 eq) evacuated and refilled with argon. Stock solution of monomer **6** in methylene chloride (45 μL, 1.88 M, 5 eq) was added via Hamilton syringe and the resulting solution was stirred for 15 minutes. A second Stock solution containing termimer **4** in methylene chloride (38 μL, 0.22 M, 0.5 eq) was added and stirred for an additional 45 minutes. Again monomer stock solution (22.5 μL, 1.88 M, 5 eq) was added and the mixture was stirred for 15 minutes before a second addition of of termimer stock solution (19 μL, 0.22 M, 0.25 eq) was added. The reaction was stirred over night and finally quenched with an excess of ethyl vinyl ether (0.05 mL).

3. Results and Discussion

The most commonly used method to convert the propagating olefin metathesis complex into a non-metathesis active species is its reaction with ethyl vinyl ether. This reaction proceeds regioselectively and transfers a methylene residue onto the polymer chain end while turning the catalyst into a Fischer-carbene complex. The reactivity of Fischer-carbene complexes in metathesis reactions with olefins is lowered to such an extent that virtually no further olefin metathesis is observed and the propagation can be regarded as terminated.[22]

With the aim of designing a highly reactive and functionalizable end-capping reagent the synthesis of a substituted *cis*-vinyl ether was addressed as *cis* olefins typically react faster than the corresponding *trans* olefins in olefin metathesis reactions. An activated ester was chosen as the functionalizable moiety as these are tolerated by the olefin metathesis reaction[23] and can thus be functionalized pre- or post polymerization.

To synthesize the desired *cis*-substituted vinyl ether derivative the Stille Coupling reaction[24] between *cis*-tributyl-(2-ethoxyethenyl)stannane and succinimidyl 4-(bromomethyl)benzoate **1** was chosen (Figure 1, top). This route is especially interesting since *cis*-tributyl-(2-ethoxyethenyl)stannane is commercially available. With this strategy *cis*-succinimidyl 4-(3-ethoxyallyl)benzoate **2** was successfully synthesized as the functional end-capping reagent for ROMP (Figure 1, top).

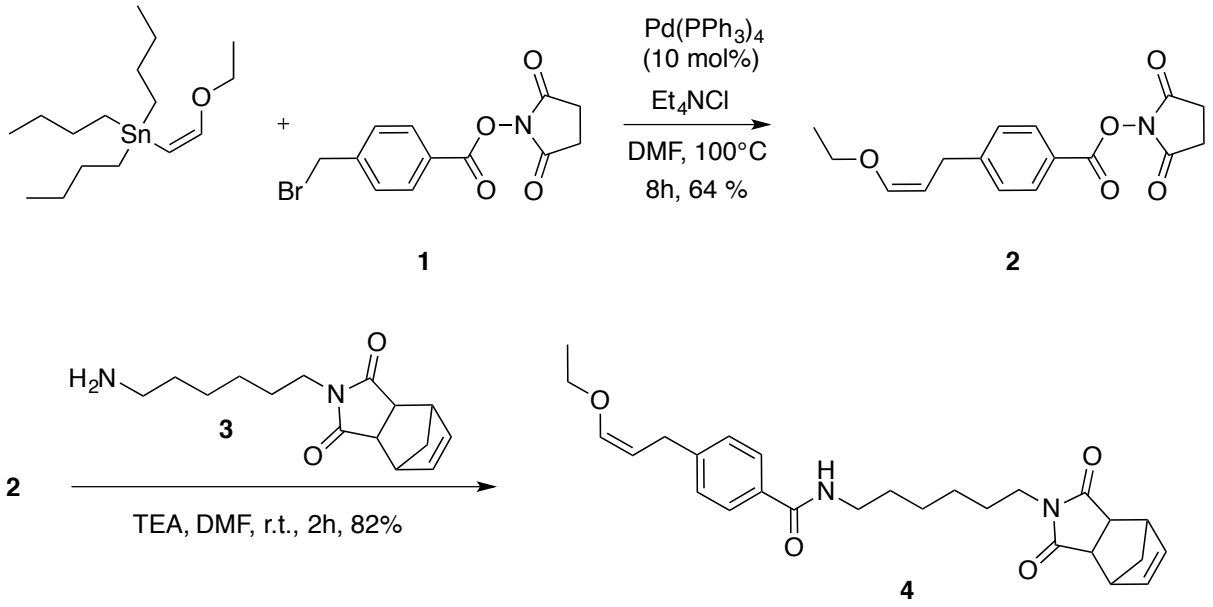


Figure 1. *Top*: Palladium catalyzed Stille coupling of an activated ester **1** with *cis*-tributyl-(2-ethoxyethenyl)stannane for the synthesis of *cis*-succinimidyl 4-(3-ethoxyallyl)benzoate **2**. *Bottom*: Synthesis of the ROMP termimer **4** from the universal end-capping reagent **2**.

The reaction of substituted vinyl ether **2** with a 1st generation Grubbs catalyst (benzylidene-bis(tricyclohexylphosphine)dichlororuthenium = **C1**, 3 equivalents) was followed by time resolved ^{1}H NMR spectroscopy in methylene chloride-d_2 (400 MHz), indicating fast termination kinetics for the *cis*-vinyl ether **2** (supporting information, Figure SI-1). To emphasize the *cis*-selectivity of **C1** we carried out a further ^{1}H NMR spectroscopy experiment in which a *cis/trans* mixture of *cis*-tributyl-(2-ethoxyethenyl)stannane (*cis/trans* = 75/25) was reacted with a 3-fold excess of initiator **C1** for 21h (methylene chloride-d_2, 400 MHz). A fast decrease of the concentration of the *cis*-isomer was observed (Figure 2). However, even though an excess of **C1** was present in the reaction mixture, the *trans*-tributyl-(2-ethoxyethenyl)stannane concentration did not significantly diminish over the period of 21 hours emphasizing the remarkable difference in reaction kinetics between the two isomers. This result certainly underlines the significance of stereo-controlled syntheses of substituted vinyl ether terminating reagents to improve substrate economy and reaction rates and thereby the definition of the resulting polymers.

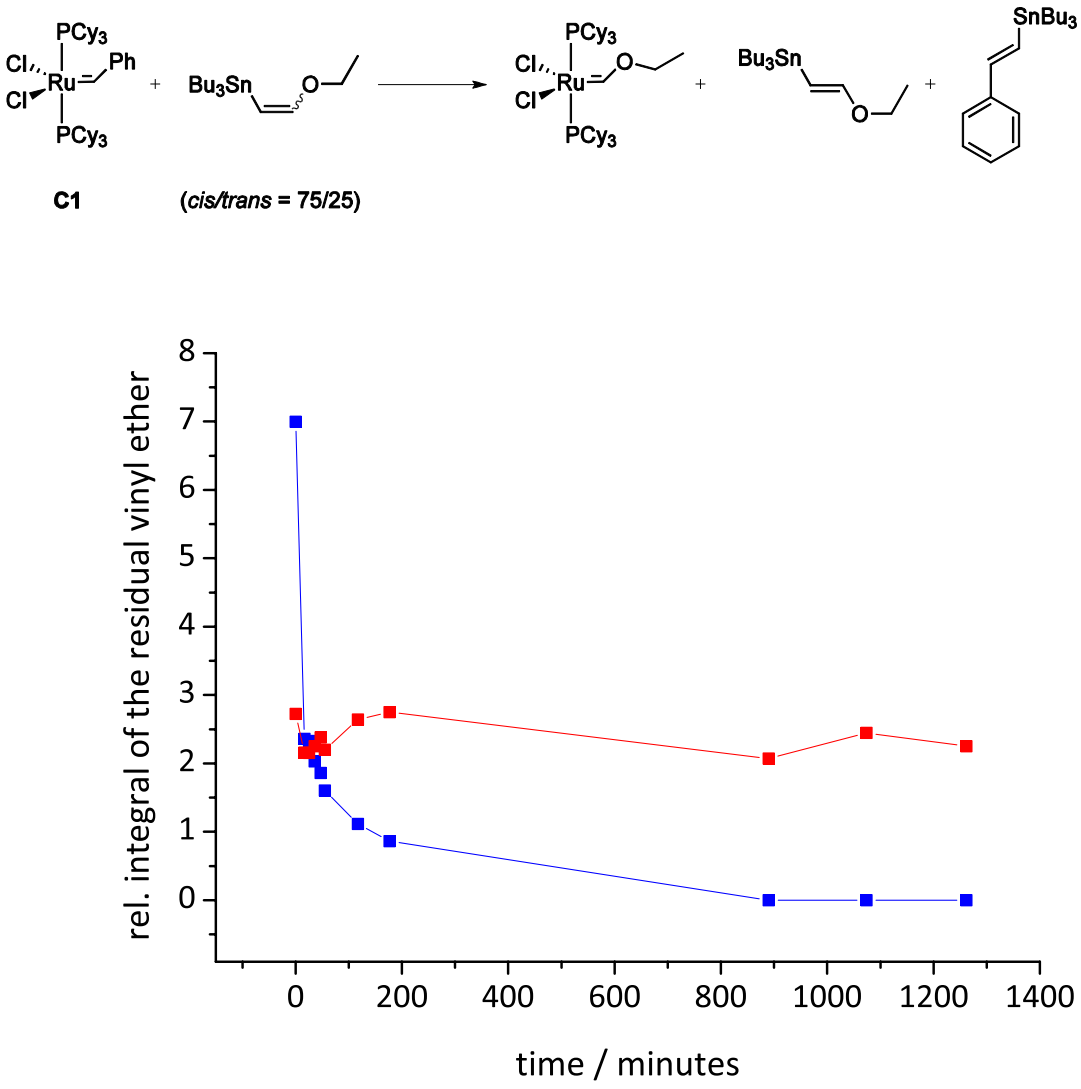


Figure 2. *Top*: Model reaction investigated over time by ^{1}H-NMR spectroscopy. *Bottom*: Time resolved ^{1}H NMR spectroscopy (methylene chloride-d_2, 400 MHz). An isomeric mixture of tributyl-(2-ethoxyethenyl)stannane (*cis/trans* = 75/25) was reacted with a 3-fold excess of catalyst **C1** over 21 hours. The signals of the *cis* (blue) and *trans* (red) isomer were integrated with respect to TMS as internal standard. The experiment indicates high substrate selectivity towards the *cis*-vinyl ether.

To verify whether a propagating ruthenium carbene is terminated with the same success under polymerization conditions, *exo*-*N*-cyclohexyl-norbornene-2,3-dicarboximide **5** (CyNI) was initiated with **C1**. After polymerization of **5**, the reaction was terminated with an excess of **2**. The ^{1}H NMR spectrum of the resulting poly(CyNI) showed the focal styryl residue transferred

by the initiator **C1** as well as the terminal succinimidyl 4-ethenylenebenzoate group transferred during termination with **2** (supporting information, Figure SI-3). MALDI-FT-ICR mass spectrometry confirmed the successful functionalization of poly(CyNI) (supporting information, Figure SI-4).

To demonstrate the versatility of the new end-capping reagent, **2** was derivatized with an amino-functional norbornene **3** (Figure 1, bottom). The resulting compound **4** represents both, a monomer and a terminating agent for ROMP and is therefore referred to as a termimer.[25]

Such a termimer allows the functional termination of a propagating polymer chain with a polymerizable unit, i.e. a norbornene derivative. When added in sub-stoichiometric amounts (with respect to the ruthenium carbene) to a living ROMP, branching of the linear chains will occur. This strategy has already been successfully used in the stepwise convergent synthesis of dendritic polymers using living anionic polymerization.[26] However, to our best knowledge, this approach has never been used with living ROMP. The functional or non-functional termination of ROMP is typically achieved by using large excesses of ethyl vinyl ether,[27] vinyl lactones[12] or other terminating agents[6,7,8,9] in order to ensure high reaction rates. As only sub-stoichiometric amounts of a termimer must be employed to achieve hyperbranching of the linear polymer chains, the termination rate of the termimer must be very high. An insufficiently reactive termimer would immediately lead to a loss of control over the ratio between branching units and propagating polymer chains. We therefore believed that the high reactivity of our *cis*-vinyl ether termimer **4** was an excellent candidate to fulfill the above requirement.

To test our hypothesis, Grubbs' 3rd generation initiator ($(H_2IMes)(3\text{-Br-Py})_2(Cl)_2Ru{=}CHPh$ = **C3**) was used to initiate 5 equivalents of exo-*N*-methylnorbornene imide **6** (MNI). After monomer consumption (reaction time of 15 minutes)[28] 0.5 equivalents of termimer **4** (with respect to the propagating ruthenium carbene species) was added. This should ideally transform 50% of the living polymer chains into linear norbornene-terminated polymer

chains, i.e. macromonomers. These macromonomers were expected to react readily with the remaining 50% of the active propagating ruthenium carbenes creating a singly branched propagating polymer (Figure 3, top). After 45 minutes of reaction time with the termimer **4**, the reaction mixture was quenched with excess ethyl vinyl ether. Analysis of the sample by GPC showed a bimodal molecular weight distribution with the first maximum at a molecular weight of 1500 $gmol^{-1}$ and a second maximum at 3500 $gmol^{-1}$ (Figure 4, dashed line). These correspond to a linear oligomer with eight repeat units and a branched oligomer with an average of 16.5 repeat units and one branching unit from **4**. MALDI-ToF MS analysis of the polymer sample revealed a mixture of linear non-functional, linear norbornene-functionalized (macromonomer) and singly branched non-functional polymers (supporting information, Figures SI-5 - SI-8). This clearly indicates that although the highly reactive *cis*-vinyl ether was used in termimer **4**, its reaction rate was still insufficient for complete conversion at this concentration. The fact that norbornene-terminated linear polymer (macromonomer) was observed in the MALDI-ToF-MS spectrum indicates that the terminal norbornene unit of the macromonomer has most likely a reduced reactivity due to steric hindrance.

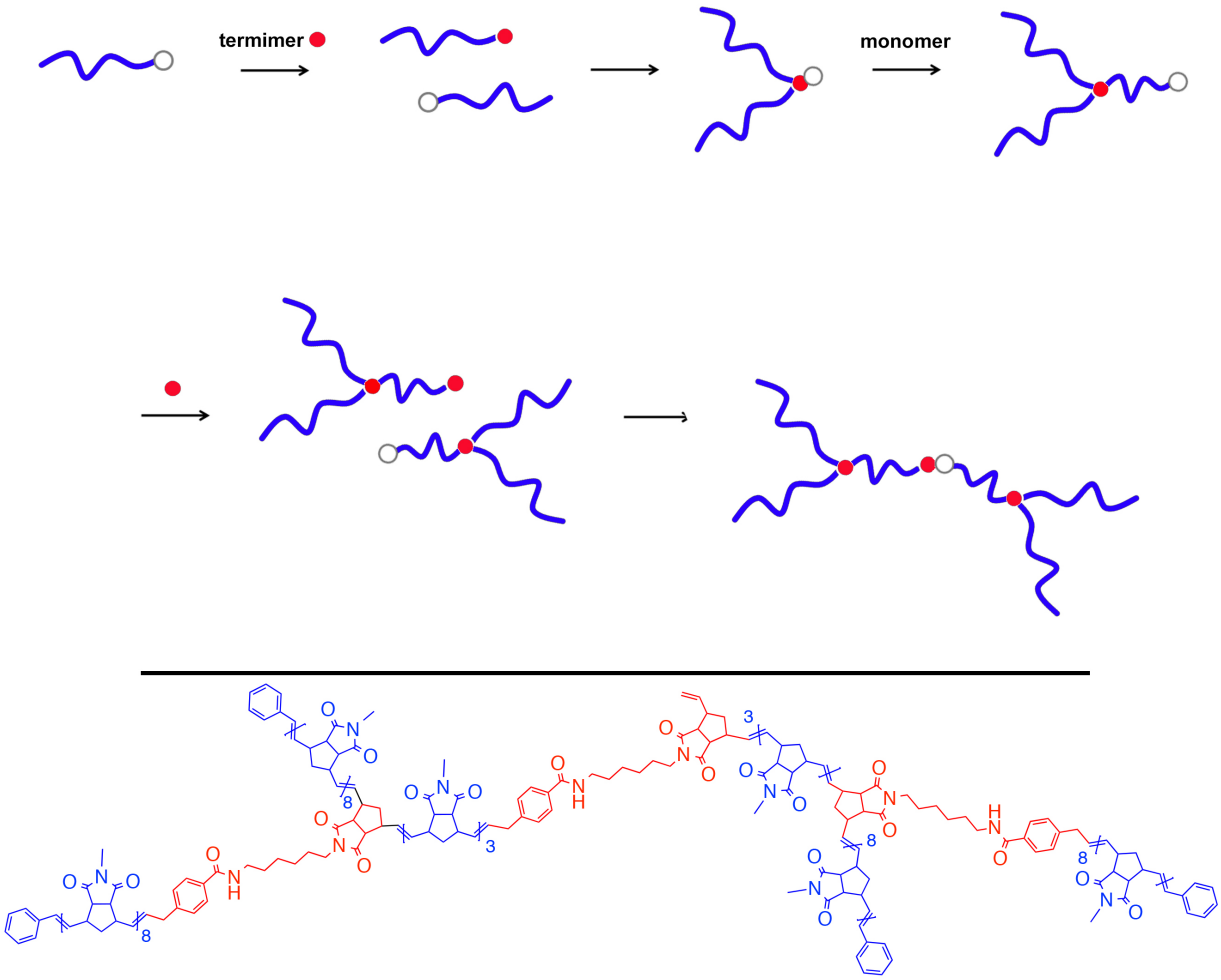


Figure 3. *Top:* Schematic representation of the stepwise convergent synthesis of dendritic olefin metathesis polymers using a termimer (filled red circle). Propagating end-groups are represented as empty circles, linear monomer (MNI) is represented as blue lines. *Bottom:* Idealized structure of the dendritic poly(MNI) when 50% of all propagating chains are functionally terminated twice.

Nonetheless, the majority of the sample consisted of singly branched polymer carrying an active ruthenium carbene. This prompted us to repeat the experiment as described above up to the point where the singly branched polymer was formed. To this mixture 5 equivalents (with respect to all active ruthenium carbene species) of monomer **6** were added. We expected this to result in a linear propagation of all active ruthenium carbene species (Figure 3, top) thereby moving the active propagating center away from the sterically demanding branching unit.

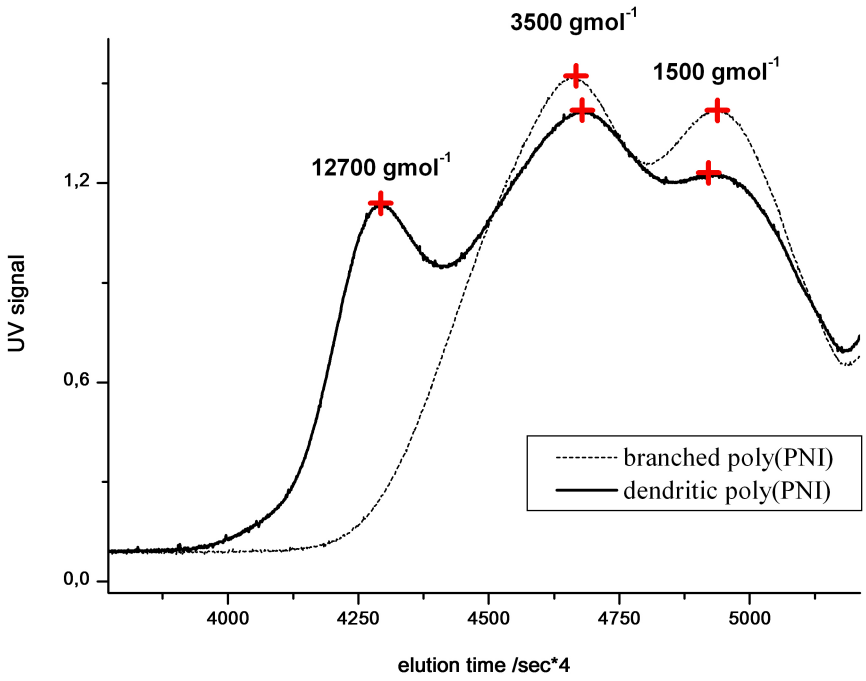


Figure 4. GPC analysis of the synthesized poly(PNI). Mixture of linear and branched poly(PNI) (---). Third distribution appears corresponding to dendritic poly(PNI) (—).

After consumption of monomer **6** (after 15 minutes), 50% of termimer **4** (with respect to the active ruthenium carbene species, i.e. half the amount of the first addition of **4**) was added to form a 2nd generation dendritic structure. The reaction mixture was quenched with excess ethyl vinyl ether after 12h and GPC analysis was performed. In addition to the previously observed bimodal molecular weight distribution, a third distribution with a maximum at 12700 $gmol^{-1}$ (Figure 4, solid line) was observed which we attribute to a 2nd generation hyperbranched polymer, each arm consisting of the former branched oligomer with an additional linear oligomer of 3 monomeric repeating units (Figure 3 bottom). Importantly no elution time shift of the maxima for the linear and the single branched oligomer units can be observed indicating that the third peak observed in the GPC trace results from recombination rather than from a linear growth of the former two species. While this method of branching is less efficient than that reported for other polymerization methods[29] it illustrates that

hyperbranching is in principle possible in ROMP. Gaining better control over complete branching in ROMP is clearly only related to the reactivity of the terminating part of the terminer (here the vinyl ether). Syntheses in analogy to similar reported systems giving access to hyperbranched[30], starlike-shaped[31], aborescent[32] or pom-pom[33] architectures should be straightforward to be carried out and we are currently underway to establish the synthetic protocols for such olefin metathesis polymers with complex architectures.

We believe that, with this initial communication, we can prove the principle of this approach while continuing to investigate new methods for faster regioselective termination reactions for ROMP.

4. Conclusions

We report for the first time a convergent approach to synthesize dendritic olefin metathesis polymers. The development of a new and highly efficient end-capping reagent for ROMP based on a functionalizable cis-vinyl ether allowed the synthesis of a so-called terminer, a monomer capable of propagation and termination. This ROMP termimer allows the combination of two propagating ROMP chains into one branched structure which carries the metathesis active ruthenium carbene complex close to its centre. GPC and MALDI ToF MS analyses strongly indicate that a high, albeit not complete, degree of branching is occurring when the termimer is introduced to a propagating ROMP polymer solution. This new route to stepwise convergent dendritic olefin metathesis polymers is an example highlighting the high reactivity of our new end-capping reagent. The end-capping reagent represents a versatile tool either for the functional termination of linear ROMP polymers or in its functionalized form as a termimer for a new approach to systematic branching of ROMP polymers.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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Keywords: ring opening metathesis polymerization, functional termination, hyperbranched polymer, Grubbs catalyst

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[1] **Supporting Information** is available online from the Wiley Online Library or from the author.

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