Telechelic Polynorbornenes with Hydrogen Bonding Moieties by Direct End Capping of Living Chains

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ABSTRACT: We present two novel symmetric olefins bearing hydrogen bonding moieties for the direct capping of living ring opening metathesis polymerization-chains using Grubbs catalyst 1st- and 3rd-generation. The symmetric olefins are generated via homo metathesis of the corresponding α-olefins under aid of microwave irradiation and are used to prepare polynorbornene-chains (M_n = 4,000–10,000 g/mol, M_w/M_n = 1.1–1.4) bearing barbiturate and thymine-moieties. A qualitative and quantitative analysis of the generated polymers is done via MALDI-TOF MS proving the introduction of hydrogen-bonding moieties into the polymer chain and revealing the strong dependence of the desorption on the chemical structure of the different polymer species and high efficiencies for the end group introduction (90–99%). The efficiency of this process depends strongly on the reaction time and the equivalents of terminating agent with respect to the living end. The best results for the end group introduction are achieved by reacting the living chains with an excess of the terminating agent (5–20 equiv) for 100 h. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5522–5532, 2010

KEYWORDS: cross metathesis; direct capping; functionalizational polymers; hydrogen bonding moieties; living polymerization; MALDI; ROMP; symmetric olefins

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INTRODUCTION Living ring opening metathesis polymerization (ROMP) has become a valuable tool for the synthesis of homo and block copolymers, as a large number of functional groups can be introduced easily and with high precision into the main-chain of the resulting polymers.[1,2] With the advent of well-defined catalysts based on molybdenum and ruthenium a large plethora of different polymeric architectures could be prepared,[3] with the Grubbs-catalysts based on ruthenium being often better suited due to their broader tolerance of functional groups. Especially within the field of supramolecular chemistry, the introduction of complex functional groups at the specific positions of a polymer chain is an important task to be fulfilled precisely.[4] Among the many supramolecular moieties known, hydrogen bonding moieties have gained special interest since they can be used to transform a random chain assembly into an ordered supramolecular structure.[5] Thus, we have accomplished the introduction of complex hydrogen-bonding moieties via a combination of ROMP with "click"-chemistry methods,[6–8] as the direct copolymerization of many monomers with complex functional groups, such as hydrogen bonds or nitroxide-moieties often leads to uncontrolled polymerization reactions with sometimes broad molecular weight distributions.[9,10] A still challenging task however, is the introduction of a functionalized end group via ROMP to one or both sides of a polymer chain, which can be achieved with different methods often including the reaction of the respective living chain end with functionalized enolethers[5,11–18] or oxygen.[19] Other approaches to such telechelic polymers rely on the use of functionalized catalysts,[17] chain transfer agents,[20,21] sacrificial synthesis[22,23] or the quench with vinyllactones.[24] However, most of the introduced functional groups are simple in their chemical structures, containing only alkyl- or carbonyl-type moieties. A significant progress in this respect has been accomplished by Weck and coworkers,[16,17] who has used functionalized enolethers to introduce pyridine and cyanurate-end groups into polynorbornenes. In a similar manner telechelic polymers from cycloctene with a chain transfer agent bearing thymine[25] and palladated sulfur-moieties were prepared. However, the synthesis of the respective functionalized enolethers requires multistep-procedures, which therefore preclude a general application of this methodology.

Recently, Grubbs and Matson published the direct capping of living chains with internal olefins[26,27] using $\sim$5 equivalents of a symmetric olefin and moderate reaction times of $\sim$6 h. Efficiencies for the end group introduction in most cases reached $\sim$90% and more, depending on the moieties pendant to the respective *cis*-olefin. As catalysts, Grubbs catalyst 3rd-generation and Grubbs-Hoveyda 2nd-generation were applied. Using this methodology, Madkour et al.[28] attached

Additional Supporting Information may be found in the online version of this article. Correspondence to: W. H. Binder (E-mail: wolfgang.binder@chemie.uni-halle.de)
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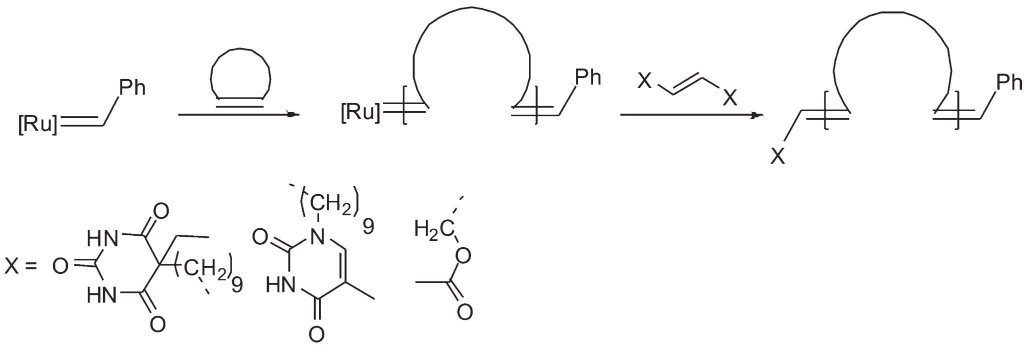


SCHEME 1 General reaction scheme for the end functionalization of ROM-polymers.

fluorescent dyes on polyoxonorbornenes with terminating agents based on *cis*-1,4-dihydroxy-2-butene. Of course, the advantage of the direct capping of living chains lies in the simple one step reaction and the avoidance for subsequent post functionalization processes.

In the present publication we report on the introduction of hydrogen bonding moieties via a direct quench of living ROMP-polymers using symmetric olefins with hydrogen bonding moieties as shown in Scheme 1.

Conceptually, we needed an attachment of the hydrogen bonding moieties to the polymer via C—C-bonds, which provides a higher thermal stability when compared to the often used ether- and ester-bonds in other synthetic strategies.[26–28] Besides the purely synthetic approach, the analysis of the quenching reaction and the evaluation of the quenching efficiency is reported, relying on a previously developed MALDI-method,[9] which enables a relatively precise evaluation of the individual species during and after the quenching reaction.

EXPERIMENTAL

All chemicals were purchased from Sigma Aldrich and were used without further purification. Dichloromethane and dimethylsulfoxide were predried over calcium chloride. Tetrahydrofuran was predried over KOH. Dichloromethane and dimethylsulfoxide were distilled over calcium hydride and degassed with argon prior to use. Tetrahydrofuran was distilled over sodium, benzophenone, and degassed with argon prior to use. Grubbs catalysts 1st-, 2nd- and 3rd-generation were purchased from Sigma Aldrich. Catalyst **4** was prepared analogously to the literature.[29] Monomer **5** was prepared analogously to the literature.[30] NMR-spectra were measured on Varian Gemini 2000 FT NMR spectrometer (200 and 400 MHz, 500 MHz) using chloroform (Isotec 99.8 atom% D) as solvent. For analysis of the FIDs Mestrec-software 4.7.0.0 was used. Chemical shifts were recorded in parts per million (δ) and referenced to residual protonated solvent [$CDCl_3$: 7.26 ppm (^1H), 77.0 ppm (^{13}C)].

Thin Layer Chromatography

Thin layer chromatography (TLC) was performed with TLC aluminium sheets silica gel 60 F_{254} being purchased from "Merck." As oxidation reagents a cerium molybdate solution – "blue stain" – [1 g $Ce(SO_4)_2 \bullet 4H_2O$, 2.5 g $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$, 6 mL conc. H_2SO_4 and 90 mL H_2O] and a solution of [1 g $Ce(SO_4)_2 \bullet 4H_2O$, 2.75 mL conc. H_2SO_4 and 47 mL H_2O] were used.

Microwave Reactions

Microwave reactions were performed with a CEM Discover 908010 in sealed tubes equipped with a Teflon-coated stirring bar.

GPC Measurements

GPC measurements were done at Viscotek GPCmax VE 2001 with a Styragel linear column GMH_{HR}; THF was used as carrier-solvent at 1 mL/min at RT. The sample concentration was ~3 mg/mL. Polystyrene standards (M_p = 1050–1,870,000 g/mol) were used for conventional external calibration standards, using a Waters RI 3580 refractive index detector.

MALDI-TOF MS Measurements

MALDI-TOF MS measurements were done at Bruker Autoflex III Smartbeam, equipped with a nitrogen laser (337 nm), in the linear positive mode. As matrix dithranol was used as solution of 20 mg/mL in THF. Polymer samples were dissolved in THF at a concentration of 10 mg/mL. As salts sodium trifluoroacetate was used as solution of 20 mg/mL in THF. In a typical sample preparation a solution was mixed with a ratio of 100:40:10 with regard to matrix:polymer:salt and spotted on the MALDI-target.

Diethyl-2-ethyl-2-(undec-10-enyl)malonate (9)[31]

All reaction steps were performed under an atmosphere of argon. Sodium hydride (60% mineral oil dispersion, 650 mg, 16.32 mmol) was dissolved in 17 mL of anhydrous tetrahydrofuran. To this mixture a solution of 2-ethyl-malonic acid diethyl ester (3.23 g, 17.18 mmol) in 3 mL anhydrous THF was added dropwise at room temperature. After the evolution of hydrogen gas ceased, 11-bromoundecene (2.67 g, 11.45 mmol) were added in one shot to the reaction mixture. The later was refluxed and the conversion was monitored via TLC. After complete conversion, the solvent was removed. The crude product was dissolved in $CHCl_3$ (100 mL). After addition of a small amount of water the phases were allowed to separate in a separation funnel. The organic layer was dried with brine and Na_2SO_4 and concentrated under reduced pressure. Final purification was performed via silica gel chromatography (hexane/ethylacetate = 10/1) giving the product (**9**) as colorless oil (3.7 g, 63%).

^{1}H NMR (400 MHz. $CDCl_3$, 27 °C, ppm) 5.80 (tdd, $J_1 = 6.7$ Hz, $J_2 = 10.2$ Hz, $J_3 = 16.9$ Hz, 1H), 4.98 (d, $J = 17.1$ Hz, 1H), 4.92 (d, $J = 10.2$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 4H), 2.03 (q, $J= 6.9$ Hz, 2H), 1.92 (q, $J = 7.5$ Hz, 2H), 1.85 (m, 2H), 1.24 (m, 20H), 0.81 (t, $J = 7.5$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, 27°C, ppm) 171.8, 139.1, 114.0, 60.8, 58.0, 33.8, 31.6, 29.9, 29.5, 29.4, 29.3, 29.1, 28.9, 25.2, 23.9, 14.1, 8.4.

5-Ethyl-5-(undec-10-enyl)pyrimidine-2,4,6-trione (10)[31]

Sodium hydride (60% mineral oil dispersion, 0.94 g, 23.50 mmol) was added to a solution of urea (7.2 g, 117.4 mmol) in 25 mL anhydrous DMSO. After the evolution of hydrogen gas ceased, compound **9** (2.0 g, 5.88 mmol) was added drop wise via a dropping funnel. The reaction mixture was stirred at room temperature for 6 days during which the conversion was monitored via TLC. After showing complete conversion the reaction mixture was poured onto 200 mL ice water and the resulting solution was neutralized with $KHSO_4$. After extracting the solution with chloroform (overall 1L) the combined organic layers were concentrated under reduced pressure. The crude product was dissolved in ethyl acetate. To this solution was added 100 mL, 10% aqueous NH_4Cl solution. After drying with brine and Na_2SO_4 the solvent was removed under reduced pressure. Pure compound **10** was obtained after silica gel chromatography (hexane/ethylacetate = 3/1) as white solid (1.3 g, 63%).

^{1}H NMR (400 MHz. $CDCl_3$, 27°C, ppm) ppm 8.89 (s, 2H), 5.80 (tdd, $J_1 = 6.7$ Hz, $J_2 = 10.1$ Hz, $J_3 = 16.9$ Hz, 1H), 4.98 (d, $J = 17.1$ Hz, 1H), 4.92 (d, $J =10.2$ Hz, 1H), 2.03 (m, 6H), 1.23 (m, 14H), 0.89 (t, $J = 7.4$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, 27°C, ppm) 172.6, 148.9, 139.1, 114.1, 57.46, 38.8, 33.7, 32.5, 29.5, 29.4, 29.4, 29.2, 29.1, 28.9, 25.2, 9.5.

5,5′-(Icos-10-ene-1,20-diyl)bis(5-ethylpyrimidine)-2,4,6-trione (6)

Compound **10** (200 mg, 0.65 mmol) and Grubbs catalyst 2nd-generation (27 mg, 0.032 mmol) were weighed into a vial equipped with a magnetic stir bar. The vial was flushed with argon and sealed with a rubber septum. After dissolving the mixture with dry dichloromethane (5 mL) the vial was placed in a microwave oven (heating up with 100 W to 100 °C, 30 W, 100 °C for 15 h). Formed ethylene was removed by purging the solution every 2 h with argon. Final quenching was done with ethylvinylether. The solvent was evaporated and the crude mixture was purified via silica gel chromatography (ethyl acetate/hexane = 1/1). (140 mg, Yield 74%).

^{1}H NMR (400 MHz. $CDCl_3$, 27 °C, ppm) ppm 8.81 (s, 4H), 5.36 (m, 2H), 2.05 (m, 12H), 1.23 (m, 28H), 0.89 (t, $J = 7.4$ Hz, 6H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 172.8, 149.1, 130.3, 129.8, 57.5, 38.9, 32.5, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.8, 27.1, 25.3, 9.6.

5-Methyl-1-undec-10-enyl-1H-pyrimidine-2,4-dione (11)

A mixture of thymine (1.12 g, 8.9 mmol), 1,1,1,3,3,3-hexamethyldisilazane (HMDS, 5.7 mL, 27 mmol), and trimethylchlorosilane (TMSCl) (1.1 mL, 8.9 mmol) was refluxed under nitrogen atmosphere until a clear solution was obtained. The excess of HMDS was then evaporated with a rotary evaporator (10 mbar, 40 °C). To the resulting crude 2,4-bis(trimethylsilyl)thymine were added dry DMF (7.5 mL) and 11-bromo-1-undecene (2.5 g, 10.7 mmol). The mixture was stirred for 11 days at 80 °C under an inert atmosphere. After removal of the solvent, the remaining solid was chromatographed (hexane/ethylacetate = 20/1) to yield 2.1 g (61%) of compound **11**.

^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, ppm) 8.39 (s, 1H), 6.96 (s, 1H), 5.81 (m, 1H), 4.96 (dd, $J_1 = 13.6$ Hz, $J_2 = 23.0$ Hz, 2H), 3.68 (t, 2H, $J = 4.5$ Hz), 2.04 (dd, $J_1 = 6.9$ Hz, $J_2 = 14.0$ Hz, 2H), 1.92 (s, 3H), 1.67 (m, 2H), 1.28 (m, 12H), ^{13}C NMR (100 MHz, $CDCl_3$, 27°C, ppm) 164.0, 150.7, 140.4, 139.1, 114.1, 110.5, 48.6, 33.8, 29.4, 29.3, 29.3, 29.1, 29.1, 29.0, 28.9, 26.4, 12.3.

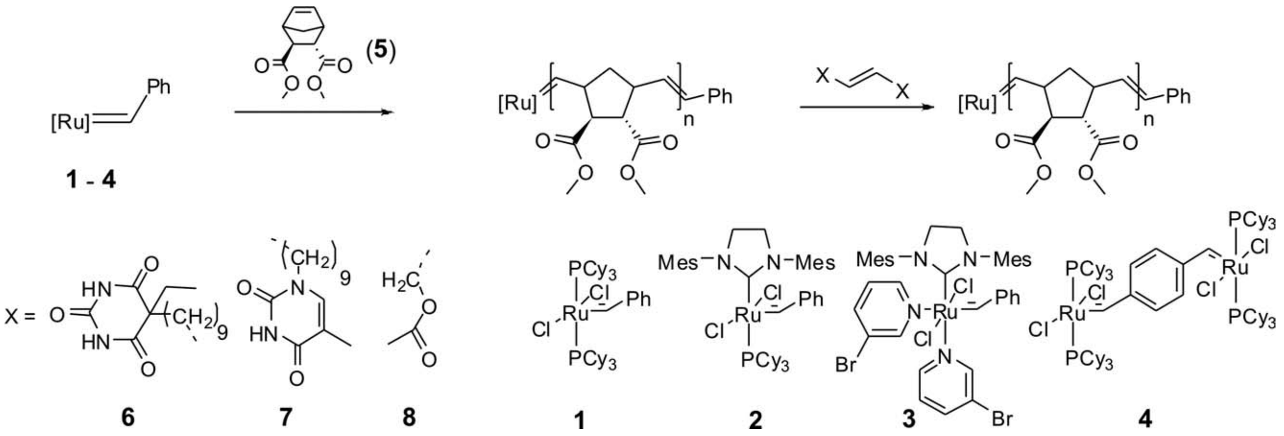
1,1′-(Eicos-10-ene-1,20-diyl)bis(5-methyl-1H-pyrimidine-2,4-dione) (7)

Compound **11** (200 mg, 0.72 mmol) and Grubbs catalyst 2nd-generation (30 mg, 0.036 mmol) were weighed into a vial equipped with a magnetic stir bar. After flushing with argon the vial was sealed with a rubber septum. The mixture was dissolved with dry dichloromethane (5 mL) and was then placed in a microwave oven (heating up with 100 W to 100 °C, 30 W, 100 °C for 15 h). Gaseous ethylene was removed by purging the solution every 2 h with argon. The mixture was quenched with ethylvinylether and after solvent evaporation the crude mixture was purified via silica gel chromatography (ethyl acetate/hexane, 1/1). (114 mg, Yield 60%).

^{1}H NMR (400 MHz. $CDCl_3$, 27 °C, ppm) 8.71 (s, 2H), 6.97 (s, 2H), 5.37 (m, 2H), 3.68 (m, 4H), 1.92 (s, 6H), 1.65 (m, 4H), 1.31 (m, 28 H), ^{13}C NMR (100 MHz, $CDCl_3$, 27°C, ppm) 163.9, 150.6, 140.2, 130.2, 110.4, 109.9, 48.6, 32.6, 29.6, 29.4, 29.3, 29.2, 29.1, 26.5, 12.4.

ROMP Polymerization

The polymerization of monomer **5** with Grubbs-1st-generation catalyst is provided as an example with quencher **6**. Thus, a heated out vial equipped with a magnetic stir bar was charged with monomer **5** (50 mg, 0.24 mmol), flushed with argon and sealed with a rubber septum. 1st-generation Grubbs catalyst (7.8 mg, 0.0095 mmol) was dissolved in anhydrous dichloromethane (1.5 mL) and was injected into the vial. The resulting solution was stirred for 1 h to complete the polymerization. Compound **6** (26.8 mg, 0.047 mmol) was dissolved in anhydrous dichloromethane and injected into the polymerization solution. The resulting solution was stirred for 100 h, after which all of the monomer had been consumed. Final quenching was done by adding cold ethylvinylether (3 drops) and stirring for another hour. After solvent evaporation the crude mixture was purified by column chromatography with hexane/ethylacetate (3:1) to remove



SCHEME 2 End functionalization of polynorbornenes via symmetric terminating agents.

the excess of compound **6**. The polymer was obtained by flushing the column with ethylacetate.

Alternatively, the polymer was separated by removing the solvent, dissolving in a minimum amount of dichloromethane and precipitation in methanol. The fine precipitate was separated by ultracentrifugation. Yield: 34 mg (62%) ($M_n = 4400$ g/mol, $M_w/M_n = 1.3$).

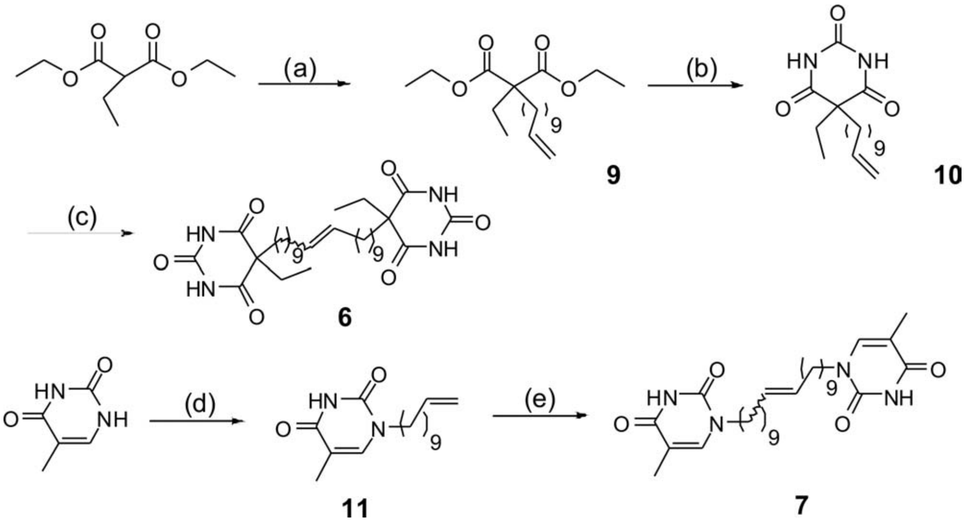
RESULTS AND DISCUSSION

The concept of the presented synthetic approach relies on the use of the bivalent quenching agents **6**, **7** which are prepared by a crossmetathesis reaction of the respective monovalent olefins bearing the respective hydrogen bonding moieties using Grubbs catalyst 2nd-generation (**2**) as catalyst (Scheme 2). Monomer **5** was chosen, as it can be polymerized well with the catalysts **1**, **3**[9] and **4** and the resulting polymers can be easily analyzed via MALDI-TOF-MS methods, as demonstrated by us recently.[9,10]

Thymine and barbituric acid moieties **6**, **7** were selected as end groups, as they represent often used hydrogen bonding motives in supramolecular polymer chemistry by us[4,6–8,32–36] and others.[25,37–42] Terminating agent (**8**) was used as a model system for the introduction of end groups via direct end capping since it is commercial available. Recent works by Matson and Grubbs[27] showed that compound **8** and its derivatives can be successfully applied for the direct end capping of living chains. The bivalent, internal olefins **6** and **7** were used as terminating agents since the respective α-olefins tend to generate exclusively vinyl capped polymer (vide infra), which can be explained by complexation of the polar groups to the ruthenium core or steric hindrance. Therefore, a simple approach toward symmetric olefins bearing the respective hydrogen-bonding moieties was investigated before conducting the quenching reactions on the polymer (Scheme 3).

Synthesis of the Terminating Agents

Quencher **6** was synthesized in a three step process starting from commercial available diethyl-2-ethylmalonate which was converted to compound **9** by nucleophilic substitution with 11-bromoundecene, followed by ring closing with urea to give compound **10**. Compound **11** was prepared by protection of thymine with HMDS and TMSCl and subsequent nucleophilic substitution with 11-bromoundecene. The



SCHEME 3 Synthesis of the terminating agents **6** and **7**; (a) 11-bromoundecene, sodium hydride (63%), (b) urea, sodium hydride (63%), (c) Grubbs catalyst 2nd-generation (74%), (d) HDMS, TMSCl, 11-bromoundecene (61%), (e) Grubbs catalyst 2nd-generation (60%).

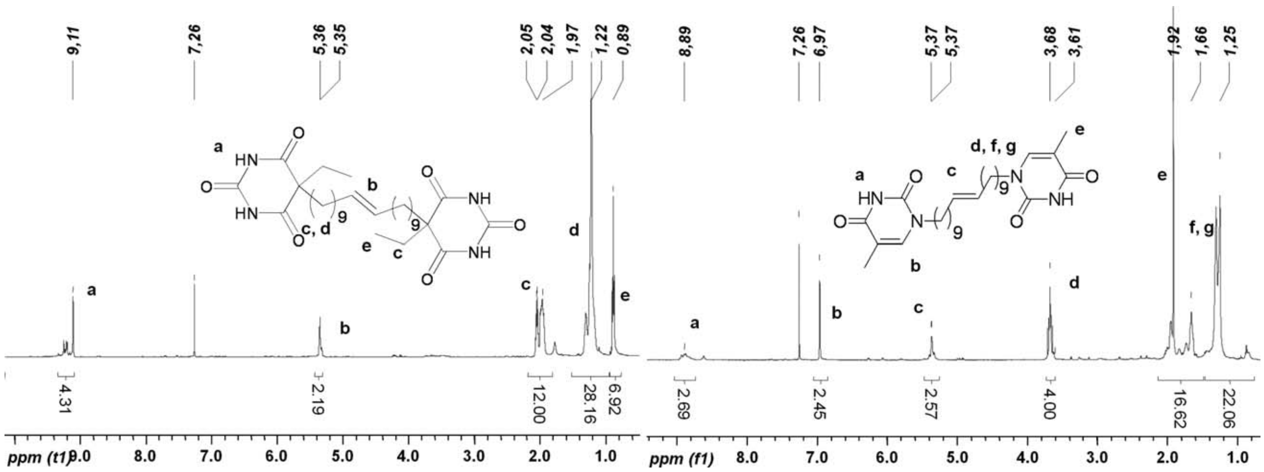


FIGURE 1 ^{1}H NMR spectra of symmetric terminating agents **6** and **7**, (a) compound **6**, (b) compound **7**.

respective mono-olefinic compounds **10** and **11** were then converted to the symmetric bivalent olefins **6** and **7** in a homometathesis step probing several Grubbs-catalysts. The best results in this metathesis step were achieved with Grubbs 2nd-generation catalyst in dichloromethane at 100 °C with a microwave-irradiation power of 30 W. The formation of the internal olefins **6** and **7** can be observed by the formation of the resonance at 5.36 and 5.37 ppm, respectively (Fig. 1), together with a disappearance of the resonances of the vinyl-group from the α-olefins **10** and **11**. The generated products are a mixture of *cis-* and *trans*-olefins, e.g., compound **6** displays two resonances in the carbon-NMR at 130.35 and 129.86 ppm which could be assigned to carbons of a *trans-* and *cis*-double bond, respectively (see Supporting Information Fig. S5).[43] The ratio of *trans-* to *cis*-double bonds can be estimated to be 3.3 to 1 for compound **6** and 2.1 to 1 for compound **7**.

Quenching Reactions

As a test system of the end groups introduction we have chosen poly-**5** initiated with Grubbs catalyst 1st-generation (**1**) and Grubbs catalyst 3rd-generation (**3**). The polymerization yielded living polymers with narrow PDI's and controllable molecular weight as described earlier.[9] Moreover this polymer can be desorbed well using MALDI-methods, thus representing an ideal model system for proving the final end group-functionalization.[9,10] Grubbs catalyst 2nd-generation could not be applied since it is generating high molecular weight poly-**5** due to the known small k_i/k_p ratio.[44] The generated polymers have molecular weights of 4000 to 10,000 g/mol with polydispersities $M_w/M_n = 1.1$ to 1.4 (Tables 1–3).

First, we reacted poly-**5** with the α-olefin **10** as a model-system. The formation of vinyl-terminated polymer is preferred but in a subsequent step the polymer acts itself as α-olefin and reacts in a cross metathesis step with the functionalized catalyst. The quenching efficiency was calculated to be 38% (Table 1, entry 1), (Supporting Information Fig. S9). The MALDI-TOF spectrum (Supporting Information Fig. S9) displays two series which could be assigned to vinyl capped poly-**5** ionized with sodium (main series) and barbiturate capped poly-**5** ionized with sodium (side series). Since this reaction did not lead to satisfying results, we concluded that internal olefins are better suitable to generate end capped polymers. This can be easily explained due to the symmetric structure of these olefins which generate just one set of products.

TABLE 1 GPC and MALDI-TOF MS Results for Polymers Quenched with Compounds **8** and **10**

Entry	Cat.	TA	Equiv TA	Time (h)	M_n (GPC) (g/mol)	PDI (GPC)	M_n[a] MALDI m/z	PDI[a] MALDI	M_P[b] MALDI m/z	I(vin)/I(eg)[c]
1	**1**	**10**	10	24	4200	1.18	3,993	1.11	3,911.1	49
2	**1**	**8**	10	24	5000	1.21	4,614	1.13	5,228.4	0.21
3	**3**	**8**	10	24	9700	1.19	13,317	1.05	14,917.5	[d]
4	**4**	**8**	10	24	6400	1.39	8,200	1.24	8,920.6	[e]

[a] Calculated with Polytools software.

[b] Mass of the peak with the highest intensity.

[c] Ratio of intensities of vinyl terminated poly-**5** and poly-**5** bearing functionalized end group.

[d] Full conversion, no vinyl-species detected.

[e] Ratio monotelechelic to telechelic acetoxy capped polymer = 0.09, monomer to initiator ratio (calculated molecular weight): 25 (5640 g/mol) for entry 1, 25 (5431 g/mol) for entry 2, 30 (6482) for entry 3, 25 (5530 g/mol) for entry 4.

TABLE 2 GPC and MALDI-TOF MS Results for Polymers Quenched with Compound **6**

Entry	Cat.	Equiv TA (6)	Time (h)	M_n (GPC) g/mol	PDI (GPC)	M_n[a] MALDI m/z	PDI[a] MALDI	M_P[b] MALDI m/z	I(vin)/ I(barb)[c]	Corrected Value[d]
1	**1**	1	2	5,500	1.15	5,969	1.05	4,750.6	50	1.61 (38.5%)
2	**1**	2	2	5,400	1.31	5,861	1.05	4,960.8	14.3	0.47 (68.0%)
3	**1**	5	2	5,400	1.23	5,724	1.05	5,380.9	3.2	0.11 (90.0%)
4	**1**	10	2	5,200	1.22	5,907	1.03	5,590.4	2.4	0.077 (93.0%)
5	**1**	5	20	6,500	1.24	6,172	1.06	4,751.3	1.6	0.050 (95.2%)
6	**1**	5	100	4,400	1.32	4,661	1.03	4,332.8	1.4	0.046 (95.6%)
7	**3**	5	50	8,000	1.18	10,583	1.05	11,547.0	2.0	0.064 (93.8%)
8	**3**	20	50	7,600	1.19	9,867	1.07	11,267.1	0.47	0.015 (98.5%)
9	**3**	20	100	6,400	1.15	7,429	1.03	7,346.2	0.17	0.005 (99.5%)

[a] Calculated with Polytools software.

[b] Mass of the peak with the highest intensity.

[c] Ratio of intensities of vinyl terminated poly-**5** and poly-**5** bearing barbiturate end group.

[d] Corrected intensity ratio by applying the desorption ratio from the quantification, monomer to initiator ratio (calculated molecular weight): 25 (5640 g/mol) for entries 1–6, 30 (6691 g/mol) for entries 7–9.

The first reactions with internal olefins were conducted with *cis*-1,4-bisacetoxy-2-butene (**8**) (Table 1, entry 2–4), similar to the work of Matson and Grubbs.[27] This compound showed high reactivity toward the living chains generating monotelechelic acetoxy capped poly-**5**. In the case of Grubbs catalyst 1st-generation (**1**) the MALDI-TOF spectrum [Fig. 2(a)] shows acetoxy capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{19}C_{11}H_{12}O_2Na]^+$ as main series, a side series can be assigned to vinyl terminated poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{20}C_8H_8Na]^+$. Complete conversion was achieved with Grubbs catalyst 3rd-generation (**3**) where the MALDI-TOF spectrum [Fig. 2(b)] displays just one series which could be assigned to acetoxy capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{62}C_{11}H_{12}O_2Na]^+$. Telechelic acetoxy capped polymer could be prepared with the bivalent catalyst **4**. Besides the main series showing telechelic acetoxy capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{28}C_{16}H_{18}O_4Na]^+$ a side-series could be assigned to monotelechelic acetoxy capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{29}C_{13}H_{14}O_2Na]^+$ [Fig. 2(c,d)]. These results are in good agreement with the work of Matson and Grubbs,[27] showing efficiencies for the end group introduction for compound **8** of upto 97% as proven by NMR-spectroscopy.

The system was then expanded to the terminating agents (TA) **6** and **7** which were reacted in a cross metathesis step with living poly-**5**-chains initiated with catalysts **1** and **3**. After addition of the terminating agents **6** or **7**, ethylvinylether was added as a final quencher to terminate the remaining chains. The excess of the terminating agent was subsequently removed by column chromatography or precipitation. Reaction conditions were varied in time and amount of compounds **6** and **7**, probing ratios of the quenching agents with respect to the living end group of 1/1 up to 20/1 (see Table 2, entries 1, 4, 8) and (Table 3, entries 1, 3). The incorporation of the end group could be proven by NMR-spectroscopy as shown in Figure 3 for poly-**5** reacted with 2 equiv of compound **6** for a reaction time of 2 h. Thus, at 6.40 ppm the protons (b) in α-position to the phenyl group can be seen. The resonances *d* and *i* at 4.99 and 0.87 ppm can be assigned to the methylidene protons and the methyl group of the barbiturate end group, respectively. The integration of these resonances gives a ratio of 1.33/1 of the barbiturate-end groups vs. the vinyl-end groups thus indicating an efficiency of the quenching reaction of 57%.

TABLE 3 GPC and MALDI-TOF MS Results for Polymers Quenched with Compound **7**

Entry	Cat.	Equiv TA (7)	Time (h)	M_n (GPC) (g/mol)	PDI (GPC)	M_n[a] MALDI m/z	PDI[a] MALDI	M_P[b] MALDI m/z	I(vin)/ I(thym)[c]	Corrected Value[d]
1	**1**	1	100	5,600	1.22	4,929	1.12	4,961.7	2.03	0.113 (89.9%)
2	**1**	2	100	5,900	1.19	5,106	1.12	4,962.1	2.00	0.111 (90.0%)
3	**1**	5 (35°C)	100	5,800	1.22	5,695	1.12	4,961.7	1.49	0.083 (92.3%)
4	**3**	5	100	8,700	1.15	8,682	1.03	9,166.4	2.42[e]	0.134 (88.2%)

[a] Calculated with Polytools software.

[b] Mass of the peak with the highest intensity.

[c] Ratio of intensities of vinyl terminated poly-**5** and poly-**5** bearing thymine end group.

[d] Corrected intensity ratio by applying the desorption ratio from the quantification.

[e] Only the sodium series were considered for the quantification, monomer to initiator ratio (calculated molecular weight): 25 (5610 g/mol) for entries 1–3, 30 (6661 g/mol) for entry 4.

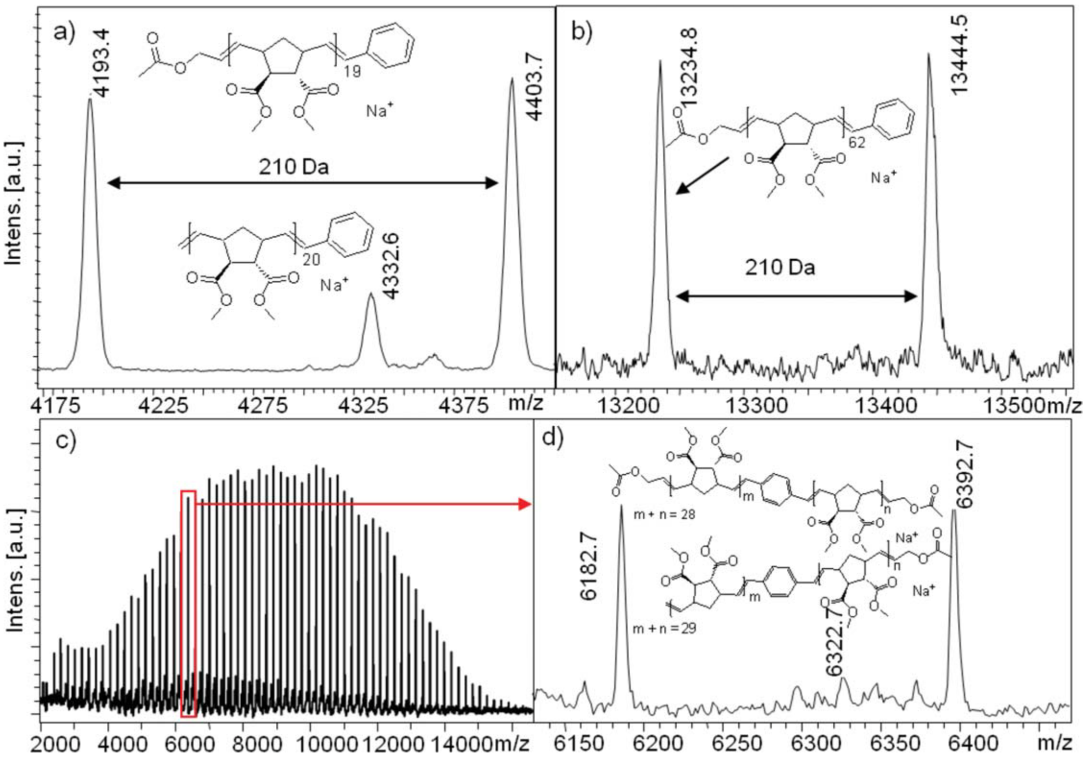


FIGURE 2 MALDI-TOF MS spectra of poly-**5** quenched with *cis*-1,4-bisacetoxy-2-butene (**8**), (a) with Grubbs catalyst 1st-generation, 10 equiv of **8**, 24 h, enlargement from 4175 to 4425 m/z, (b) initiated with Grubbs catalyst 3rd-generation, 10 equiv of **8**, 24 h, enlargement from 13150 to 13500 m/z, (c) with bivalent catalyst **4**, 10 equiv of **8**, 24 h, full spectrum, (d) enlargement from 6100 to 6500 m/z.

The resulting polymers were intensively investigated via MALDI-TOF MS as mass spectrometric methods have become important tools for the characterization of synthetic polymers.[9,45] The mass-spectra (Figures 4–6) of the end functionalized polymers showed in the most cases two series, which could be assigned to the functionalized polymer and vinyl capped polymer. The peaks of each series are separated by $m/z = 210$ Da which corresponds to the mass of monomer **5**. The MALDI-TOF spectrum of poly-**5** initiated with catalyst **1** and quenching with terminating agent **6** (5 equiv, 100 h) is shown in Figure 4. The enlarged spectrum [Fig. 4(b)] displays two series, which could be assigned to vinyl-capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{20}C_8H_8Na]^+$ as main series and barbiturate capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{19}C_{23}H_{32}N_2O_3Na]^+$ as side series. Figure 5 displays the MALDI-TOF spectrum of poly-**5** initiated with catalyst **3** and quenching with terminating agent **6** (20 equiv, 100 h). The enlarged spectrum [Fig. 5(b)] displays three series with the barbiturate capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{32}C_{23}H_{32}N_2O_3Na]^+$ as main series. Barbiturate capped poly-**5** ionized with lithium $[(C_{11}H_{14}O_4)_{32}$-$C_{23}H_{32}N_2O_3Li]^+$ and vinyl-capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{33}C_8H_8Na]^+$ could be assigned as side series. In the case of terminating agent **6** the change from Grubbs catalyst 1st (**1**) to Grubbs catalyst 3rd-generation (**3**) leads to a significant decrease of the vinyl capped species in the MALDI-TOF spectra [Figs. 4(b), 5(b)], showing nearly an inverse picture compared to poly-**5** initiated with Grubbs catalyst 1st-generation. The best results for the terminating agent **6** were achieved with catalyst **3** and reaction with an excess of terminating agent (20 equiv) for 100 h (Table 2, entries 8 and 9). These results can be explained due to the higher reactivity of catalyst **3** toward internal olefins.

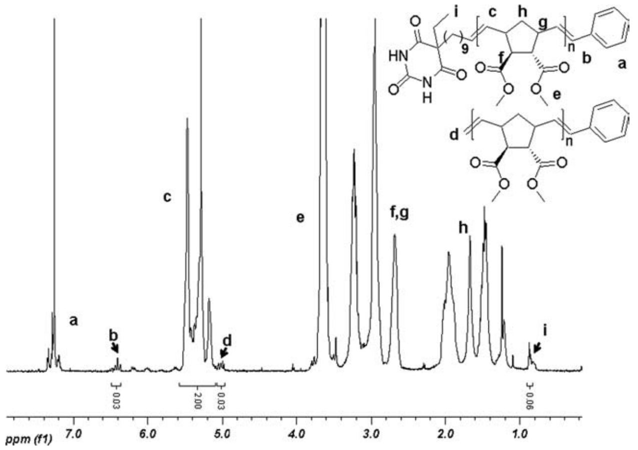


FIGURE 3 ^{1}H NMR-spectrum for poly-**5** initiated with Grubbs catalyst 1st-generation, quenched with 2 equiv of compound **6** for 2 h.

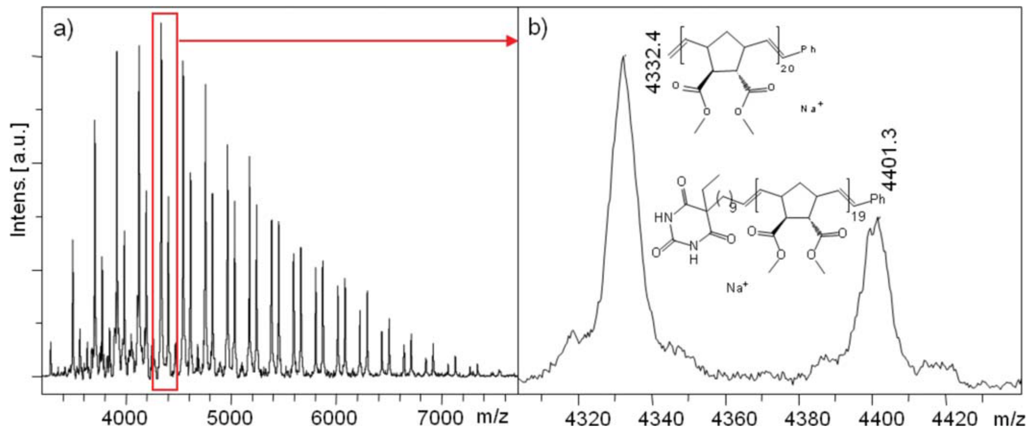


FIGURE 4 MALDI-TOF MS spectrum of poly-**5** initiated with Grubbs catalyst 1st-generation and quenched with TA **6**, 5 equiv, 100 h, (a) full spectrum (b) enlargement from 4310 to 4430 m/z. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

Terminating agent **7** was reacted analogously with poly-**5** initiated with catalyst **1** and **3** with a reaction time of 100 h. In Figure 6(a) the enlarged MALDI-TOF spectrum of poly-**5** initiated with catalyst **1** and quenched with compound **7** (5 equiv, 100 h) is shown. The main series is vinyl capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{23}C_8H_8Na]^+$, the side series could be assigned to thymine capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{22}C_{22}H_{30}N_2O_2Na]^+$. Figure 6(b) shows the enlarged MALDI-TOF spectrum of poly-**5** initiated with catalyst **3** and quenched with compound **7** (5 equiv, 100 h). The main series is vinyl capped poly-**5** ionized with sodium $[(C_{11}H_{14}O_4)_{42}C_8H_8Na]^+$, two other series could be assigned to thymine capped poly-**5** ionized either with lithium $[(C_{11}H_{14}O_4)_{41}C_{22}H_{30}N_2O_2Li]^+$ or with sodium $[(C_{11}H_{14}O_4)_{41}C_{22}H_{30}N_2O_2Na]^+$. The fourth series could not be assigned but it might overlap with vinyl capped poly-**5** ionized with potassium $[(C_{11}H_{14}O_4)_{42}C_8H_8K]^+$. In contrast to terminating agent **6** the change from Grubbs catalyst 1st-generation to Grubbs catalyst 3rd-generation did not lead to a significant change in the intensity ratio of vinyl capped to thymine capped poly-**5**-species (Table 3, entries 3, 4), [Fig. 6(a,b)]. In the case of catalyst **3** additional polymer-species ionized with lithium appear in the mass spectrum.

MALDI-TOF Analysis

The fraction of functionalized polymer increases with increasing reaction-time and amount of added terminating agent **6** (Table 2, entries 1, 3, 4, 6). A further increase by prolonging the reaction time after 100 h was not observed. By changing from catalyst **1** to **3** and by using higher excess of the terminating agent the fraction of barbiturate capped polymer could be further increased (Table 2, entries 8, 9). Similar observations were made for the reaction of living poly-**5** with terminating agent **7.** The fraction of thymine-capped poly-**5** could be increased by using higher amounts of the terminating agent (Table 3, entries 1 and 3). No further increase in the fraction of thymine-capped poly-**5** was observed by changing from catalyst **1** to catalyst **3** (Table 3,

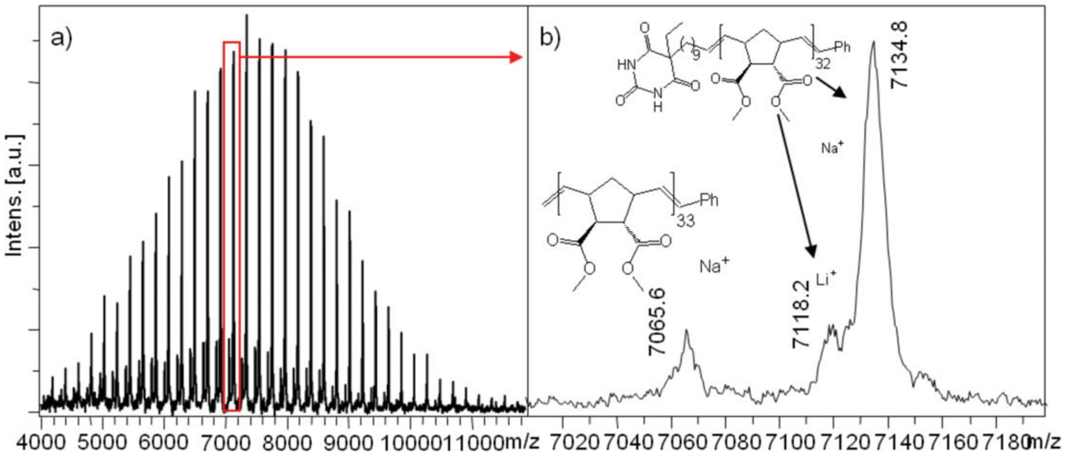


FIGURE 5 MALDI-TOF MS spectrum of poly-**5** initiated with Grubbs catalyst 3rd-generation and quenched with TA **6**, 20 equiv, 100 h (a) full spectra (b) enlargement from 7000 to 7200 m/z. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

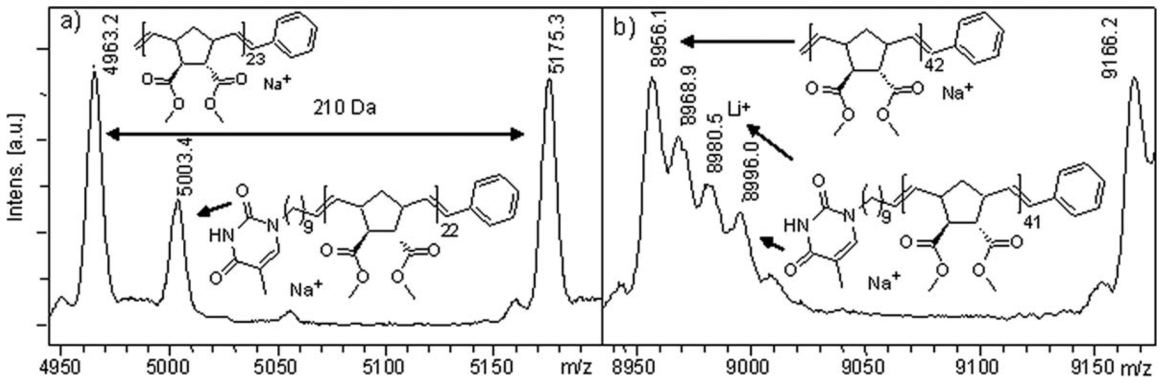


FIGURE 6 MALDI-TOF MS spectra of poly-**5** quenched with terminating agent (**7**), (a) initiated with catalyst (**1**), 5 equiv (**7**), 100 h, enlargement from 4950 to 5200 m/z, (b) initiated with catalyst (**3**), 5 equiv (**7**), 100 h, enlargement from 8950 to 9170 m/z.

entries 3 and 4). Since desorption of the specific polymer-species depends strongly on the chemical structure, a quantification of the different polymer species was done via MALDI-TOF MS. This method was already applied for the quantification of block copolymers in one of our previous papers[9] based on the works of Chen et al.[46,47] For the quantification a sample of the end functionalized polymer was measured in different mixtures with vinyl capped poly-**5**. The slope of the curve (Fig. 7) gives the desorption ratio between vinyl capped poly-**5** and poly-**5** with the functional end group. As the curves have a linear slope showing values of 18 for thymine and 30 for barbiturate the capped polymer, respectively, these values indicate that the vinyl capped polymer is preferentially desorbed. Therefore, the fraction of the end functionalized polymer is strongly underestimated by the determined factor. The values for the intensity ratio of vinyl capped poly-**5** against end group functionalized poly-**5** in Tables 2 and 3 were then corrected by the desorption ratio to give an estimation of the content of functionalized polymer. For the quantification just the species ionized with sodium were taken into consideration. By applying this correction we could determine that the fraction of barbiturate capped polymer in the mixture is between 38 and 99%. The best result with quencher **6** could be achieved by using the more reactive catalyst **3** with an excess of 20 equivalents of terminating agent and a reaction time of 100 h to get a fraction of functionalized polymer of 99% (Table 2, entry 9). For the polymers quenched with terminating agent **7** the fraction of thymine-capped poly-**5** is between 88 and 92%. No significant difference between the terminating agents **6** and **7** could be noticed comparing the conversion with 5 equivalents of terminating agent and a reaction time of 100 h for poly-**5** initiated with catalyst **1** (Table 2, entry 6), (Table 3, entry 3) showing a fraction of functionalized polymer of 96 and 92%, respectively.

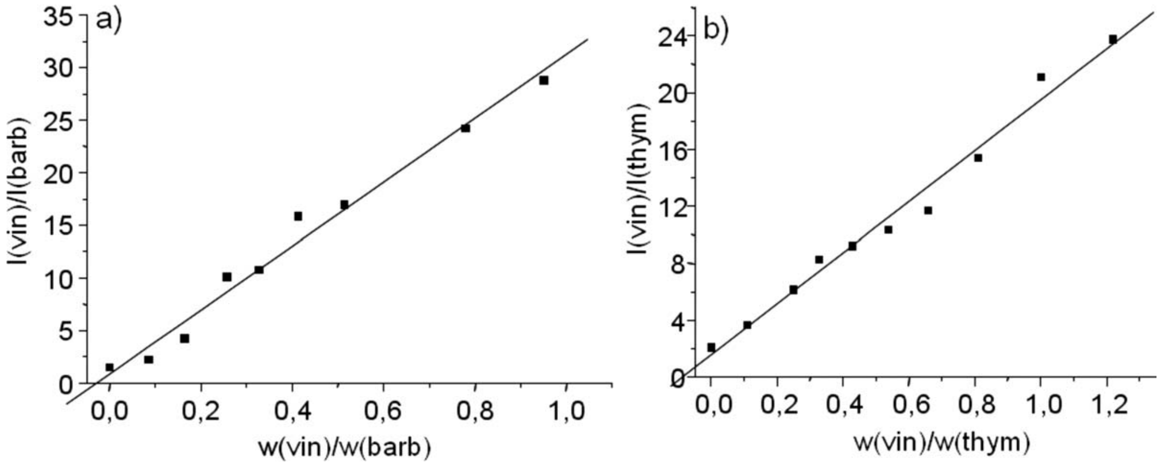


FIGURE 7 Quantification curves for poly-**5** (a) capped with barbiturate end group (**6**), (b) capped with thymine-end group (**7**), I(vinyl)/I(barb): intensity ratio of poly-**5** capped with vinyl-group against poly-**5** capped with barbiturate end group, w(vinyl)/w(barb): mixing ratio of poly-**5** capped with vinyl-group against poly-**5** capped with barbiturate end group, I(vin)/I(thym): intensity ratio of poly-**5** capped with vinyl-group against poly-**5** capped with thymine end group, w(vin)/w(thym): mixing ratio of poly-**5** capped with vinyl-group against poly-**5** capped with thymine end group.

CONCLUSIONS

In this article, we presented the successful synthesis of two new terminating agents **6** and **7** bearing hydrogen bonding moieties and their use for the end functionalization of living ROM-polymers. The terminating agents were prepared by the homo metathesis of the corresponding α-olefins with aid of microwave irradiation. Incorporation of the functional moieties onto the polymer backbone was proven by NMR-spectroscopy and MALDI-TOF MS. The efficiency of this process depends on the reaction time and on the amount of added terminating agent and can be quantified via MALDI-TOF MS. Polymers with a fraction of 99% of barbiturate-end groups could be prepared by reacting the living chains, initiated with catalyst **3**, with an excess of terminating agent **6** (20 equiv) and a reaction time of 100 h. With terminating agent **7**, it was possible to prepare polymer with a fraction of 92% of thymine-end groups by reacting the living chains, initiated with catalyst **1**, with an excess of terminating agent (5 equiv) and a reaction time of 100 h. The preparation of the terminating agents via homo metathesis with ruthenium catalysts can be applied on an array of functional moieties due to the tolerance of these catalysts on functional groups. Symmetric olefins acting as terminating agents represent a simple approach for the end group introduction by the direct capping of living chains, thus circumventing multistep organic syntheses of reactive olefinic moieties. We will further investigate this method for the preparation of supramolecular polymers.

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