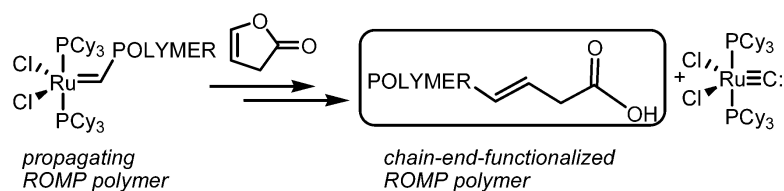


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End Capping Ring-Opening Olefin Metathesis Polymerization Polymers with Vinyl Lactones

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Abstract: The selective placement of a functional group at the chain end of a ring-opening metathesis polymer using ruthenium carbene initiators has been a significant limitation. Here we demonstrate a highly effective and facile end-capping technique for ROMP with living ruthenium carbene chain ends using single-turnover olefin metathesis substrates. Vinylene carbonate and 3*H*-furanone are introduced as functionalization and termination agents for the ruthenium-initiated ring-opening metathesis polymerization. This leads directly to the formation of functional polymer end groups without further chemical transformation steps. Aldehyde and carboxylic acid end groups can be introduced by this new method which involves the decomposition of acyl carbenes to ruthenium carbides. The high degrees of chain-end functionality obtained are supported by ¹H NMR spectroscopy, MALDI-ToF mass spectrometry, and end-group derivatization.

Introduction

The ring-opening olefin metathesis polymerization (ROMP) is a powerful polymerization technique.¹ Early well-defined catalyst systems based on titanium,² molybdenum³ and tungsten⁴ showed rather low functional group tolerance. While this was undesirable for the polymerization of functional monomers, it could be exploited in the introduction of functional end groups. The high oxophilicity of the metal carbenes allowed end functionalization via addition of substituted aldehydes to the polymerization mixture.⁵ Such functionalized polymers have been employed in a number of applications such as the formation of hybrid materials with interesting architectures.⁶

With the recent advances in functional group tolerant olefin metathesis catalysts based on ruthenium carbenes,⁷ the ring-opening metathesis polymerization (ROMP) has been established

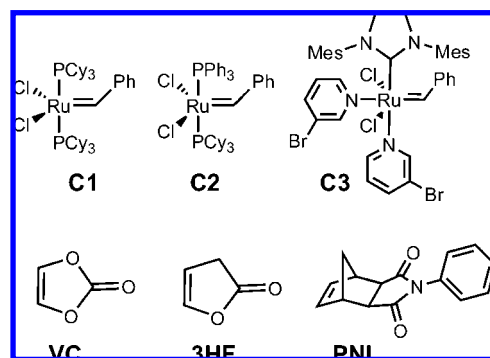


Figure 1. Top: Ruthenium carbene initiators **C1**, **C2**, and **C3** employed in this study. Bottom: Polymer end functionalization agents vinylene carbonate (**VC**) and 3*H*-furanone (**3HF**) and monomer *exo-N*-phenyl-norbornene-2,3-dicarboximide (**PNI**).

as a commonly employed polymerization technique.⁸ Highly active ruthenium carbene initiators for instance those featuring pyridine ligands⁹ (e.g., **C3**, see Figure 1) are able to polymerize a large variety of low strain cyclic olefins in a living manner while tolerating many polar functional groups and solvents.¹⁰

Lack of synthetic routes toward end-functional materials has prevented this otherwise very attractive polymerization technique

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to gain ground in areas still dominated by classical anionic polymerizations. Most efforts to date have been conducted toward ROMP polymers with highly functional pendant groups via polymerization of functional monomers.¹¹ Many such examples have been described ranging from bioactive groups^{12,13} to ionic groups^{14,15} to noncovalent binding motives.¹⁶

End-functionalized telechelic polymers are also easily accessible using ruthenium carbene initiators in the presence of chain transfer agents. A number of functional groups such as hydroxyl groups¹⁷ or amino and carboxylic acid groups¹⁸ have been introduced in this manner.

One of the great limitations of the olefin metathesis polymerization has been the introduction of end-functional groups while maintaining full control over the molecular weight distribution. Most other living polymerization techniques, such as carbanionic polymerization,^{19,20} RAFT,²¹ ATRP,²² or anionic ring-opening polymerization offer straightforward routes to either functionalize the living polymer chain end or start the polymerization with a functional initiator.

The above-mentioned route to telechelic polymers offers a very useful route to introduce functional end groups to ROMP polymers, however, at the price of broad molecular weight distributions of the resulting polymers with typical polydispersity indices (PDI) of 2 and cannot give only one functional end group exclusively.

Several attempts have been made at functionalizing the living end groups of ROMP polymers using substituted vinyl ethers. These deactivate and remove the catalytic center from the chain end while leaving the desired functional group behind.²³ Other research groups have employed molecular oxygen,²⁴ stoichiometric amounts of a specifically functionalized monomer,²⁵ or

specially functionalized ruthenium initiators²⁶ to place functional end groups at exactly one chain end of the ROMP polymer while maintaining the living nature of the polymerizations. However, the functionalization reactions were often reported to be slow, gave low end group conversions, or were not applicable in general.

Vinyl esters carry an electron deficient double bond that can deactivate ruthenium metathesis catalysts in a manner comparable to vinyl ethers.²⁷ Furthermore, they contain a fragile C–O bond which could be useful in releasing functional groups. In fact, as the pioneering work of the Johnson group demonstrated,²⁸ the carbenes of vinyl esters decompose, readily forming a carboxylic acid and a ruthenium complex bearing a carbido-ligand.

We recently reported a general synthetic route to overcome many of the above-mentioned limitations using a sacrificial diblock copolymer route.^{29,30} There, the living ROMP polymer to be functionalized was turned into a diblock copolymer by polymerizing dioxepine monomers onto the first polymer block. The polyacetal block could then be cleaved under acidic conditions to leave exactly “half a dioxepine”, i.e. a hydroxyl group at the chain end of the original polymer. Hydroxy-end functional polymers prepared via this route have already been used for the synthesis of graft³¹ and block copolymers.³² While this route gives particularly high degrees of chain-end functionalization (>97%) it requires a postpolymerization transformation, i.e. the hydrolysis of the acetal groups.

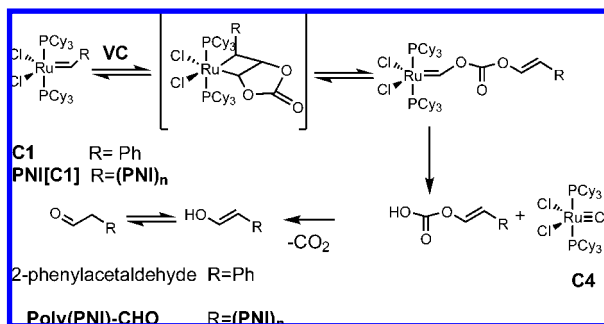
Here we present a new end-functionalization procedure for ROMP polymers. Polymers are initiated with the most common ruthenium initiators for living ROMP **C1**, **C2**, or **C3** (Figure 1) and rapidly chain-end-functionalized using the quenching agents vinylene carbonate (VC) or 3*H*-furanone (3HF) to give aldehyde- or carboxylic acid polymer end groups without the need of further chemical transformations. PNI was chosen as the monomer in this study as poly(PNI) can be readily analyzed by MALDI-ToF mass spectrometry.

Results and Discussion

Functionalization with Vinylene Carbonate. Vinylene carbonate (VC) is a small five-membered ring with little or no ring strain. It therefore appears to be a poor choice for metathesis termination at first glance. However, this vinyl lactone contains a strongly electron deficient double bond which allows the formation of Fischer-type carbenes upon reaction with ruthenium carbenes. In addition, the cis double bond is substituted symmetrically, thus eliminating regioselectivity problems during the metathesis reaction. A reaction of VC with a living polymer ruthenium carbene end group would result in the formation of

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Scheme 1. Proposed Mechanism for the Functionalization Reaction with VC

a Fischer-type carbene linked to the polymer chain end via a carbonate (Scheme 1).

Acyl- and halide-substituted carbenes, such as the one shown in Scheme 1, are known to decompose to the corresponding acid and a ruthenium-carbido complex that cannot undergo further metathesis reaction unless reactivated.³³ The ring-opening of the vinylene carbonate would therefore trigger the cleavage of the ruthenium complex from the polymer chain end making further end-group modifications unnecessary.

We were interested whether this reaction would allow us to introduce functionality by applying the classical “quenching of living end group” approach to ruthenium carbenes. The proposed mechanism of the reaction of initiator or living polymeric end group **C1** with VC is outlined in Scheme 1. After the ring-opening metathesis reaction of VC has occurred, the ester bond toward the ruthenium center is cleaved during the formation of the ruthenium-carbido complex **C4**. The resulting semiester of a carbonic acid then decomposes releasing carbon dioxide and phenylacetaldehyde or an aldehyde polymeric end group.

In a first model reaction, a large excess of VC was reacted with Grubbs first generation catalyst (**C1**). The reaction could be followed with the naked eye as the color of the reaction mixture changed from purple to yellow within a few minutes with the characteristic smell of phenylacetaldehyde emerging from the reaction vessel. In further model reactions catalysts **C1** and **C2** were used to initiate the polymerization of PNI to give living polymers with ruthenium carbene end groups. Upon addition of VC, similar color changes of the solutions toward yellow were observed. An image of the solutions of the uninitiated, initiated, and terminated catalyst **C1** can be found in the Supporting Information (S-1). The UV–vis absorption spectrum (see Supporting Information, S-2) showed complete loss of absorption bands characteristic of catalysts **C1** (absorption band at 520 nm) and catalyst **C2** initiated with *exo-N*-phenyl-norbornene-2,3-dicarboximide (PNI) (absorption bands at 400 and 330 nm). An FD-MS (field desorption mass spectrometry) analysis of the reaction mixture of initiated catalyst **C1** quenched with VC showed peaks that could be assigned to tricyclohexyl phosphine dissociated from the catalyst, short oligomers of the monomer bearing a terminal aldehyde (see Supporting Information for FD-MS) and phenylacetaldehyde from uninitiated catalyst **C1**.

In order to characterize the reaction kinetics and extent of reaction, time-resolved ¹H NMR spectroscopy was performed. The reaction of catalyst **C1** with VC proceeds at a moderate rate when equimolar amounts of the reactants were used (*c* =

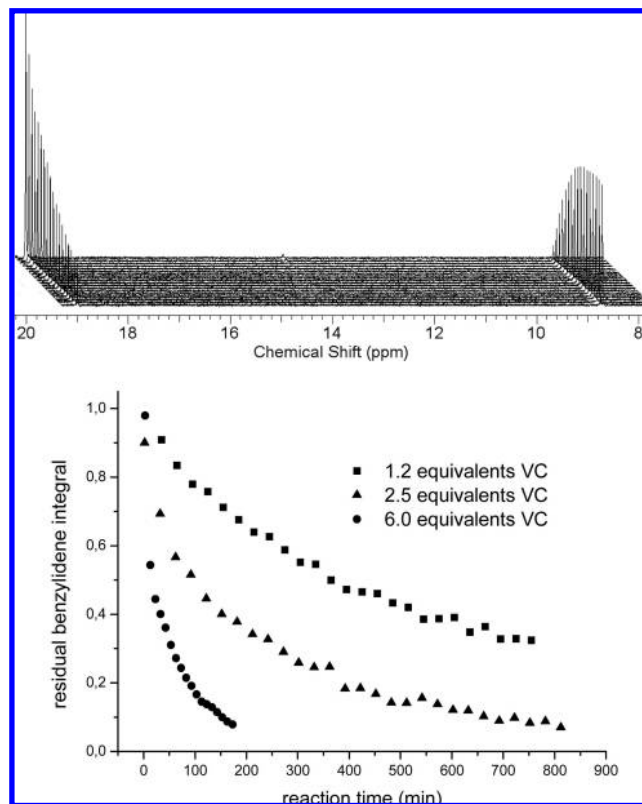


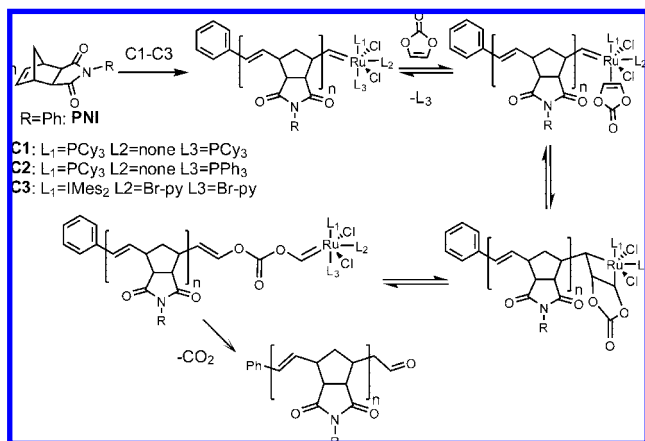
Figure 2. Reaction between benzylidene catalyst **C1** and VC. Top: Reaction with 8 equiv of VC (time increases from back to front). The time difference between individual ¹H NMR-spectra is 30 min. Bottom: Change of the benzylidene signal in the ¹H NMR spectrum over time for 1.2, 2.5, and 6.0 equiv of VC.

0.026 mmol L⁻¹). The time-resolved ¹H NMR spectrum given in Figure 2 shows the process of the reaction of **C1** with 8 equiv of VC. The benzylidene signal (at 20.05 ppm) slowly diminishes over the course of the experiment (14 h) while the aldehyde signal forms at a similar rate (taking into account proton–deuterium exchange). A Fischer-carbene type intermediate can only be seen at the very beginning of the reaction, where the formation of the intermediate is faster than its decomposition. With higher excesses of VC, this carbene can be monitored for a longer period which shows that the formation and decomposition reaction steps are not concerted.

When the same reaction is carried out between catalyst **C2** and VC, the reaction is much slower than with catalyst **C1**. The reaction rate is strongly dependent on the amount of PPh₃ added to regulate the catalyst’s activity. For **C2**, the equilibrium of phosphine dissociation, which is a key step for metathesis activity, is shifted toward the coordinated species. Because of the low reaction rate, no intermediates could be found by ¹H NMR spectroscopy.

Adding VC to catalyst **C3**, the benzylidene signal in the ¹H NMR spectrum disappears five times faster than in the case of catalyst **C1**. Two intermediate species can be found in the ¹H NMR spectrum. The signal at 17.9 ppm presumably represents the ruthenium complex carrying VC as a ligand (see Supporting Information). The same observation is made with initiated catalyst **C3**. The resonance of the Fischer carbene can be found at 14.3 ppm as expected, while the aldehyde group gives a signal at 9.6 ppm. Again, the decomposition of the Fischer carbene is faster than its formation, so the signal of this intermediate state is small and vanishes over time.

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Scheme 2. Mechanism of the Termination of Ruthenium Carbene End Groups with VC

Upon initiation of the three catalysts **C1**, **C2**, and **C3** with PNI, the reaction with VC becomes much faster. The reactivity increase is caused by electronic effects as the rather stable benzylidene is replaced with a more reactive alkylidene.²⁷

Addition of equimolar amounts of VC terminates the PNI-initiated catalyst **C1** much more rapidly than benzylidene catalyst **C1**. However, the determination of stoichiometrical factors is difficult because of incomplete initiation of **C1** even with 15 equiv of monomer (PNI).

PNI-initiated catalyst **C2** reacts with VC at a rate similar to the uninitiated (benzylidene) catalyst **C1**. Both active species present in this catalytic system (18.7 ppm with PPh₃ dissociated and 17.6 ppm with PCy₃ dissociated, see Supporting Information)³⁴ react at a similar rate. No Fischer-carbene intermediate could be observed by ¹H NMR spectroscopy; however, aldehyde formation proceeded cleanly.

The reaction between PNI-initiated catalyst **C3** and VC is extremely fast. Different reaction stages can be found in the ¹H NMR spectrum. Similar to the uninitiated (benzylidene) catalyst **C3**, the PNI-initiated catalyst forms a complex with VC quantitatively within 5 min (carbene signal at 17.3 ppm, see Supporting Information) with little more than 1 equiv of the terminating agent (VC) added. This complex then forms the intermediate Fischer carbene before decomposing to the aldehyde functionalized polymer chain.

In order to prove the formation of the proposed carbide complex (Scheme 1), ¹³C NMR spectroscopy was performed on the reaction mixture of the above experiments. A carbon signal at 472 ppm could be detected. This matches the signal reported by the first group to synthesize **C4** (see Supporting Information).³⁵

The mechanism for the termination reaction with VC is shown in Scheme 2. All intermediate steps proposed in Scheme 2 represent species that would be expected from the generally accepted mechanism of ruthenium catalyzed olefin metathesis.³⁶ All intermediates (except for the metalla-cyclobutane transition state) could be observed by ¹H NMR spectroscopy (see above).

Table 1. Termination Constants with VC^{a,b}

catalyst	equiv of PPh ₃	equiv of PNI	k _t L/mol·s
C1	0	0	0.073
C1	0	20	0.117
C2	3.4	0	<0.001 ^a
C2	3.4	20	0.065
C2	1.2	20	0.104
C3	0	0	0.366
C3	0	20	>100 ^b

^a Too slow to determine half life within 14 h measurement. ^b Too fast to be measured by ¹H-NMR spectroscopy (t_{1/2} below 30 s).

Kinetic measurements were repeated at different concentrations of VC. The termination reaction proceeds with first-order kinetics with respect to the terminating agent (VC). The overall kinetics are expected to be second order; however, reactions on a polymer chain end typically suffer from steric hindrance and diffusion phenomena. From as little as 4–6 equiv of VC with respect to ruthenium carbene end groups, reactions followed a pseudo-first-order behavior. In order to determine the kinetic rate constants, second-order kinetic constants were calculated from the pseudo first-order constants obtained from integration of the benzylidene signals over time, according to literature procedures.³⁷ Kinetic constants derived from the time-resolved ¹H NMR spectroscopic measurements are summarized in Table 1. In all cases with initiated catalysts, reactions reached complete conversions even with small excesses of VC. The ¹H NMR spectra indicated no side reactions.

For polymer synthesis the degree of functionalization and the molecular weight distribution are key factors. Catalysts **C1–C3** are known to polymerize many strained olefins in a living manner, yielding polymers with narrow molecular weight distributions. In order to achieve full termination and chain-end functionalization, chain transfer, reinitiation, and nonfunctionalizing side reactions have to be excluded. Because of the nature of the termination reaction with VC, chain transfer and nonfunctionalizing termination can be excluded if the quenching reaction is given time to complete.

Reinitiation of monomer with a carbide complex is a known phenomenon although it requires the addition of a strong acid. A moderate rate of termination is undesirable, as it can lead to considerable broadening of the molecular weight distribution in cases where the polymerization was incomplete at the time the quenching agent was added. In order to facilitate the termination of polymer chains, 10–20 fold excesses of the terminating agent can be applied. If instant termination of all metathesis activity is needed, a large excess of the terminating agent (>50 equiv) has to be added.

The intermediate Fischer-carbene chain end itself represents a vinyl ester which could, in theory, undergo a second metathesis reaction with a living chain end. This side reaction would yield two coupled polymer chains with no functional group at the chain end. The results of our kinetic study of the termination reaction, however, render the probability of this reaction diminishingly small since the decomposition of this carbene is faster than its formation so that the concentration of this intermediate is extremely low. In addition, we found no evidence for the formation of stilbene as a coupling product in reactions with uninitiated (benzylidene) catalysts.

A number of polymers of PNI with different molecular weights were synthesized and functionalized with this method.

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Table 2. GPC-RI Results for Aldehyde-Terminated Polymers

entry	catalyst	<i>n</i>	<i>M_n</i> (theor)	<i>M_n</i> (GPC)	<i>M_w</i> (GPC)	PDI
1	C1	18	4420	7500	9500	1.25
2	C1	25	6010	9000	10800	1.20
3	C1	60	14450	15500	18600	1.20
4	C2	10	2500	2500	3000	1.17
5	C2	12	2980	3000	3600	1.20
6	C2	18	4420	4600	5500	1.20
7	C2	50	12070	12600	14100	1.12
8	C3	18	4420	4600	4900	1.07

GPC analysis of the resulting materials gave narrow molecular weight distributions typical of catalysts **C1**–**C3** as summarized in Table 2. The average molecular weight of the polymer matches the calculated values as expected from a living polymerization. In the case of catalyst **C1**, it has to be noted that the initiation efficiency is <1 as known from literature when aiming for low molecular weight polymers.³⁴ Any occurrence of broadened molecular weight distributions or higher molecular weight shoulders can be linked to incomplete polymerization reactions before the end-capping agent is added. In this case, unreacted chains continue to polymerize any residual monomer until all catalytic centers have been terminated. This can be avoided by addition of larger excesses of VC (see below).

Aldehyde ¹H NMR signals often give lower integrals than expected because of proton–deuterium exchange. Therefore, the total degree of functionalization was determined by absence of nonfunctional end groups and also by derivatization of the terminal aldehyde with 2,4-dinitrophenylhydrazine to give the respective hydrazone. In order to terminate all residually active catalyst, ethyl vinyl ether was added after the termination reaction with VC was finished. The terminal olefinic end groups produced by the reaction with ethyl vinyl ether can easily be detected by ¹H NMR spectroscopy as demonstrated in Figure 3.

The derivatization reaction with 2,4-dinitrophenylhydrazine gave distinct end-group signals that could be evaluated quantitatively in the ¹H NMR spectra and compared to the end-group signals generated by the initiator (c.f. Supporting Information, S-8 for further details). Integration of the respective proton signals confirmed degrees of functionalizations exceeding 95%.

In addition, MALDI-ToF MS showed attachment of an aldehyde end group to the polymer. As shown in Figure 4, the obtained mass spectrum reflects almost exclusively the aldehyde-functionalized polymer chains. The mass difference between signals corresponds to the molecular weight of the PNI repeat unit. The minor peaks represent polymer chains with an olefinic end group produced by termination with ethyl vinyl ether. However, the total amount of these chains is extremely low (invisible by NMR and <1% by MALDI ToF MS).

The functional group produced by addition of VC is set free during the course of the catalyst deactivation reaction without the need of further chemical transformations. This is a distinct advantage over the classical molybdenum-initiated ROMP polymerizations which cannot tolerate the unprotected functional group. In the case of molybdenum-initiated ROMP, the newly formed terminal aldehyde would undergo a secondary termination reaction giving incompletely functionalized and partially coupled polymer chains.

Vinylene carbonate is a particularly fast and efficient functionalizing agent for ROMP using ruthenium initiators. The reaction is applicable not only to small molecules, but also to polymer chemistry. It proceeds by selectively attaching exactly one aldehyde group onto every polymer chain end.

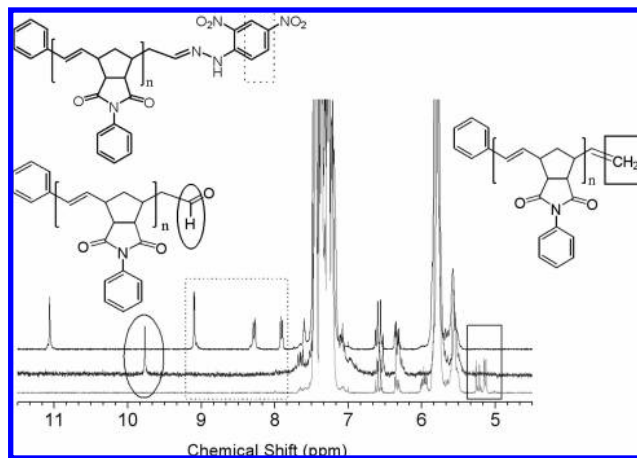


Figure 3. ¹H NMR spectroscopic (CDCl₃) determination of the degree of functionalization. Middle: poly(PNI)-CHO; top: 2,4-Dinitrophenyl hydrazone of poly(PNI)-CHO; bottom: poly(PNI)=CH₂ (all polymers, entry 6, Table 2).

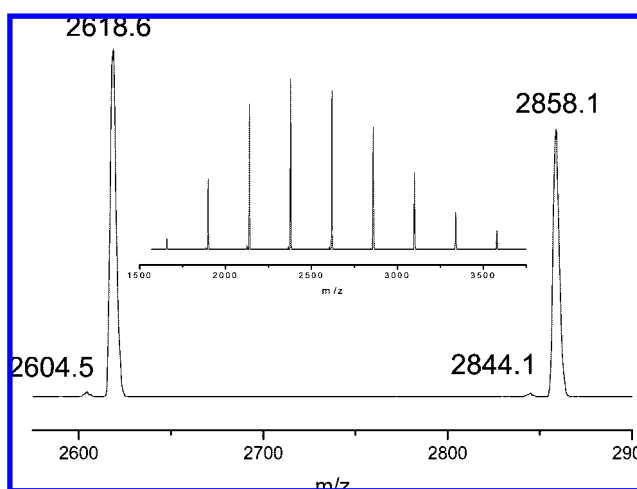
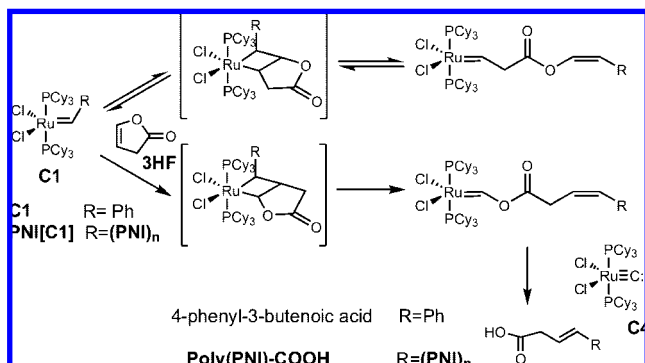


Figure 4. MALDI-ToF MS of aldehyde functionalized poly(PNI) (entry 5, Table 2).

In order to prove that polymer functionalization with VC can be performed on highly functionalized polymers, the polymerization of *exo-N*-(2-hydroxyethoxy)ethyl-2,3-norbornenedicarboximide (HEENI) was initiated with **C1** and terminated with VC, giving a polyalcohol bearing exactly one aldehyde group on every chain end (see Supporting Information, S-9).

Functionalization with 3H-Furanone. 3H-Furanone (3HF) is an asymmetric vinyl lactone, which can be easily synthesized in one step by the Baeyer–Villiger oxidation of furfural.³⁸ Given its lower degree of conjugation within the five-membered ring, it is expected to react more readily with ruthenium metathesis catalysts than VC. However, as 3HF does not carry a symmetrically substituted double bond, the question of regioselectivity during the metathesis step is immanent. As shown in Scheme 3, two transition states of the metathesis step can be proposed, which lead to different products. Only the metathesis step leading to a Fischer-type carbene (Scheme 3, bottom pathway) is irreversible and leads to the desired acyl carbene which can subsequently decompose to release the acid functionality. The second pathway (Scheme 3, top), leading to another alkyl carbene, is reversible with the reverse reaction

(38) Näsman, J.-A. H.; Pensar, K. G. *Synthesis* **1985**, 786–788.

Scheme 3. Proposed Mechanism for the Termination of **C1** with 3HF

leading to a five-membered ring. This equilibrium should force the overall reaction into the Fischer-carbene pathway ensuring high degrees of functionalization. Upon treatment with 3HF, catalyst **C1** showed the same color change as with VC, indicating a similar carbide-complex formation.

In order to determine the kinetics of this reaction, the progress of the transformation with a predetermined amount of 3HF was followed by time-resolved ^1H NMR spectroscopy. Upon addition of the quenching agent (3HF) to catalyst **C1**, the benzyldene signal vanished at a rate seven times higher than for VC (Figure 5, top). The intermediate Fischer carbene could be observed initially, confirming that the decomposition of this carbene is faster than its formation under these conditions (see Figure 5, top). The signal representing the carboxylic acid proton of the newly formed 4-phenyl-3-butenic acid is very weak owing to rapid proton exchange with the deuterated solvent during the course of the reaction. If the same reaction is carried out with catalyst **C1** initiated with PNI, the termination reaction is more than 10 times faster.

With initiated catalyst **C2**, a termination rate could be observed that is in the same range as uninitiated catalyst **C1**. In this case, the signal of the carboxylic acid group formed on the polymer chain end can be detected in the ^1H NMR spectra (see Supporting Information).

When the termination reaction was carried out on the 3-bromopyridine complex **C3**, the reaction rate jumped to 30 times the value of catalyst **C1**. This effect was even increased when the catalyst was initiated with PNI. In this case, even with low excesses (1.2 equiv) of 3HF, the reaction proceeded at such a high rate that several half-lives had passed by the time the sample had been placed in the spectrometer (see Supporting Information). Interestingly, in this case, the formation of the Fischer carbene was much faster than its decomposition leading to an intense signal of this intermediate.

During the course of the reactions, no evidence for the presence a second carbene was found that would represent the regioisomer of the Fischer carbene as described in Scheme 3. Therefore, this pathway of the proposed mechanism of 3HF-functionalization can be excluded. The slightly higher amounts of Fischer carbene observed during the time-resolved ^1H NMR spectroscopic measurements with 3HF compared to VC can be linked to the higher rate of formation of the intermediate due to electronic factors.

The time dependence of the catalyst deactivation could be shown by plotting the integrals of the carbene signals against time (Figure 5, bottom). Similar to the termination reaction with VC, all reactions showed second-order overall kinetics and

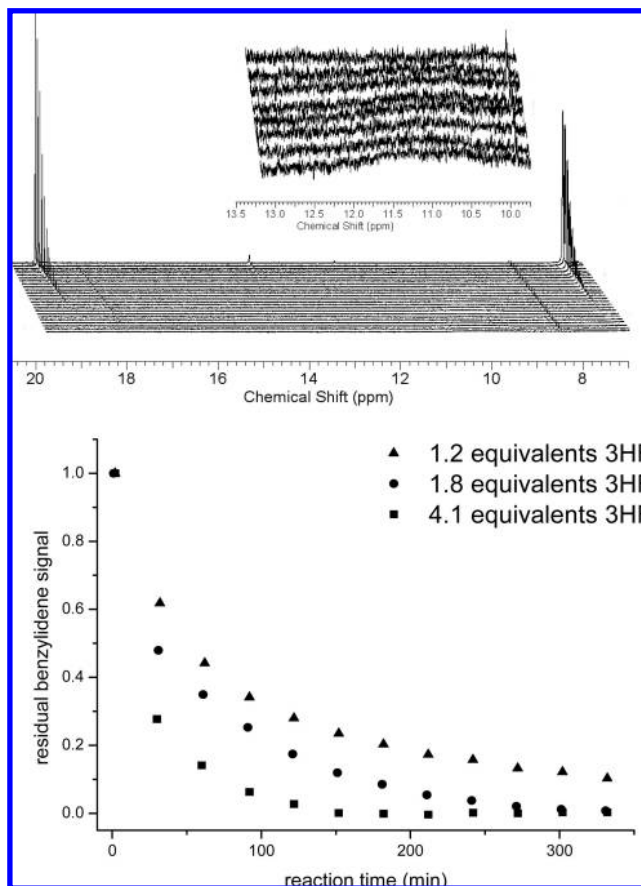


Figure 5. Reaction of benzyldene catalyst **C1** with 3HF. Top: Reaction with 4 equiv of 3HF (from back to front). The time difference between individual ^1H NMR-spectra is 30 min. Bottom: Change of the benzyldene signal in the ^1H NMR spectrum over time for 1.2, 1.8, and 4.1 equiv of 3HF.

Table 3. Initiation Constants with 3HF

catalyst	equiv of PPh ₃	equiv of PNI	k_t L/mol · s
C1	0	0	0.327
C1	0	20	3.56
C2	7.8	20	0.236
C3	0	0	11.7
C3	0	20	> 100 ^a

^a Too fast to be measured by ^1H NMR spectroscopy ($t_{1/2}$ below 30 s).

exhibited pseudo-first-order behavior when greater 4–6 equiv of 3HF were employed. All reactions were first order with respect to the concentration of the quenching reagent (3HF). In order to calculate rate constants for the termination reaction, second-order constants were calculated from the pseudo-first-order constants obtained by integration of the benzyldene signals over time. All kinetic constants obtained are summarized in Table 3. With initiated catalysts, reactions reached 100% conversion even with small excesses of 3HF and without any observed side reactions.

The functionalization of polymers with 3HF proceeds in the manner outlined in Scheme 4. All intermediates with the exception of the metallacyclobutane transition state could be observed during kinetic measurements.

With ruthenium-carbido complexes being able to be reactivated to extremely metathesis-active carbenes by strong acids, the question could arise as to whether the acid end group that is formed by this reaction is strong enough to reactivate the

Scheme 4. Polymer Functionalization with 3HF and Attachment of a Pyrene Chromophore

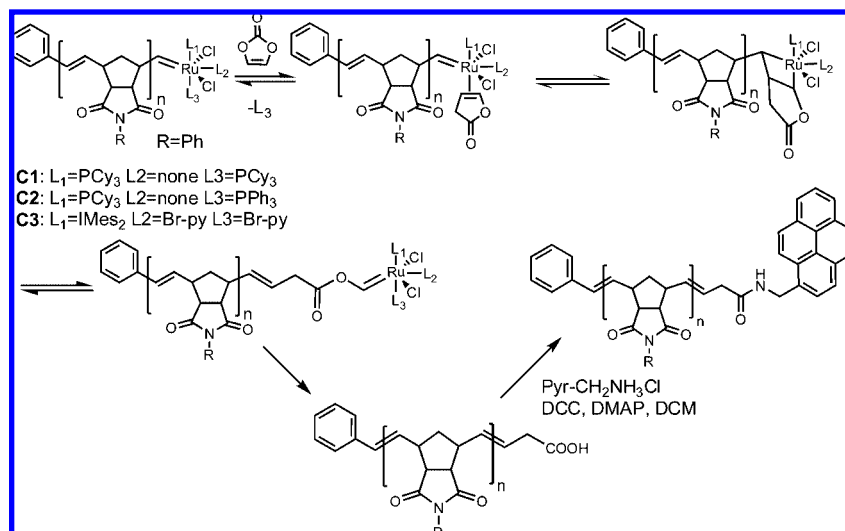


Table 4. GPC-RI Results for Poly(PNI)-COOH with Different Catalysts

entry	catalyst	<i>n</i>	<i>M_n</i> (theor)	<i>M_n</i> (GPC)	<i>M_w</i> (GPC)	PDI
9	C1	18	4400	8400	10500	1.25
10	C1	25	6100	9300	11300	1.22
11	C1	50	12000	13300	15900	1.20
12	C2	18	4400	4400	5200	1.14
13	C2	25	6100	6200	7000	1.14
14	C2	50	12000	12600	14200	1.12
15	C3	18	4400	4300	4700	1.08

catalyst. During kinetic measurements, no signals were found that could be assigned to such a newly formed carbene proton.

3HF functionalization was deployed on an array of polymers, initiated by different catalysts and varying in molecular weight, in order to demonstrate the versatility of the method and the applicability to different catalytic systems. GPC analyses of the resulting polymers are summarized in Table 4. All polymerizations gave narrow molecular weight distributions typical of catalysts C1–C3, and the average molecular weight could be controlled by the monomer-to-initiator ratio as expected for living polymerizations. This also demonstrates that no undesired metathesis reactivation by the carboxylic acid end group occurred.

Similar to the reaction with VC, the termination reaction with 3HF is slower than the polymerization of typical metathesis monomers based on norbornene derivatives. In order to obtain molecular weight distributions as narrow as possible, either full monomer conversion has to be reached before the terminating agent (3HF) is added or a large excess (20–50 equiv) has to be added in order to terminate the metathesis reaction instantly.

In order to confirm that the attachment of an acid functionality to the polymer chain, this end group was derivatized with a chromophore. 1-Pyrenemethylamine hydrochloride was reacted to the terminal polymeric carboxylic acid using standard coupling chemistry, employing the well-established dicyclohexylcarbodiimide/*p*-dimethylaminopyridine system. Detection of the chromophore was performed by GPC-UV detection at the absorption maximum of the dye (340 nm). The presence of a signal in the polymer region proved the attachment of the amine to the polymer and hence the presence of a carboxylic acid (Supporting Information).

The total degree of functionalization with 3HF can be determined by the absence of nonfunctional groups in the ¹H NMR spectrum and by esterification of the terminal carboxylic acid with an alcohol, giving distinct ¹H NMR signals. 2,2,2-Trichloroethanol was chosen for esterification since its methylene protons can be easily detected and analyzed quantitatively (cf. Figure 6). ¹H NMR quantification of the trichloroethyl ester and comparison to the styryl end group generated by the initiator typically gave total degrees of functionalization >97% (cf. Supporting Information, S-13) This derivatization reaction as well as the one described above (see Figure 3) shows clearly that terminating with excess ethyl vinyl ether after functional capping with either VC or 3HF is sufficient to evaluate the degree of end functionalization by ¹H NMR.

The MALDI-ToF mass spectrum of polymers functionalized by 3HF shows signals at masses that represent functionalized polymer chains exclusively. Olefin-terminated polymer chains could not be detected. Minor signals between the expected poly(PNI)-COOH signals most likely represent macromolecules with neutralized chain ends (Figure 7). These signals could not be assigned to any intermediate, side product, or the product of regioisomeric metathesis reactions of the 3HF.

The feasibility of this functionalization reaction could be shown by functionalizing poly(norbornene-5-carbaldehyde)

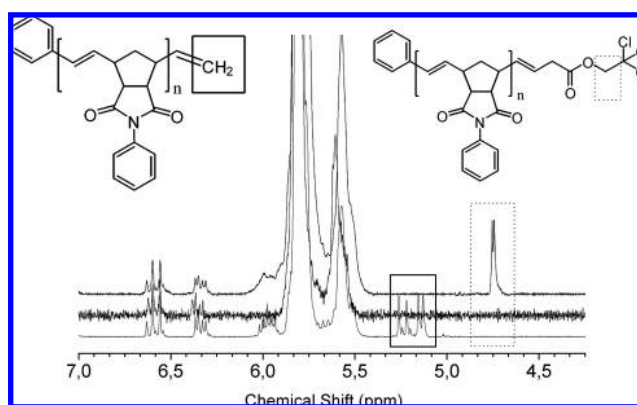


Figure 6. ¹H NMR spectroscopic characterization (CDCl₃) of degree of functionalization. Middle: poly(PNI)-COOH, Top: Trichloroethyl ester of poly(PNI)-COOH; bottom: Poly(PNI)=CH₂ (all polymers, entry 13, Table 4).

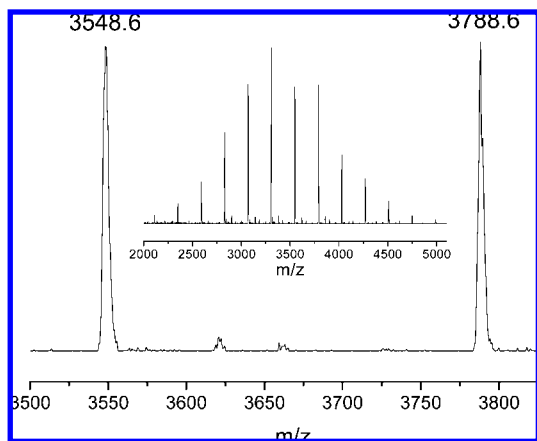


Figure 7. MALDI-ToF MS of acid functionalized poly(PNI) (entry 12, Table 4).

(initiated with **C3**) giving carboxylic acid functionalized poly-aldehydes with excellent degrees of chain-end functionalization (ca. 95%, see Supporting Information, S-14).

3*H*-Furanone (3HF) can therefore be seen as a versatile functionalizing reagent for ROMP polymers. It terminates the catalytically active chain end efficiently and selectively. The formation of the terminal carboxylic acid functionality proceeds smoothly while the former catalytic center is cleaved off the polymer chain simultaneously. As with VC, 3HF quenching can not be performed on molybdenum-initiated ROMP polymerizations since free carboxylic acids are incompatible with these catalysts.

Experimental Section

General. ^1H NMR spectra were recorded at 300 MHz on a Bruker AC300 or a Bruker AMX400, and kinetic ^1H NMR was conducted on a Bruker ARX400. ^{13}C NMR spectra were measured on a Bruker DRX400 at 100.15 MHz. All spectra were referenced internally to residual proton or carbon signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Gel permeation chromatography in chloroform was performed on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P100 pump and a set of three PSS SDV columns ($10^4/500/50 \text{ \AA}$). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm unless otherwise stated) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service. Field desorption mass spectra were measured on a Finnigan MAT 95. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) measurements were performed on a Shimadzu Axima CFR MALDI-TOF mass spectrometer equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Dithranol (1,8-dihydroxy-9(10*H*)-anthracetone, Aldrich 97%), was used as matrix. Potassium (Aldrich, 98%) or silver trifluoroacetate (Aldrich, 99.99%) were added for ion formation. Best results were obtained for samples which were prepared from THF solution by mixing matrix (10 mg/mL), polymer (10 mg/mL), and salt (0.1 N solution) in a ratio of 10:1:1. A volume of 0.9 μL was given onto the MALDI sample slide and allowed to dry at room temperature for 2 h prior to measurement.

exo-N-Phenyl-2,3-norbornenedicarboximide and other monomers were synthesized as described in earlier publications. Vinylene carbonate was purchased from Aldrich and used as received, Grubbs first and second generation catalysts were obtained from Materia, Inc. The bromopyridine complex **C3** was synthesized as described

elsewhere.³⁹ All solvents and other reagents were purchased from Acros. All polymerization reactions were carried out under nitrogen using Schlenk techniques. Dichloromethane as the solvent was dried over P_2O_5 and freshly distilled under nitrogen. 3*H*-Furanone was obtained in good yield and purity as described by Näsman et al.³⁸

Preparation of Kinetic ^1H NMR Samples. A 15 mg (18 μmol) amount of **1** was added to 0.7 mL of dichloromethane- d_2 in a nitrogen-filled glovebox. In cases where a phosphine was added, the applicable amount of PPh_3 was added to this solution and was allowed to stand for 15 min. The solution was transferred into an NMR tube, which was sealed with a rubber septum. Upon measurement of a reference spectrum, the quenching reagent (1.2 μL of vinylene carbonate or 1.3 μL of 3*H*-furanone for 1 equiv) was added by microsyringe, and kinetic measurement was commenced immediately. Formation and decomposition of the Fischer carbene was monitored by ^1H NMR spectroscopy in the 13–15 ppm region.

General Procedure for the Synthesis of Poly(PNI)-CHO and Poly(PNI)-COOH with Grubbs First Generation Catalyst (C1**).** A solution of the monomer in dry, degassed dichloromethane (1 mL per 100 mg monomer) was added to an equal volume of a rapidly stirred dichloromethane solution of the calculated amount of catalyst at r.t. After the polymerization reaction was well finished (ca. 1 h for 5000 g/mol), a large excess of the quencher was added (50 equiv of vinylene carbonate or 20 equiv of 3*H*-furanone) and the stirring was continued until the solution had turned yellow (formation of **C4**). The Fischer carbene was not isolated, and no further addition of reagents was needed to induce decomposition to the functional group and complex **C4**. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (> 100 equiv) and stirring was continued for another 30 min. The resulting polymer was precipitated in methanol. The collected solids were redissolved in chloroform, reprecipitated in methanol, collected, and dried under vacuum overnight, affording a colorless polymer material in good yield (>90% typical).

General Procedure for the Synthesis of Poly(PNI)-CHO and Poly(PNI)-COOH with Catalyst **C2.** To a stirred dichloromethane solution of the calculated amount of catalyst (5 mL dichloromethane per 100 mg of catalyst) was added twice the mass of PPh_3 (6.3 equiv) at r.t. The mixture was allowed to react for 15 min before a solution of the monomer in dichloromethane (1 mL per 100 mg monomer) was added. After the polymerization reaction was finished (ca. 8 h for 5000 g/mol), a large excess of the quencher was added (50 equiv of vinylene carbonate or 20 equiv of 3*H*-furanone) and stirring was continued overnight or until the solution had turned yellow. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (> 100 equiv) and stirring was continued for another 2 h. The polymer was precipitated in methanol, collected, redissolved in chloroform, reprecipitated in methanol, collected, and dried under vacuum overnight to give a virtually colorless solid in good yield (>90% typical).

General Procedure for the Synthesis of Poly(PNI)-CHO and Poly(PNI)-COOH with Bromopyridine Poly Complex (C3**).** A solution of *exo-N*-Phenyl-2,3-dicarboximide in dry, degassed dichloromethane (1 mL per 100 mg monomer) was added to an equal volume of a rapidly stirred dichloromethane solution of the calculated amount of freshly prepared catalyst **3** at r.t. After the polymerization reaction was finished (ca. 15 min for 10 000 g/mol), an excess of the quencher was added (20 equiv of vinylene carbonate or 10 equiv of 3*H*-furanone) and the stirring was continued until the solution had turned yellow. In order to terminate all residual living chains, a large excess of ethyl vinyl ether was added (> 100 equiv) and stirring was continued for another 10 min. The polymer was precipitated in methanol and collected. The solids were redissolved in chloroform, reprecipitated in methanol, col-

(39) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035–4037.

lected, and dried under vacuum overnight to give a colorless solid in good yield (>90% typical).

Synthesis of Poly(PNI)-CONH-CH₂-Pyrene. A mixture of 50 mg of poly(PNI) ($M_n = 4400$, PDI = 1.13 (RI detection); 11.4 μmol), 20 mg (84 μmol) of 1-pyrenemethylamine hydrochloride, 50 mg (242 μmol) of dicyclohexylcarbodiimide, and 50 mg (409 μmol) of 4-dimethylaminopyridine was weighed into a 50 mL Schlenk flask, degassed, and dissolved in 10 mL of dry dichloromethane. After being stirred at r.t. for 14 h, the turbid mixture was concentrated at the rotary evaporator, taken up with a small amount of chloroform, and precipitated in methanol. The resulting solids were collected and dried in vacuo yielding 40 mg (ca. 80%) of a colorless material. GPC: $M_n = 4200$, PDI = 1.13 (RI detection).

Conclusions

Both, vinylene carbonate (VC) and 3*H*-furanone (3HF) are powerful end-capping reagents for ruthenium-catalyzed ROMP. As vinyl lactones have not been used for the functionalization of polymers to date, they represent a new class of single-turnover metathesis functionalizing reagents. Both new quenching agents represent five-membered cyclic molecules, that combine an easily cleavable lactone with an electron-deficient all-cis double bond. This reduces the steric hindrance for the coordination of the olefin to the metal center. The self-deprotection of the functional group caused by the instability of the intermediate acyl carbene makes this innovative method uniquely versatile and exclusive to ruthenium-based ROMP catalysis.

Methods have been developed to quantify the total degree of functionalization by classical derivatization reactions. The functionalization efficiency of both VC and 3HF could be shown to be extremely high or even quantitative. The simpler determination method of the degree of functionalization involving secondary termination with ethyl vinyl was proven to give reliable functionalization values.

In addition, further polymer analogous transformations become obsolete as the ring-opening metathesis reaction of the quenching agent triggers its decomposition into a ruthenium carbide complex and the functionalized polymer chain end. Our study on the two reagents VC and 3HF could show both the selectivity and the efficiency of the catalyst deactivation and polymer functionalization.

In addition, VC is the first commercially available end-capping reagent for the metathesis polymerization that installs a functional group on the polymer chain end. The regioselectivity of the metathesis step is not critical because of the symmetry of the double bond in VC.

The second end-capping reagent, 3HF, which is readily available in one step from furfural, has demonstrated high regioselectivity during the metathesis step, thus producing carboxylic acid-functionalized polymer chain ends exclusively. As carboxylic acids represent one of the most interesting functional end groups that can be attached to a polymer, we believe that this functionalization method is of great synthetic value.

The progress of the functionalization reactions with VC and 3HF is independent of the nature of the ruthenium-alkylidene or -benzylidene as could be shown using a variety of different catalyst systems. As no further chemical transformation is needed to release the functional end group, even sensitive and labile functional groups can be present along the main chain of the polymer. Therefore, the functionalization with the two vinyl lactones presented here can be expected to be generally applicable.

Finally, the versatility of vinyl lactone functionalization, virtually eliminating the need for workup and further deprotection steps, together with the ready availability of the quenching reagents, renders this new method extremely useful for polymer science.

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Supporting Information Available: Experimental procedures, UV-spectroscopic data, ¹H NMR spectra, GPC traces, and kinetic NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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