208 *Macromolecules* **2010**, *43*, 208–212
DOI: 10.1021/ma902074y

Macromolecules
ARTICLE

Heterotelechelic Ring-Opening Metathesis Polymers

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Received September 17, 2009; Revised Manuscript Received November 2, 2009

ABSTRACT: By combining sacrificial synthesis with the vinyl lactone termination technique, heterotelechelic polymers were synthesized. The nonterminating nature of sacrificial synthesis was utilized to introduce a hydroxyl group at the start of the polymer chain. Lactone termination was used to functionalize the chain ends with aldehydes or carboxylic acids. The synthesis of well-defined heterotelechelic polymers was thus accomplished employing the Grubbs' first generation catalyst as the initiator. The living nature of this polymerization allowed for precise control over the molecular weight and guaranteed full functionalization of both polymer chain ends. The presence of the functional groups is shown by MALDI-ToF and NMR measurements. Also, labeling experiments with chromophores were conducted to demonstrate the utility of such heterotelechelic polymer chains.

Introduction

The synthesis of heterotelechelic polymers is a particularly sophisticated aspect of macromolecular synthesis research. In contrast to their simpler homotelechelic relatives, i.e., those polymer chains carrying identical functional groups at either chain end, this class of materials carries different reactive end groups on both chain ends. In the case of orthogonal reactivity this allows the chemist to address and functionalize either chain end individually. Precision in placement of functional groups is the basis for the synthesis of complex macromolecular architectures from heterotelechelic starting materials. In addition, such materials are of tremendous relevance in many other fields of research such as materials and life sciences. Heterotelechelic polymeric materials can for example be used to covalently link different molecules such as biologically active peptides or receptor sites[1] with e.g. fluorescent labels or proteins.[2] However, not only interdisciplinary applications but also polymer synthesis requires strategies for the synthesis of heterobifunctional polymer chains. They can act as linkers between different synthetic macromolecules or as building blocks in block copolymer synthesis. They are also employed for the construction of a number of interesting polymeric architectures.[3]

Most heterotelechelic syntheses rely on living polymerization methods. Carb-anionic[4] and oxy-anionic[5] polymerization methods are among the most utilized strategies for the formation of heterotelechelic polymers. This trend is mainly caused by the availability of appropriate functional termination agents which provide access to the chain-end functionality. This polymerization technique, however, also offers the potential for introducing functional groups at the start of every polymer chain using functional initiators.[6]

Furthermore, strategies for the use of controlled radical polymerization techniques for the synthesis of heterotelechelic polymers have been developed.[7] They make use of the relatively high functional group tolerance of the radical polymerization and therefore often do not require protective groups. Yet, even free radical polymerizations have been employed to prepare telechelic polymers.[8]

Less well-defined telechelic polymers can be synthesized by step-growth polymerizations.[9] Polycondensation and polyaddition polymers are easily accessible and typically give extremely high degrees of chain-end functionalization. Nonetheless, they typically give broad molecular weight distributions and little control over the average chain length.

Telechelic polymers can also be prepared via the ring-opening metathesis polymerization (ROMP). Three different approaches are known to date, using two different synthetic methods. Using chain-transfer agents (CTA), homobifunctional olefins have been synthesized with a broad variety of functional groups including carboxylic acids, alcohols, and amines.[10] Statistical copolymers of ROMP monomers with cyclic olefins containing a cleavable site such as an acetal also gave telechelic polymers after hydrolysis.[11] Both approaches, however, are strictly limited to homobifunctional telechelics due to the low regioselectivity of ROMP. Also, they give ill-defined polymeric materials with respect to molecular weight distributions. Both methods rely on statistical polymerizations or equilibration reactions which inevitably lead to a broader molecular weight distribution. The third method is based on the concept of sacrificial synthesis for the placement of hydroxyl groups at polymer chain ends. There, the controlled formation of (multi)block copolymers of sacrificial and hydrolysis stable monomers gives rise to well-defined telechelic polymers.[12]

Over the past 3 years, we have reported various strategies for the functionalization of ROMP polymers.[13] The aforementioned unique sacrificial synthesis[14] strategy does not require a termination reaction for the placement of the functional group, in contrast to the established quenching reactions involving vinyl ethers.[15] Chain-end functionalization in sacrificial synthesis relies on a macroinitiation step.[16] The living chain end retains its activity and can be used to polymerize additional polymer blocks. Cyclic acetals were introduced for the formation of hydroxyl end groups; the use of dithiepines could be employed in generating thiol end groups.[17] Monofunctionalized polymers synthesized by this method have already been used for the synthesis of long-chain branched,[18] graft,[19] and block copolymers.[20]

The second method for precise and efficient functional group placement is based on the termination reaction induced by vinyl lactones.[21] The deactivated Fischer-type carbene in this case represents an acyl carbene which self-decomposes, liberating the functional group and a ruthenium−carbido complex. This method is particularly mild as no work-up or additional deprotection reactions are required.

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 Published on Web 11/16/2009

Here, we present a combination of two different synthetic approaches for the synthesis of heterotelechelic polymers. A polymer synthesis is initiated using sacrificial synthesis in order to introduce a functional group at the beginning of the chain. This is followed by polymerization of a regular monomer and finally by a lactone termination step to introduce the functionality at the chain end.

Results and Discussion

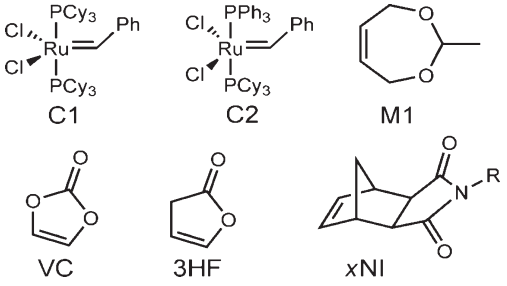
This strategy for the synthesis of heterotelechelic polymers is based on the nondeactivating characteristics of sacrificial block copolymer synthesis for the introduction of functional chain ends (start/end groups). If such a sacrificial block is synthesized as the first block of a block copolymer synthesis, the "start" group of this chain is functionalized. After polymerizing a ROMP monomer to the desired molecular weight, the second chain end can be functionalized easily using the established terminating reactions to give either aldehyde or carboxylic acid groups.

In order to introduce the functional group at the beginning of the polymer chain, a cleavable block was initially polymerized from 2-methyl-1,3-dioxepine (**M1**) using Grubbs' first generation catalyst (**C1**) or its derivative **C2** (Scheme 1) which gives better molecular weight distributions at low molecular weights.[22] These initiators were chosen as they have been proven to be functional group tolerant and stable. Furthermore, they have also been shown to be efficient in block transfer reactions from a dioxepine block to classical ROMP monomer block. Norbornene imides (**DNI**: exo-*N*-dodecyl-2,3-norbornene dicarboximide; **HNI**: exo-*N*-hexyl-2,3-norbornene dicarboximide) were chosen as the stable (nonhydrolyzable) monomer since this class of monomer is highly variable in its imide substituents and can be synthesized easily from the readily available exoanhydride. The termination of the living ruthenium sites on the active chains was conducted by application of vinylene carbonate (**VC**) to generate aldehyde end groups or by addition of 3*H*-furanone (**3HF**) when carboxylic acid end groups were to be attached to the polymer chain ends.

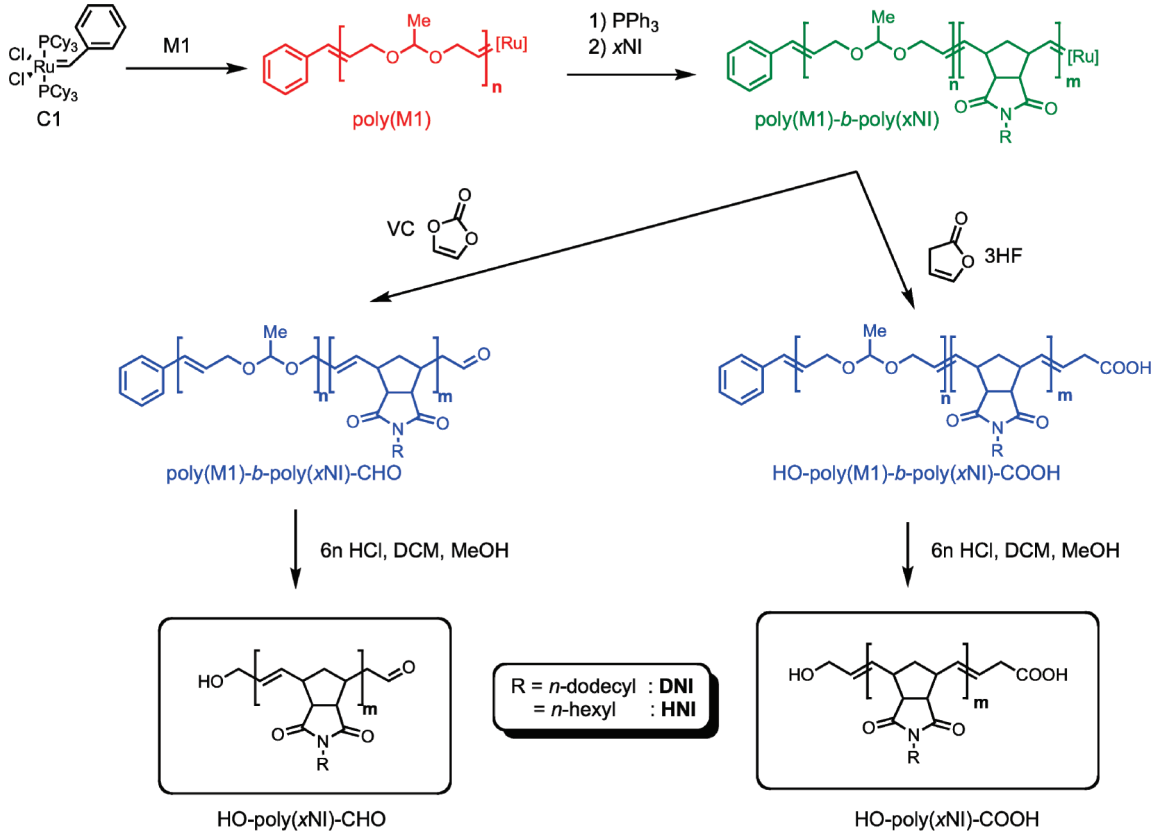
The synthetic pathway leading to heterotelechelic is illustrated in Scheme 2. Here, a methyldioxepine block is polymerized as the first block, the block copolymer is formed by addition of norbornene imide monomers, and termination is facilitated by addition of a vinyl lactone which produces the second functional end group. The first functionality is then liberated by acidic hydrolysis of the poly(**M1**) block cleaving the acetal moieties included in the monomer structure.

In a first attempt, the polymerization of the sacrificial diblock copolymer was carried out using catalyst **C1**. The synthesis of the diblock copolymer worked well, according to a blockwise analysis of the constituting polymer blocks. The polymers were obtained in good definition (PDI ~ 1.2). After acidic hydrolysis of the sacrificial block, however, a material was obtained that showed a significantly broadened molecular weight distribution in all cases (Figure 1). Elevated PDIs of 1.35−1.5 were observed. Apparently, the termination in presence of poly(**M1**) led to side

Scheme 1. Monomers, Initiators, and Terminating Agents Used in This Study (DNI: R = *n*-Dodecyl; HNI: R = *n*-Hexyl)



Scheme 2. Synthesis of Heterotelechelic ROMP Polymers via Sacrificial Synthesis and Lactone Quenching



reactions such as secondary metathesis reactions which we had not observed previously in lactone quenching.[19]

In order to improve the definition of the final polymer, the method of Bielawski was tested, adding an excess of PPh_3 to the polymerization mixture.[20] A test polymerization of **M1**, however, unveiled incomplete polymerization of the acetal monomer after 10 h, presumably due to an extremely slow propagation. An extensive purification of the poly(**M1**) macroinitiator would therefore have been necessary in order to avoid contamination of the second polymer block with residual **M1** monomer which would scramble the stable block into statistically distributed and incorrectly functionalized chains.

Hence, we decided to carry out a combined approach using the polymerization characteristics of **C1** for the **M1** block and making use of the easy conversion from **C1** to **C2**, whose improved polymerization characteristics for norbornene imides should then lead to better polymer definition in the second (stable) polymer block. Again, the stepwise construction of the block copolymer and the termination were monitored by stagewise analysis by SEC. All samples were terminated additionally by conventional ethyl vinyl ether termination in order to avoid further reactions in the analytical samples and to mark the nonterminated and therefore unfunctionalized polymer chains of the final materials with terminal olefins. The SEC traces obtained for the formation of OH/COOH and OH/CHO telechelics are given in Figure 2.

From the block samples, the clean construction of the sacrificial diblock copolymer can be observed. Interestingly, a small decrease in the average molecular weight can be found after termination of the diblock copolymer with **3HF**, which is not observed when the reaction was terminated with **VC**. Considering the chemical nature of the newly formed functional group, a carboxylic acid, a minor hydrolytical decomposition of the **M1** block can be imagined. The acidic cleavage of the sacrificial block worked well and gave exceptionally well-defined heterotelechelic polymers (PDI $\sim$ 1.15).

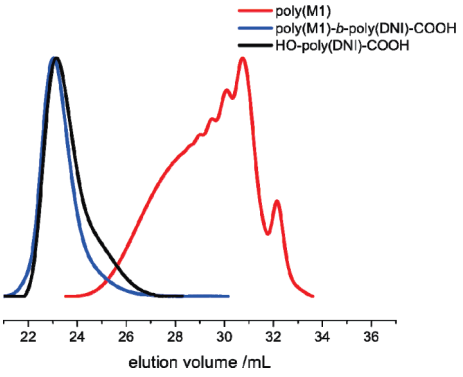


Figure 1. Blockwise SEC (chloroform) analysis of the heterotelechelic polymers initiated by **C1**.

Both functional groups can be found by ^{1}H NMR spectrometry. The spectra given in Figure 3 show examples of both types of heterotelechelic polymers synthesized in this study. As we had shown in the previous publications on the single functionalization methods, the hydroxyl groups introduces by sacrificial synthesis can be characterized by the allyl-protons in the direct neighborhood of the hydroxyl group (δ = 4.14 ppm, integral A in Table 1). The absence of nonfunctionalized chains on the hydroxyl end can be rationalized by the absence of initiator groups, which would give signals in the δ = 6.1−6.6 region caused by the styryl groups introduced by Grubbs' first generation catalyst (integral B in Table 1). This group is cleaved off the polymer chain during the hydrolysis step of sacrificial synthesis when functionalization is successful. The total degree of functionalization of the hydroxyl end of the polymer chains was calculated by comparison of the integral B given by the styryl group signals caused by unsuccessful sacrificial synthesis with the integral for the successfully end-capped polymer chains given by the integral A. Typically, degrees of hydroxyl functionalization of the first chain end ranged from 77% to 96%.

The second functional group on every polymer chain can also be found in the respective spectra (at δ = 9.8 ppm (aldehydes group) or δ = 11.2 ppm (carboxylic acid group)); however, it cannot be quantified due to proton−deuterium exchanges of the particular functional groups with the NMR solvent. The versatility of lactone termination, giving completely functionalized materials has, however, been shown before and is also indicated by the absence of ethyl vinyl ether functionalized chains, which would be detected as two doublets at δ = 5.0−5.1 ppm in the same spectra (integral C in Table 1). Spectral reference information for comparison, including those of nonfunctionalized polymers, can be found in the original publications of the respective functionalization methods.[14,16,21] In order to quantify the success of lactone capping on the second chain end, the integrals of terminal olefins caused by the additional ethyl vinyl ether termination (integral C) were compared to the molecular weight obtained from the same spectra using the backbone olefin signals and all end group signals of the first end. A high degree of functionalization of $>$89% is also demonstrated for the second chain end which, in most cases, even exceeds the degrees of functionalization obtained for the first end group. This effect can be explained by the irreversibility of the functionalization by lactone termination due to the catalyst inactivation during this method.

Furthermore, the heterotelechelic polymers were analyzed by MALDI-ToF MS. Figure 4 shows the spectrum obtained for a poly(**HNI**) heterotelechelic polymer carrying a hydroxyl function and a carboxylic acid. In the case of heterotelechelic

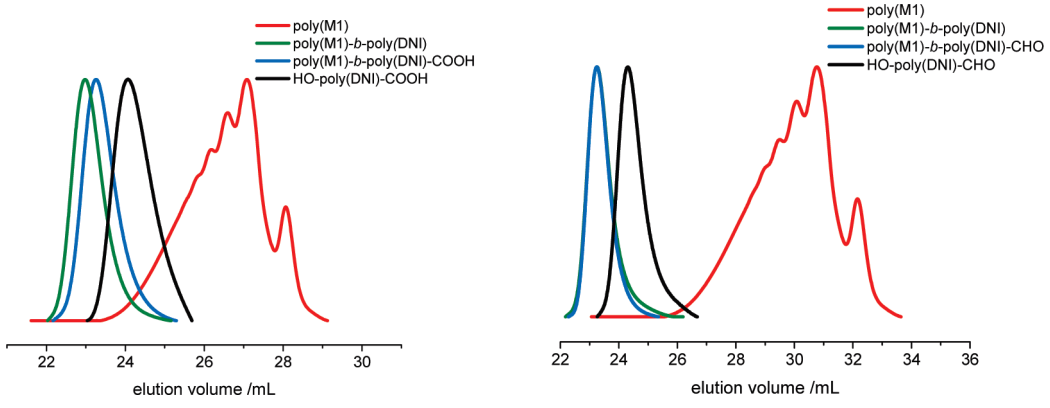


Figure 2. Blockwise analysis of the construction of OH/COOH (left) and OH/CHO (right) heterotelechelic polymers employing catalyst **C2**.

polymers, the carboxylic acid was a sodium salt in contrast to the monofunctional polymers observed in our lactone termination study under the same conditions where the protonated species were detected. No matrix/ionization agent could yet be found for the OH/CHO telechelic polymers.

A number of polymers were synthesized and heterobifunctionalized using this strategy. The characterization results for the various samples are listed in Table 1. The use of catalyst **C2**, which has an increased initiation efficiency when rather short polymer chains are synthesized, allowed for the precise synthesis of defined polymers. We have therefore been able to develop a facile and versatile method for the synthesis of heterotelechelic polymers based on ROMP using commercially available catalysts as well as readily available monomers and functionalization agents.

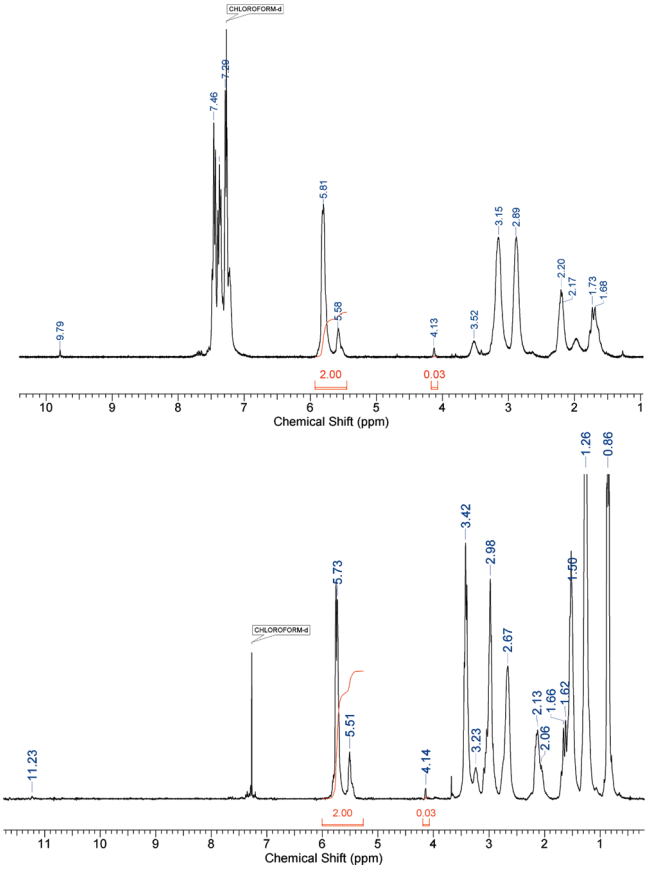


Figure 3. ^{1}H NMR spectra of heterotelic polymers. Top: HO-Poly(**PNI**)−CHO (entry 15 in Table 1). Bottom: HO-Poly(**HNI**)-COOH (entry 3 in Table 1). The functional group signals can be found at δ = 4.1 ppm (CH_2−OH), δ = 9.8 ppm (CHO), and δ = 11.2 (COOH).

Experimental Section

General. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400 MHz on a Bruker ARX400. All spectra were referenced internally to residual proton signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Gel permeation chromatography in tetrahydrofuran or chloroform was performed on an instrument consisting of a Waters 717 plus autosampler, a TSP Spectra Series P100 pump, and a set of three PSS SDV columns ($10^5/10^3/10^2$ Å). 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. 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.

exo-N-Dodecyl-2,3-norbornene dicarboximide (DNI), *exo-N*-phenyl-2,3-norbornene dicarboximide (PNI), and *exo-N*-hexyl-2,3-norbornene dicarboximide (HNI) as well as 2-methyl-1,3-dioxepine (M1) were synthesized as described in earlier publications.[13,18,23] Grubbs' first generation catalyst was obtained from Materia, Inc. All solvents and other reagents were purchased from Aldrich or Acros. All polymerization reactions were carried out under argon using standard Schlenk techniques unless otherwise stated. Dichloromethane as the polymerization solvent was dried over P_2O_5 and distilled under a nitrogen atmosphere. 2-Methyl-1,3-dioxepine was degassed by repeated freeze−pump−thaw−purge cycles using argon as the inert gas.

Synthetic Procedures. *General Procedure for the Synthesis of Heterotelechelic Polymers Using Catalyst **C1***. To a stirred solution of Grubbs' first generation catalyst (**C1**) (164 mg in 3 mL of dichloromethane) was added 1.0 mL of 2-methyl-1,3-dioxepine. After 1 h, the solvent and all residual monomer was removed by high vacuum under gentle warming with a room temperature water bath. After evacuating the flask was evacuated for 30 min, 3 mL of dichloromethane was added to dissolve the solid residues, and the flask was evacuated again for 30 min. The living polymer was then redissolved in 10 mL of dichloromethane, and the calculated amount of monomer (1 g in 5 mL of dichloromethane for 5000 g/mol, 1.4 g in 5 mL of dichloromethane for 7000 g/mol, or 2 g in 10 mL of dichloromethane for 10 000 g/mol) was added by syringe. After the polymerization

Table 1. Polymerization Results for the Heterotelechelic Polymers

entry	monomer	FG[a] (A/B)	$M_{n,calc}$/g mol^{-1}	$M_{n,SEC}$/g mol^{-1}	PDI	^{1}H NMR integral A[b]	^{1}H NMR integral B[b]	^{1}H NMR integral C[b]	% FG[c] (A/B)
1	**HNI**	OH/COOH	6000	6700	1.18	0.033	0.002	0.002	88/94
2	**HNI**	OH/COOH	7500	8400	1.20	0.026	0.002	0.003	85/89
3	**HNI**	OH/COOH	10000	9000	1.12	0.025	0.003	0.001	76/96
4	**PNI**	OH/COOH	6000	6200	1.16	0.036	0.003	0.002	83/94
5	**PNI**	OH/COOH	7000	6600	1.20	0.033	0.002	0.000	88/100
6	**PNI**	OH/COOH	10000	9500	1.17	0.023	0.002	0.002	83/91
7	**DNI**	OH/COOH	4000	4600	1.27	0.048	0.002	0.001	76/98
8	**DNI**	OH/COOH	6000	6400	1.14	0.034	0.004	0.001	77/97
9	**DNI**	OH/COOH	7000	7100	1.20	0.031	0.002	0.002	87/94
10	**HNI**	OH/CHO	5000	6800	1.26	0.041	0.002	0.003	90/93
11	**HNI**	OH/CHO	10000	10300	1.29	0.027	0.003	0.002	78/93
12	**HNI**	OH/CHO	15000	15500	1.13	0.018	0.001	0.000	89/100
13	**PNI**	OH/CHO	4000	4200	1.21	0.067	0.003	0.002	91/97
14	**PNI**	OH/CHO	7000	7600	1.18	0.037	0.002	0.001	89/97
15	**PNI**	OH/CHO	10000	10300	1.18	0.027	0.002	0.000	85/100
16	**DNI**	OH/CHO	5000	5700	1.23	0.049	0.003	0.002	88/96
17	**DNI**	OH/CHO	7000	7500	1.24	0.037	0.003	0.002	84/95
18	**DNI**	OH/CHO	10000	12000	1.22	0.023	0.002	0.001	83/96

[a] FG = functional group. [b] Calculated as denoted in the text; integral for backbone olefins = 2. [c] % FG = degree of functionalization in percent.

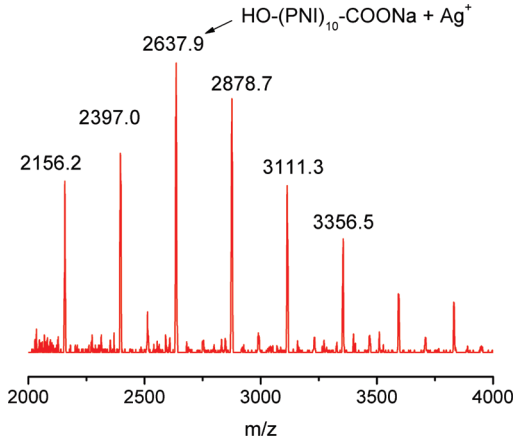


Figure 4. MALDI-ToF MS of HO-(**HNI**)$_n$-COOH (entry 1 in Table 1).

had finished (typically 1 h for 10 000 g/mol), 300 μL of the termination agent (VC for aldehydes 3HF for carboxylic acids) was added. After another 2 h, after which the color of the solution had typically changed from a brown color to yellow, the polymer was precipitated in methanol, collected, and dried overnight in a vacuum oven to give a brownish solid in good yield (> 90% typically).

*General Procedure for the Synthesis of Heterotelechelic Polymers Using Catalyst **C2***. The polymerization of the dioxepine block was carried out under the same conditions and with the same catalyst as described for catalyst **C1**. Catalyst **C2** was generated during the reaction as follows: After the vacuum removal of all solvents and residual M1 monomers, a solution of 240 mg of triphenylphosphine (4 equiv of the catalyst) dissolved in 10 mL of dichloromethane was used to redissolve the living poly(**M1**). After 10 min, the calculated amount of monomer (2 g in 10 mL of dichloromethane for 10 000 g/mol) was added by syringe. After the polymerization had finished (typically 14 h for 10 000 g/mol and 7 h for 5000 g/mol), 300 μL of the termination agent (VC for aldehydes 3HF for carboxylic acids) was added. The mixture was left to terminate for 14 h. The color change during the termination of catalyst **C2** is less pronounced than with **C1**. After the termination was finished, the polymer was precipitated in methanol, collected, and dried overnight in a vacuum oven giving a brownish solid in good yield (> 90% typically).

*General Procedure for the Hydrolysis of the **M1** Block*. The polymer bearing a poly(2-methyldioxepine) block was dissolved in dichloromethane (ca. 20 mL per 1 g of polymer). 10 mL of methanol and 10 mL of 6 N HCl were added, and the mixture was stirred vigorously. After one night, the polymer was precipitated by adding methanol. After collecting, redissolving in chloroform, and reprecipitation in methanol, the polymer was obtained as an off-white solid in good yield (> 75% typically).

Conclusions

The synthesis of heterotelechelic polymers bearing hydroxyl groups on one chain end and an aldehyde or a carboxylic acid at the other has been accomplished by a combined approach using sacrificial synthesis and the vinyl lactone termination. The nonterminating placement of exactly one hydroxyl group via a cleavable acetal polymer allowed for the precise functionalization of the first chain end, while the second functionality was introduced by a termination reaction.

The polymerization of the chain-end functionalized sacrificial diblock copolymer was carried out using initiators of the first generation of Grubbs' catalysts. Best polymerization results were achieved when the catalyst activity was tailored to the necessities of each polymer block. For the polymerization of the first, sacrificial, block, catalyst **C1** was used to promote the polymerization. Before the second, stable, monomer was added, the catalysts activity was changed by addition of PPh_3, thus forming **C2**.

This pathway gave rise to very well-defined heterotelechelic material which will certainly be of considerable interest in polymer chemistry as now ROMP polymers can bear not only a variety of interesting functional groups along the chain but also two different, precisely placed, reactive end groups on the two chain ends.

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft (DFG) for funding and Materia Inc. for a kind donation of olefin metathesis catalysts. Nils Hanik is greatly acknowledged for many helpful discussions. Uli Kemmer-Jonas, Sabrina Samer, and Ines Wollmer are acknowledged for laboratory assistance.

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