Functionalized Polymers

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Monofunctional Metathesis Polymers via Sacrificial Diblock Copolymers**

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Ring-opening olefin metathesis polymerization (ROMP) is a powerful tool for the synthesis of highly functionalized polymers.[1] The first well-defined ROMP catalyst systems based on titanium,[2] molybdenum, and tungsten[3] exhibited relatively low tolerance toward functional groups. This low tolerance could be exploited in the end-functionalization of metathesis polymers. The high oxophilicity of the metal centers made end functionalization possible by addition of aldehydes to the polymerization mixture.[4] Late-transition-metal catalysts based on ruthenium[5] do not allow for olefin metathesis functionalization with aldehydes. Nonetheless, several pathways have been described in the literature for the end functionalization of ruthenium-catalyzed metathesis polymers.

The most common method of terminating a ruthenium carbene at the chain end of a polymer is achieved by adding ethyl vinyl ether.[6] A methylene group is transferred onto the polymer while cleaving the catalyst off the polymer chain end at the same time. It could be shown that the cleaved-off Fischer-type carbene can undergo further olefin metathesis reactions under certain conditions.[7] For most polymer synthetic applications, however, this species can be regarded as inactive. In the presence of vinyl sulfides it could be shown that such "Fischer carbenes" react as chain-transfer agents to yield monofunctional polymers.[8] The polymers that were prepared in this way show broad polydispersity indices (PDI between 1.3 and 3).

Substituted methyl vinyl ethers have also been used for the termination of living metathesis polymers.[9] In this way, a variety of functional groups could be transferred to the polymer chain end. Gibson and co-workers reported an end-capping reaction whereby the polymerization reaction mixture was exposed to an oxygen atmosphere, which resulted in

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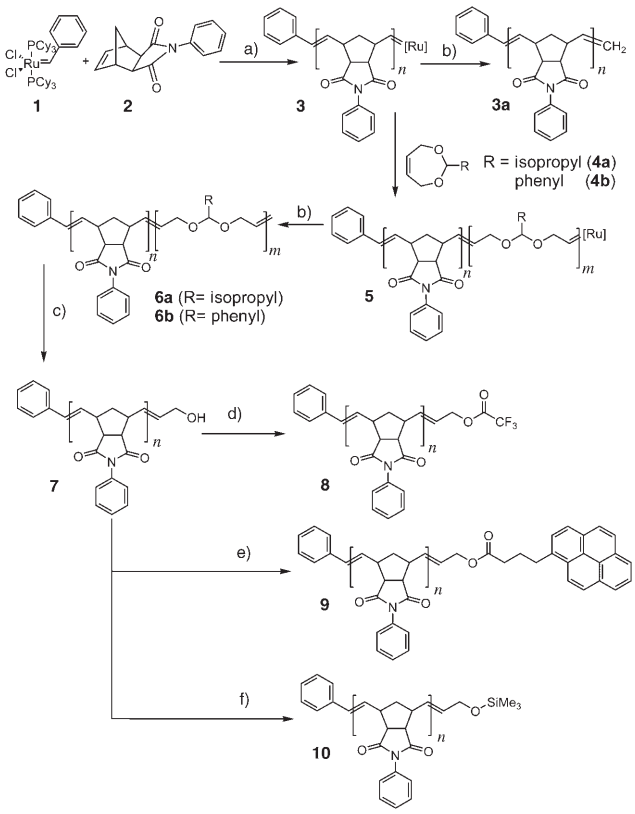
an aldehyde end group after a reaction time of 24 hours.[10] A further method describes the stoichiometric addition of one equivalent of functional monomer to the catalyst, thereby turning the catalyst into a monofunctional initiator.[11]

The end-functionalization reactions described above suffer from several drawbacks. They typically take several hours to complete, during which the metathesis-active catalytic species can undergo further polymerization or secondary metathesis reactions. These end-capping methods can therefore not be employed in the presence of residual monomer without significant broadening of the molecular weight distribution. Even in the absence of residual monomer, long reaction times for the termination reaction can lead to molecular weight broadening as a result of chain-transfer reactions to the polymer (back-biting), a fact that is exploited in the equilibration of telechelics.[12] True monofunctionality is also not guaranteed rigorously by some of the above examples. It is important to stress that the presence of exactly one functional group at the chain end is essential for many applications, such as the synthesis of block copolymers, the synthesis of conjugates with biomacromolecules like proteins, polysaccharides, or polynucleotides, or the functionalization of surfaces and nanoparticles. Today, many of these applications employ monofunctional polymers that are prepared by anionic polymerization.

Herein, we describe the monofunctionalization of the chain end of ruthenium-catalyzed metathesis polymers, which can be carried out in the presence of residual monomer, yields narrow molecular weight distributions, and allows the presence of functional groups in the monomer structure. To prove our synthetic concept, we chose *exo*-*N*-phenylnorbornene-2,3-dicarboximide (PNI) as the monomer as it can be polymerized in a living fashion.[13] PNI was initiated with catalyst **1** (Scheme 1) and polymerized to only 60% conversion. Polymerization to low monomer conversion allowed us to evaluate the influence of residual monomer on the polydispersity of the monofunctional polymer. An analytical sample was taken and quenched with ethyl vinyl ether. Next, a large excess of dioxepine monomer **4a** or **4b** was introduced into the reaction mixture, thereby resulting in the formation of a diblock copolymer, which was quenched with excess ethyl vinyl ether.

Figure 1 shows gel permeation chromatography (GPC) traces of the first block **3a** and diblock **6a**, which clearly show that the living chain end of **3** was an effective initiator for the second monomer **4a**. As the first monomer had only been consumed to about 60%, the second block was most likely a statistical mixture of monomers **2** and **4a**. Polymerization of **2** to higher conversions (60–90%) before addition of the second monomer was also successful. Molecular weight control of the first polymer block is therefore possible by either varying the reaction time before adding the second monomer or by varying the monomer/catalyst ratio. After isolation and purification, the block copolymer was dissolved in a mixture of methanol/dichloromethane/HCl to cleave the acetal groups of the second block.[14] As can be seen in Scheme 1, cleavage of the acetal groups decomposes the second polymer block (to form **7**) but leaves half a monomer unit of **4a** attached to the first block at a C–C double bond.



Scheme 1. Synthesis and cleavage of the block copolymers. a) PPh_3, dichloromethane, room temperature; b) ethyl vinyl ether; c) 6 N HCl, methanol, dichloromethane; d) trifluoroacetic anhydride; e) pyrenebutyroyl chloride; f) trimethylsilyl chloride.

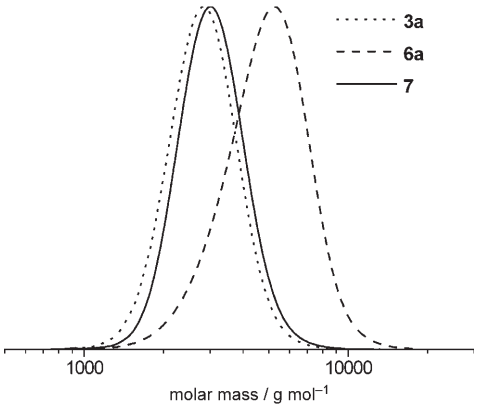


Figure 1. GPC traces (THF, calibration with polystyrene) of the first polymer block of monomer **2** (polymer **3a**, dotted line), the diblock copolymer of monomers **2** and **4a** (polymer **6a**, dashed line), and monofunctional polymer **7** (solid line).

GPC analysis revealed that the molecular weight of the first block (**3a**, Figure 1) and monofunctional polymer (**7**, Figure 1) are almost identical. Moreover, the polydispersity indices for polymers **3a** and **7** (Figure 1) are identical and very narrow (PDI = 1.1). The presence of residual monomer **2,** which can lead to severe molecular weight broadening in many of the previously reported end-capping procedures, was

shown not to have any effect on the polydispersity of the monofunctional polymer.

The same experiment was carried out with the dioxepine monomer **4b**. The GPC trace of diblock copolymer **6b** was also shifted towards higher molecular weights in comparison with that of **3a**, thus indicating good reinitiation from the first to the second block (see the Supporting Information). The monofunctional polymer **7** that was prepared by acidic cleavage of the polyacetal block of **4b** shows a virtually identical molecular weight and polydispersity index (PDI = 1.1) as the first block. It is important to stress at this point that the propagation rate of the dioxepine monomer is of no importance for successful end functionalization of the first polymer block. As the second polymer block is eventually "sacrificed", only the reinitiation of the first polymer block to the first unit of the dioxepine monomer is crucial. This incorporation of the first unit of the dioxepine monomer represents a breaking point, the junction between the end-functionalized and sacrificed polymer block.

To obtain proof for the presence of a hydroxy functionality at the polymer chain end, polymer **7** (from **6a**) was treated with pyrenebutyroyl chloride to give the corresponding ester **9**. A GPC experiment with UV detection at $\lambda = 340$ nm (characteristic for pyrenebutyric acid derivatives) showed a signal for the pyrene-functionalized polymer **9** while hydroxyl-functionalized polymer **7** shows no absorption at this wavelength (see the Supporting Information). This finding shows that the pyrene group was covalently attached to the polymer chain. The ^{1}H NMR spectrum of polymer **7** reveals a singlet at $\delta = 4.14$ ppm, which was attributed to the methylene group adjacent to the hydroxy functionality (Figure 2 bottom). Addition of trifluoroacetic anhydride to the NMR tube resulted in a shift of the peak to $\delta = 4.82$ ppm, which is in agreement with the described assignment (Figure 2 top). Furthermore, the olefinic protons H^1 and H^2 of the styrene-like initiator group can be observed in the ^{1}H NMR spectrum of **7** at $\delta = 6.33$ and 6.60 ppm. Comparing the integrals of the olefinic protons H^1 and H^2 with the integral from H^4 reveals that end functionalization in excess of 97%

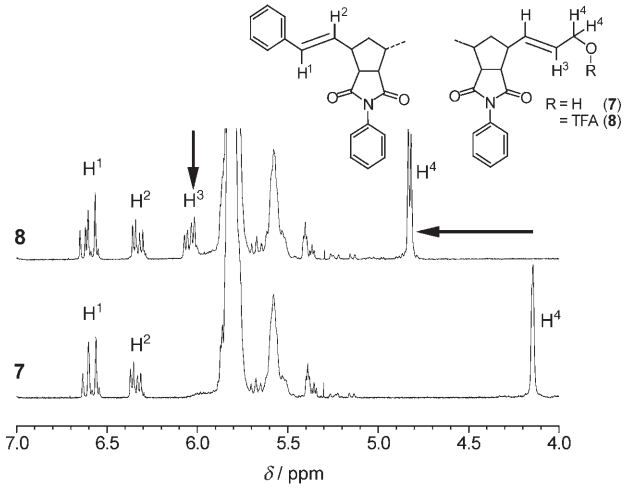


Figure 2. ^{1}H NMR spectroscopic end-group analysis of polymers **8** (top) and **7** (bottom). The structures show the two end groups of the polymer chain.

had occurred. In the ^{1}H NMR spectrum of the trifluoroacetate-functionalized polymer **8** (Figure 2 top), the terminal olefinic protons (H^3, $\delta = 6.04$ ppm) are separated from other olefinic peaks in the spectrum and can also be used for end-group analysis. Reaction of polymer **7** with trimethylsilyl chloride gave the trimethylsilyl-functionalized polymer **10**. The ^{1}H NMR spectrum revealed the methyl end groups at $\delta = 0.17$ ppm (see the Supporting Information).

Polymers **3a** and **7** were analyzed by MALDI-TOF mass spectrometry (**7** from **6a**, see Figure 3; **7** from **6b**, see the Supporting Information). The mass distribution of polymer **7**

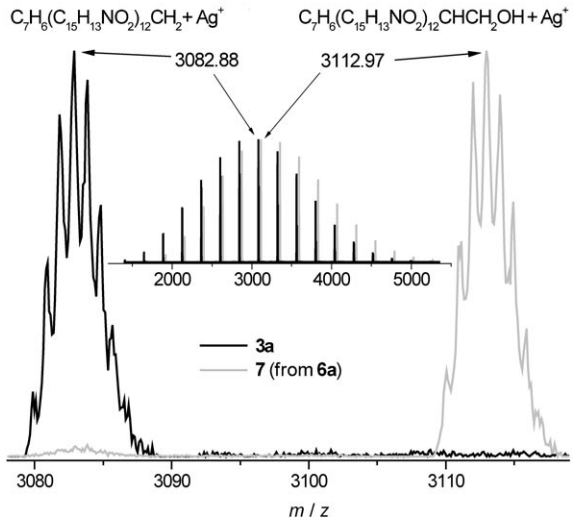


Figure 3. MALDI-TOF mass spectra of **3a** and **7** (from **6a**) showing isotopically resolved mass peaks; inset: complete mass distribution.

is shifted by m/z 30.09 compared to that of polymer **3** (the exact mass of CH_2O is 30.01 g mol^{-1}). This difference corresponds to the mass difference between the ethyl vinyl ether end-capped polymer **3a** and the hydroxy-functionalized polymer **7**. The mass distribution for polymer **7** provides no evidence for a second monomer distribution from residual dioxepine monomer. However, a very small mass distribution owing to unfunctionalized polymer **3** (which is structurally identical to **3a**) can be seen in the mass spectrum of **7** (Figure 3). The functionalization of **7** with trimethylsilyl chloride to give the silyl-protected alcohol was also successful and was confirmed by MALDI-TOF mass spectrometry (see the Supporting Information).

In conclusion, we have presented a route to monofunctionalized olefin metathesis polymers. This route allows the preparation of narrowly distributed polymers with commercially available ruthenium catalysts. Monomeric *exo-N*-phenyl-norbornene-2,3-dicarboximide was polymerized to the desired molecular weight and subsequently turned into a diblock copolymer by adding a cyclic olefinic acetal as a second monomer. The second polymer block was decomposed under acidic conditions, thereby leaving exactly one hydroxyl group at the end of the initial polymer block. We believe that this route to monofunctional ring-opening metathesis polymers presents a viable and less laborious alternative to carbanionic polymerization. Such polymers with

monofunctionalized end groups and narrow polydispersity will allow numerous new applications in fields that previously relied on monofunctionalized polymers from carbanionic polymerization.

Experimental Section

General procedure for the synthesis of block copolymers: Triphenylphosphine (6.3 equiv) and **2** were sealed in a Schlenk flask, which was evacuated and charged with nitrogen twice. Dichloromethane (ca. 10 mL per gram of monomer) was then added by cannula transfer. Polymerization was initiated by quickly adding a solution of the appropriate amount of catalyst **1** in dichloromethane (ca. 1 mL per 100 mg of **1**) by syringe to the stirred solution. Reaction times were dependent on the desired molecular weight of the polymer (7 h for 3000 g mol^{-1}, 13 h for 5000 g mol^{-1}, 24 h for 10000 g mol^{-1}, all at room temperature). Upon completion of the reaction time, the cyclic olefinic acetal was added to the mixture (1 mL of **4a** or **4b** per gram of polymer) and allowed to react for another 10 h. The reaction was quenched with ethyl vinyl ether (1 mL). The product was precipitated into methanol, dissolved in chloroform, and reprecipitated into methanol. The block copolymer was dried to yield 70–80% of a brown solid.

General procedure for cleaving of the second block: HCl (6 M, 4 mL) and methanol (2 mL) were added to a solution of the block copolymer (1 g) in dichloromethane (10 mL). The mixture was stirred for 12 h at room temperature and subsequently precipitated into methanol. The solid was recovered, dissolved in chloroform, and reprecipitated into methanol. The polymer was dried under vacuum to give a white solid (850 mg, ca. 80%, depending on the block ratio).

Detailed experimental procedures are described in the Supporting Information.

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