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Thiol-functionalized ROMP polymers via Sacrificial Synthesis

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ABSTRACT: The synthesis of well-defined and highly functionalized thiol-functionalized polymers has been accomplished via the ring-opening metathesis polymerization (ROMP). A sacrificial synthesis-based approach was chosen for this interesting functional group since it has proven to give precise control over molecular weight and selective placement of end-groups on a different functionality before. Thiol-functionalized ROMP-polymers were successfully synthesized employing thioacetal monomers, which can be cleaved by hydrogenation leaving the desired thiol group behind. The placement of this highly reactive functional group at one chain end of a poly(norborneneimide) is demonstrated by analytical methods such as MALDI−ToF mass spectroscopy and ^{1}H NMR of derivatized polymers. By kinetic measurements, the functionalization efficiency and the polymerization characteristics of the used dithiepine monomer were determined. In a first demonstration, the coating of gold nanoparticles is shown as one interesting application of such functionalized metathesis polymers.

Introduction

Within the broad field of functional reactive polymers, the thiol group has established itself as a particularly interesting target.[1] Compared to their oxo-derivatives, thiols show increased reactivity in a number of reactions including nucleophilic substitutions, transition-metal complex formation and anionic binding to metal surfaces.[2] The electronic structure of sulfur, being able to occupy d-orbitals, can stabilize reaction intermediates such as radicals and ions in a manner inaccessible to alcohols.

These additional reaction pathways and the structural similarity of sulfur-containing connecting groups compared to their oxygen analoga have had great impact in the field of bioconjugate and peptide chemistry. Especially the well-renown thiol−ene and thiol-maleimide "click" reaction[3] is of great importance in, e.g., protein coupling to other synthetic molecules. There, a relatively stable radical species is formed which attacks the electron-deficient double bond of a maleimide bearing the desired counterpart for the respective conjugate.

The thiol's tendency to form sulfur bonds to metal surfaces has been exploited largely in materials science and for analytical purposes. A number of thiol-functionalized low molecular weight molecules and polymers have been applied to gold nanoparticles and surfaces giving prefunctionalized electrode materials and synthons for derivatized nanoparticles in solid state chemistry.[4] By attaching various stimuli-responsive materials, sensoring properties[5] can be transferred to electrodes. Also, such thiol-bonding materials play an important role in surface plasmon resonance spectroscopy (SPR).[6]

Due to its high functional group tolerance, ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) has become a versatile tool in modern polymer and conjugate chemistry. A variety of interesting molecular motives have been polymerized by this ground-breaking method reaching from bioactive groups[7] to noncovalent binding motives.[8] Moreover, ROMP follows living polymerization characteristics for many monomer types, particularly strained and bicyclic olefins. The outstanding functional group tolerance, however, has limited the reaction pathways for efficient chain-end functionalization reactions to electron deficient olefins such as vinyl ethers[9] or the use of prefunctionalized catalysts[10] for a long time.

By introducing olefinic lactones[11] as a novel type of functionalizing agents, our group has recently managed to overcome many limitations of vinyl ether termination including slow kinetics of cis/trans isomeric double bonds and the need for subsequent deprotection reactions. This reaction strategy, as well as the classical vinyl ether termination, is not applicable for the attachment of thio-functionalities. It has been shown before, that vinyl thioethers rather act as a chain transfer agent as, in contrast to its oxo-analogue. The resulting thio-Fischer-carbene can undergo further metathesis steps.[12]

Sacrificial synthesis[13] follows a completely different functionalization scheme. In this case, the functional group to be attached is hidden in a cyclic monomer that can be polymerized as an additional block. Therefore, it does not involve a termination reaction, but a macroinitiation. Cyclic acetal monomers, forming a polyacetal block were used, leaving exactly "half a dioxepine", i.e., a hydroxyl group at the chain-end after hydrolysis. Monofunctionalized polymers synthesized by this method have already found application in the synthesis of graft[14] and block copolymers.[15] Due to its unique, nonterminating functionalization,[16] it could also be used for the defined synthesis of hydroxy-telechelic polymers from tri- and multiblock copolymers.[17]

Thioacetals have been largely used in organic chemistry. In particular, the C−C coupling chemistry developed by Corey and Seebach[18] relies on the special stability of these structures allowing for umpolung reactions of carbonyl centers. They have also developed a variety of cleaving conditions for this protective group.[19]

Here we present an extension of sacrificial synthesis (Figure 1) to the introduction of thiol groups at precisely one chain end. By polymerizing the sulfur-analogues **MT1** and **MT2** of previously used dioxepines, a poly(thioacetal) block is built on the desired polymer which is then selectively cleaved by subsequent

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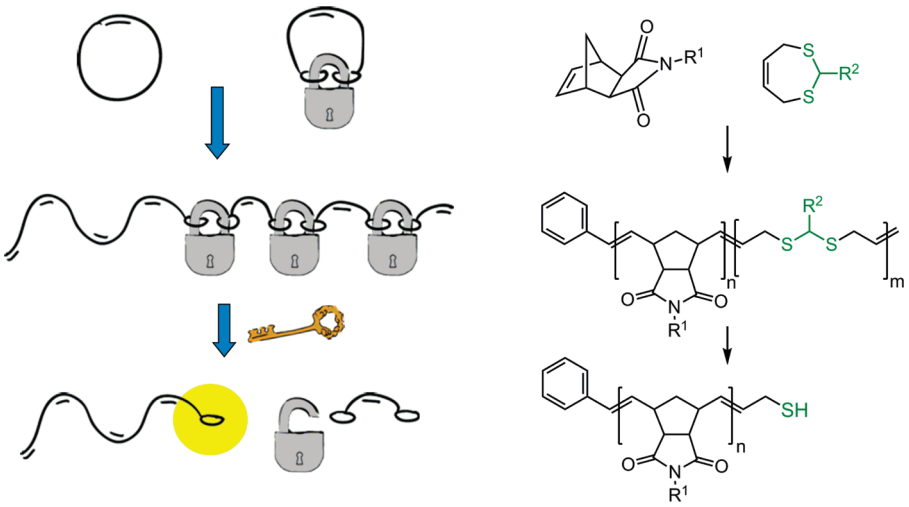


Figure 1. Principle of sacrificial synthesis of thiol-functionalized poly(norborneneimide)s. Left: Schematic representation.[16] Right: Molecular structure.

hydrogenation reaction. For this study, Grubbs' first generation catalyst **C1** and the bromopyridine complex **C2** were chosen as initiators and two different norborneneimide (**xNI**) monomers which polymerize in a living fashion (*cf.* Scheme 1). The successful placement of precisely one thiol end group on every polymer chain is proven by MALDI−ToF and ^{1}H NMR of derivatized polymer samples. In addition, the polymerization characteristics are studied by kinetic analysis.

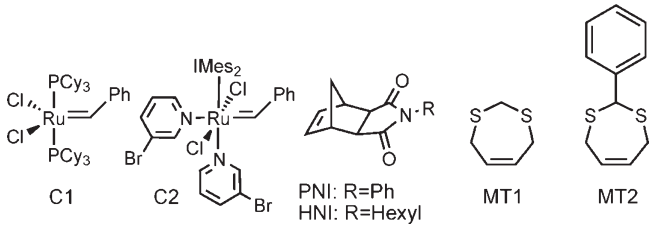
Experimental Section

General Data. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400 MHz on a Bruker ARX400. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker AC300. Time-resolved ^{1}H NMR was conducted on a Bruker ARX400. All spectra were referenced internally to carbon or residual proton signals of the deuterated solvent. Deuterated solvents were purchased from Deutero GmbH. Size exclusion chromatography (SEC) in chloroform (poly(**PNI**)) or THF (poly(**HNI**)) 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 ($10^5/10^3/10^2$ 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-Phenyl-2,3-norbornene dicarboximide (**PNI**), *exo-N*-hexyl-2,3-norbornene dicarboximide (**HNI**), and the bromopyridine complex **C2** were synthesized as described in earlier publications.[13,15] Grubbs' first generation ruthenium catalyst was obtained from Materia, inc. All solvents and other reagents were purchased from Aldrich or Acros and were used withous further purification. All polymerization reactions using initiator **C1** were carried out under argon using standard Schlenk techniques, polymerizations using initiator **C2** were conducted in a nitrogen filled glovebox. Dichloromethane as the polymerization solvent was dried over P_2O_5, distilled under a nitrogen atmosphere and stored over molecular sieves. Monodisperse gold nanoparticles with a diameter of 12.0 nm were prepared by the citrate-reduction method.[20] Substances **1**, **2** and **MT1** were synthesized as described by Harpp and Friedlander[21] with some variations:

Synthesis of cis*-1,4-Dichlorobutene (**1**)*[21]. Thionyl chloride (100 mL, 1.4 mol) was added dropwise to *cis*-1,3-butenediol

Scheme 1. Initiators and the Monomers Used for the Synthesis of Thiol-Functionalized ROMP Polymers



(50 mL, 0.6 mol) with rapid stirring under cooling with an ice bath. The reaction temperature was maintained below 10 °C at all times in order to avoid isomerization. After all thionyl chloride had been added, the mixture was allowed to react for another 4 h before the residual thionyl chloride was removed under reduced pressure. The resulting dark liquid was distilled under vacuum (bp = 67 °C, 23 mbar) to give a colorless liquid in good yield (58 g, 0.46 mol, 77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 4.12 (d, 4H, ^3J = 5.9 Hz, CH_2); 5.84, t, 2H, ^3J = 5.2 Hz, CH). The characterization of **1** was in good agreement with the literature.[21]

Synthesis of cis*-1,4-Butene−Dithioureate·2HCl (**2**)*[21]. To a solution of 28 g (0.4 mol) of **1** in 200 mL of ethanol was added 36 g (0.8 mol) of thiourea. The solution was heated to 40 °C until precipitation commenced. Heating was then discontinued as long as the reaction heat could maintain a gentle reflux. After refluxing for another 16 h, the mixture was cooled with ice and the precipitate was filtered off and dried in vacuo to give 51 g (80%) of a pale solid which was used without further purification. The characterization of **2** was in good agreement with the literature.[21]

*One-Pot Synthesis of 2-Methyl-1,3-dithiepine (**MT1**)*[21]. The thiouronium salt **2** (35 g, 0.22 mol) was dissolved in 600 mL of methanol. KOH (solid, 66 g) was added in small portions over 1 h under cooling with ice. The mixture was stirred overnight to complete the formation of the dithiolate. Then, dibromomethane (18 mL, 43 g, 0.24 mol) dissolved in 200 mL of methanol was added dropwise under cooling with ice. After the addition was completed, the reaction was allowed to finish over 60 h before the methanol was removed at the rotary evaporator. The resulting solids were separated between ether and water (3 × 200 mL) and the combined organic phases were dried with sodium sulfate. After removal of the solvent, the obtained solids were recrystallized from pentane to give colorless needles (15 g, 0.11 mol, 50%).

^{1}H NMR (300 MHz, $CDCl_3$) δ[ppm]: 3.47 (4H, d, ^3J = 6.6 Hz, CH_2); 4.01 (2H, s, S−CH_2−S); 5.9 (2H, m, double bonds). The characterization of **MT1** was in good agreement with the literature.[21]

*One-Pot Synthesis of 2-Phenyl-1,3-dithiepine (**MT2**)*. This was synthesized under the same conditions as **MT1** starting with 8 g (0.05 mol) of the thiouronium salt **2** and subsequent addition of α,α-dibromotoluene to the dithiolate over 6 h. The solids were cleaned by column chromatography over silica using petroleum ether/chloroform 9:2 (v:v) as the eluent (R_f = 0.45) yielding 5.7 g (30 mmol, 60%) of a colorless solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 3.5−3.6 (4H, m, CH_2); 5.30 (1H, s, S−CH−S); 6.0−6.1 (2H, m, double bonds); 7.28−7.45 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm]: 30.39 (2C, CH_2); 59.63 (1C, S−C−S); 127.89(1C, Ph: C_p); 128.43(1C, Ph: C_m); 128.72(1C, Ph: C_o); 129.17 (2C, C=C); 139.49 (1C, Ph: C_i). FD−MS: 208.1 m/z (calcd 208.34 g/mol).

*General Synthesis of Poly(norborneneimide-*b*-dithiepine) Block Copolymers Using Catalyst **C1***. The calculated amount of Grubbs first generation catalyst (164 mg, 2 mmol in a typical experiment) was dissolved in dichloromethane (5 mL) in a Schlenk flask. The appropriate amount of monomer **xNI** (750 mg PNI, 31 mmol, 15 equiv for 7500 g/mol poly(PNI)) was dissolved in dichloromethane (10 mL per 1 g of monomer) and added to the solution by syringe. After the polymerization had finished (ca. 1 h for 10000 g/mol), a 40-fold excess of **MT2** (850 mg, 40 mmol typically) dissolved in dichloromethane (3 mL) was added with continued stirring. The polymerization was terminated by adding ethyl vinyl ether (1 mL) after another 4 h. The polymer was obtained by precipitation in methanol and repeated redissolution in chloroform and precipitation in methanol to give a dark solid material in good yield (>80% typical).

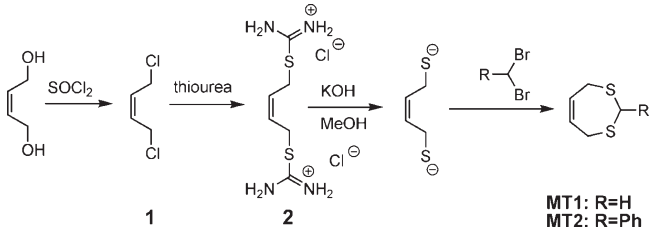
^{1}H NMR (300 MHz, $CDCl_3$) for poly(**HNI**-*b*-**MT2**) δ [ppm]: 0.8−0.9 (m, 3H, CH_3); 1.1−1.4 (m, 6H, C^3H_2−C^5H_2 hexyl chain) 1.5−2.1 (m, 4H, CH_2-bridge + C^2H_2 hexyl chain); 2.8−3.0 (m, 2H, C_3CH); 3.1−3.3 (m, 2H, C(O)CH); 3.4−3.5 (m, 2H, C^1H_2 hexyl chain); 3.2−3.5 (m, 4H, C=C−CH_2 **MT2**-block); 5.3−5.9 (m, 3H, double bonds polymer, S−CH−S in **MT2** block); 7.2−7.5 (m, 5H, Ph in **MT2** block).

*General Synthesis of Poly(norborneneimide-*b*-dithiepine) Block Copolymers Using Catalyst **C2***. In a glovebox, the initiator **C2** (42 mg, 0.5 mmol for a typical experiment) was dissolved in dichloromethane (2 mL) in a septum-capped vial. The appropriate amount of monomer **xNI** (380 mg of PNI, 16 mmol, 32 equiv for 15000 g/mol poly(PNI)) dissolved in dichloromethane (10 mL per 1 g of monomer) was added quickly by syringe with rapid stirring. After the polymerization had finished (ca. 15 min for 10000 g/mol), the calculated amount of **MT2** (104 mg, 5 mmol for 10 equivalents) dissolved in dichloromethane (1 mL) was added with continued stirring. The polymerization was terminated by adding ethyl vinyl ether (100 μL) after 1 h. The polymer was obtained by precipitation in methanol to give an off-white material in good yield (>85% typical).

^{1}H NMR (400 MHz, $CDCl_3$) for poly(**PNI**-*b*-**MT2**) δ [ppm]: 1.6−1.8, 2.0−2.2 (m, 2H, CH_2-brigde); 2.8−3.0 (m, 2H, C_3CH); 3.1−3.4 (m, 4H, C=C−CH_2 **MT2**-block); 3.4−3.6 (m, 2H, C(O)CH); 5.3−5.8 (m, 3H, double bonds polymer, S−CH−S in **MT2**-block); 7.2−7.5 (m, 10H, Ph).

General Procedure for the Hydrogenation of the Dithiepine Block. The polymer was dissolved in dichloromethane (ca. 50 mL per 1 g of polymer) and transferred into a hydrogenation reactor. A slurry of Raney nickel in methanol (solvent exchanged from water) was added (1 mL of the original 50% slurry in water per 1 g polymer) before the mixture was degassed and purged with hydrogen three times. After 14 h at 8 bar hydrogen pressure under stirring, the solution was filtered over Celite, the dichloromethane was evaporated and the polymer solution was precipitated in methanol, collected, redissolved in chloroform and reprecipitated in methanol. Colorless polymer samples were obtained when catalyst **C2** had been used to initiate the polymerization. An exemplary ^{1}H NMR spectrum for poly(**PNI**) and ^{1}H NMR and ^{13}C NMR speactra for poly(**HNI**)-SH are given in the Supporting Information (Figure SI-1).

Scheme 2. Synthesis of Dithiepines MT1 and MT2



General Procedure for the Formation of 3,5-Dinitrobenzylthioesters of the Functionalized Polymers. The thiol-bearing polymer (100 mg, ca. 0.02 mmol) was dissolved in dimethylformamide (2 mL). Dimethylaminopyridine (20 mg, 0.17 mmol) and 3,5-dinitrobenzoylchloride (30 mg, 0.13 mmol) were added and the mixture was stirred for 10 h at room temperature before the solvent was removed in vacuo. The remaining solids were dispersed in chloroform, filtered and precipitated in methanol twice to give an off-white polymer material. An exemplary ^{1}H NMR spectrum for poly(**PNI**) is given in the Supporting Information (Figure SI-2).

Results and Discussion

For the synthesis of monomers **MT1** and **MT2**, a method was chosen in which the thioacetal was formed from the readily accessible thioureate **2** precursor in a one-pot synthesis (Scheme 2). The handling of dithiol compounds could thus be avoided. The functional group in the 2-position could be varied using the respective geminal dihalide added to the dithiolate intermediate. Subsequent recrystallization or column chromatography gave pure compounds. The characterization data of **MT1** was in accordance to the data found by Harpp and Friedlander.[21] The phenyl substituted dithiepine was chosen because aromatically substituted dithioacetals could be cleaved by catalytic hydrogenation before.[22] The unsubstituted dithiepine, on the other hand, imposes minimal steric hindrance to metathesis reactions and was expected to polymerize better than the oxo-analogues used by Fraser et al.[23] and by our group.

From both thioacetal monomers, block copolymer synthesis was performed with catalyst **C1** and a norborneneimide monomer for the stable first block (Scheme 3). The GPC traces of the block-copolymerization with **MT1** revealed an incomplete block transfer to the second block (SEC given in the Supporting Information, Figure SI-3) and subsequent cleavage employing *N*-bromosuccinimide or Hg^{2+} salts resulted in cross-linked polymers or did not cause cleavage at all.

Addition of **MT2** to a polymerization initiated by **C1** gave slightly better block transfer at the same excess of the thioacetal monomer as applied for **MT1**. Virtually complete block transfer was reached only by applying large excesses (>40 equiv) of **MT2** (*cf*. Figure 2) indicating a very small k_i/k_p rate for this monomer. After the polymerization reaction had finished, ethyl vinyl ether quenching was performed in order to terminate all residual metathesis activity and remove the ruthenium species from the polymer chains.

The polymer block formed from **MT2** was then removed by hydrogenation with Raney nickel overnight. At this point, it has to be emphasized that full macro-initiation (block transfer) is a key condition for the viability of the sacrificial synthesis method, as only chains that have initiated the cleavable monomer, remain functionalized after the removal of the sacrificial block.

Figure 2 shows as an example the GPC traces of poly(**PNI**)-*b*-poly(**MT2**), initiated with catalyst **C1**. Here, 40 equiv of **MT2** were employed in this reaction, and complete block transfer can be observed. It has to be noted at this point, that the color of the polymer samples darkened strongly during the cleavage step. Almost black materials were obtained after workup of the hydrogenation. Apparently, the ruthenium catalyst had strongly coordinated to the thioacetal block avoiding removal of the ruthenium after termination of the reaction.

When catalyst **C2** was used to initiate the block-copolymerization, the shift of the molecular weight distribution after addition of **MT2** was minimal although 20 equiv of **MT2** had been added (SEC given in the Supporting Information, Figure SI-4). Given ample time to finish the metathesis reaction with the cleavable monomer, ethyl vinyl ether termination was conducted. Subsequent treatment of the obtained polymer with hydrogen under Raney nickel catalysis resulted in the formation of thiols, as their characteristic smell revealed. Virtually colorless materials were yielded in all cases. Also, thiol end groups could be found exclusively in the MALDI−ToF MS of the material (Figure 3). No indications for side reactions during the hydrogenation step

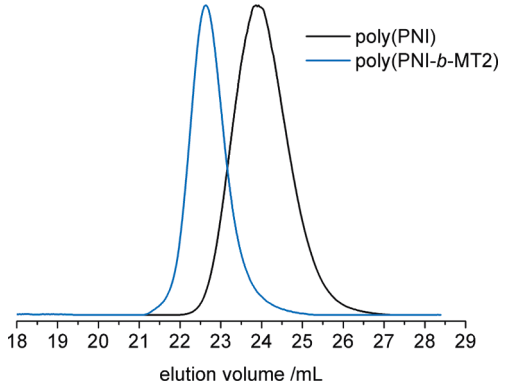


Figure 2. SEC-RI traces of poly(**PNI**) and poly(**PNI**-*b*-**MT2**) initiated by catalyst **C1** after addition of 40 equiv of **MT2**.

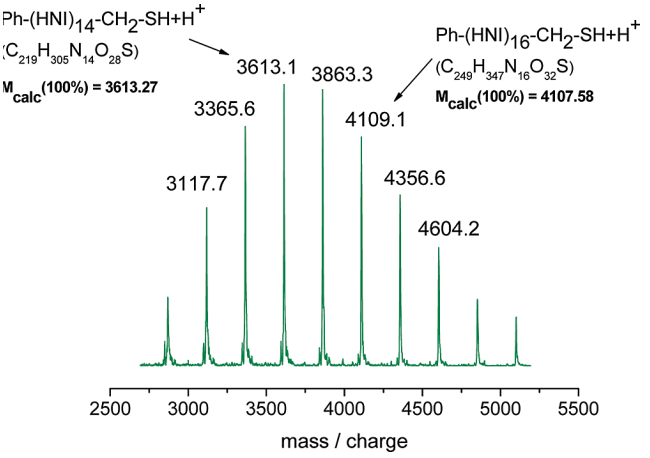


Figure 3. MALDI−ToF spectrum of poly(**HNI**)-SH. Matrix: dithranol, potassium triflate.

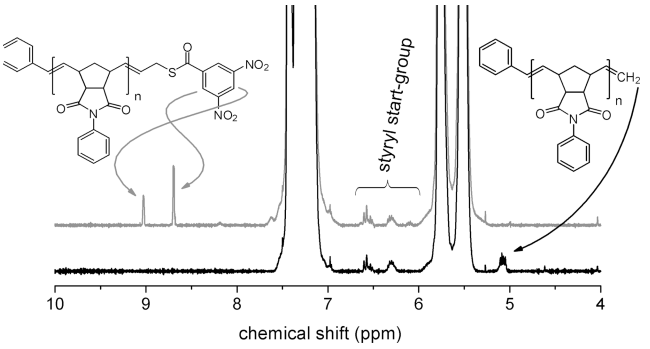
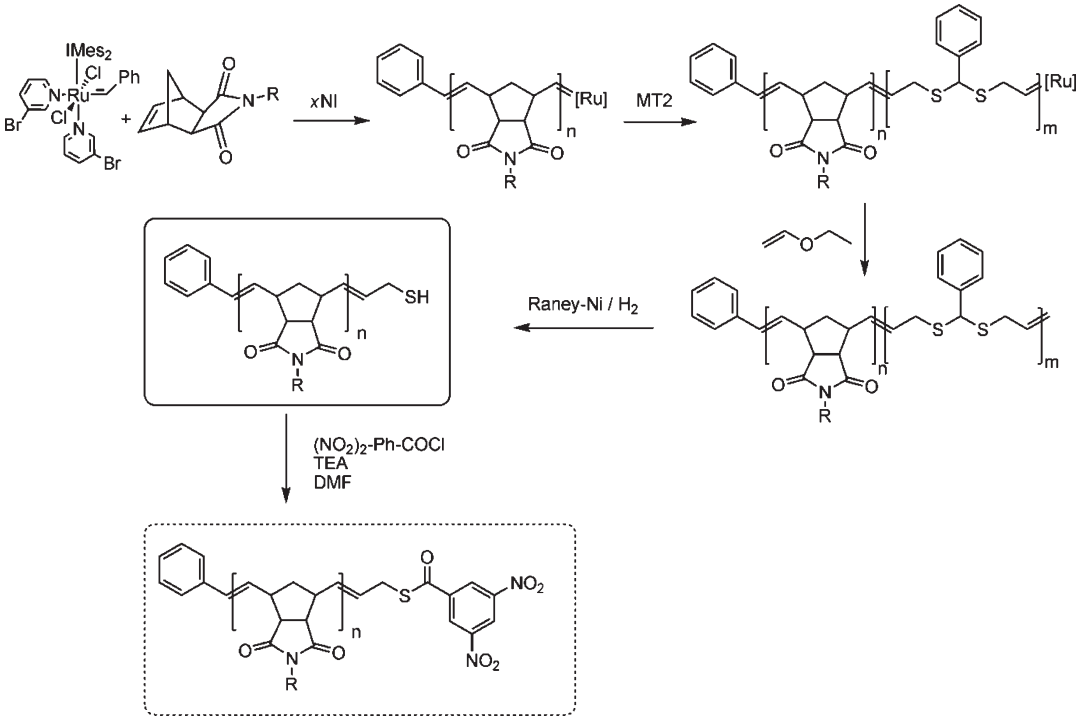


Figure 4. ^{1}H NMR determination of the total degree of functionalization after derivatization of poly(**PNI**)-SH and nonfunctionalized reference material obtained from ethyl vinyl ether termination (spectra including integrals are given in the Supporting Information).

Scheme 3. Sacrificial Synthesis of Thiol-Functionalized Poly(norborneneimide)s



such as backbone hydrogenation have been observed. This is in contrast to the hydrogenation cleavage involving Ph−dioxepine,[17] where such side reactions were observed. We believe that this is due to the poisoning of residual ruthenium by the liberated hydrogenation products thereby preventing it from hydrogenating olefins. Also, no signs of a desulfurization at the chain end has been found in the MALDI−ToF mass spectra. The degree of functionalization was determined by ^{1}H NMR of the polymer after derivatization with 3,5-dinitrobenzoyl chloride (*cf.* Figure 4).

By comparison of the resulting aromatic thioester signals (at δ = 9.04 ppm and δ = 8.70 ppm) to the signals representing the styryl end group (at δ = 6.55 ppm and δ = 6.30 ppm) (*cf.* Figure 4), which is generated during the initiation step, the percentage of polymer chains bearing the desired functional group could be determined. The overall degree of functionalization obtained by this method was >95%. This method of end-group determination assumes that all polymer chains have been initiated with the ruthenium carbene initiator and no chain transfer has occurred during the polymerization. Both are fulfilled for a living polymerization such as the one described here. In this case, comparing the integral intensity of both end groups of a polymer chain gives very accurate degrees of functionalization (see also Figure SI-2 in the Supporting Information).

In order to determine the efficiency of this functionalization method, kinetic aspects of the macroinitiation step and the following polymerization of the thioacetal block had to be determined. In analogy to our study on the behavior of different acetals, this included kinetic ^{1}H NMR observation of the initiation step. This experiment was conducted with addition of 10 equiv of **MT2** in order to ensure pseudofirst order conditions throughout the course of the reaction. It was performed on four different types of catalysts: **C1** and **C2**, as well both catalysts after initiation with 15 equiv of **PNI**, which had proven to be far more reactive toward macroinitiation in the acetal study.[16]

Catalyst **C1** showed no initiation activity on **MT2**, yet the carbene did not decompose significantly over the period of 10 h. When **MT2** had been initiated by a norbornene monomer a slow initiation could be observed. This difference in the versatility of the initiation is typically observed on most ruthenium-based catalyst systems.[11] If initiated with **PNI**, the macroinitiation step to the **MT2** block was slow (spectra given in the Supporting Information, Figure SI-5). The assumption that could be drawn from the preliminary test polymerization was therefore confirmed, which had shown that the rate of polymerization is high, while the rate of initiation is not. There, extremely large excesses of **MT2** had to be applied in order to approach complete initiation of the sacrificial block.

As a consequence, initiation of **MT2** was performed with the much more reactive catalyst **C2**. This latest-generation catalyst is well renowned for its ultrafast initiation kinetics on all kinds of even mildly reactive cyclic olefins. Partly, this outstanding property is credited to the weakly associated pyridyl ligands which facilitate the coordination of olefins. When **MT2** was applied to catalyst **C2**, a quick initiation reaction could be monitored in time-resolved ^{1}H NMR (*cf.* Figure 5). The decay of the benzylidene signal followed clear first-order kinetics and k_i could be determined from the integration data obtained (k_i = 5.5 L/mol s^{-1}). When **C2** had been initiated with 15 equiv of **PNI** before **MT2** was added, the block transfer reaction was too

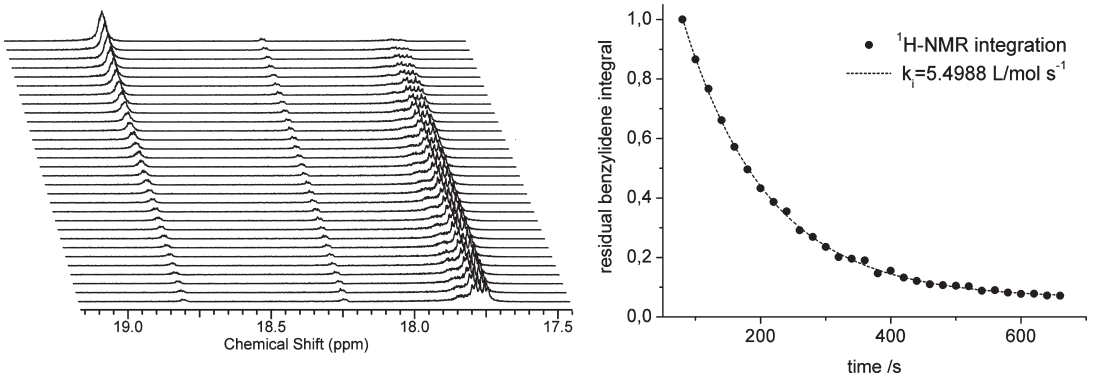


Figure 5. Time-resolved ^{1}H NMR of the reaction of initiator **C2** with 10 equivalents of **MT2** (Δt = 20 s) (*left*) and kinetic evaluation of the carbene integrals (signal at 18.8 ppm, *right*).

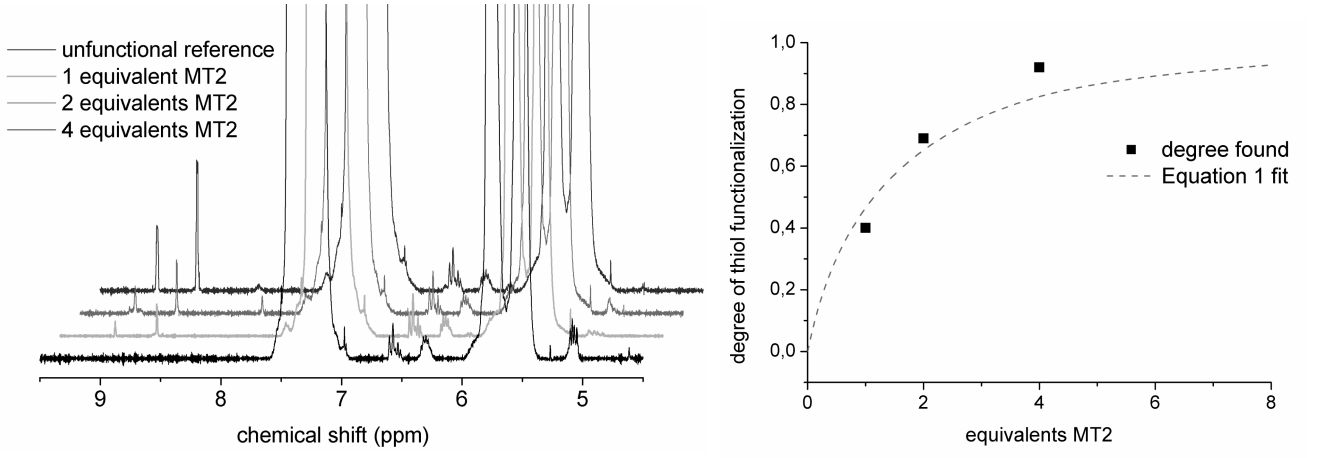


Figure 6. Functionalization series applying a different number of equivalents of **MT2**, ^{1}H NMR results after hydrogenation (*left*) and derivatization for k_i/k_p determination (*right*).

fast to be monitored by ^{1}H NMR. No residual carbene signal originating from norbornenyl carbenes ($\delta = 18.54$ ppm) could be found any more in the first measurement after the addition. The respective spectra are given in the Supporting Information (Figure SI-6). Their complete conversion to a novel carbene species at δ = 18.07 ppm demonstrated good stability of the initiator toward the thioacetal monomer. The rate of reaction was high, as more than 10 half-lives of the reaction had been passed during the first minute of the reaction.

However, no information about the actual polymerization reaction could be obtained from kinetic NMR due to strong signal overlap. Therefore, the k_i/k_p ratio could not be determined by this method. In order to fully comprehend the functionalization behavior of the thioacetal monomer, knowledge of this factor is vital. As we had shown in the acetal study,[16] this key ratio can be obtained from a series of functionalizations at different amounts of functionalizing sacrificial monomer added. The degrees of functionalization could be used in order to calculate this factor from Swarcz's equation, eq 1.[24,25]

$$\frac{M_{total}}{C_{total}} = \left(\frac{k_p}{k_i}\right)[\ln(1-f)^{-1} - f] + f \qquad (1)$$

For this, a series of functionalization reactions was conducted, followed by hydrogenation cleavage of the sacrificial block and subsequent derivatization with 3,5-dinitrobenzoyl chloride. The functionalization was calculated from the resulting ^{1}H NMR signals as shown in Figure 6. The results were used to fit eq 1 accordingly and thus obtain the k_i/k_p factor, which was determined to be k_i/k_p = 0.31. It has to be noted, that the degrees of functionalization obtained from the experiment are higher than expected from the fit when fitting is based on the values for 1 and 2 equiv of **MT2**. The same effect has been discovered for 2-phenyl-1,3-dioxepine in the sacrificial synthesis efficiency study.[16] This effect can be explained by the polymerization characteristics of the sacrificial monomer. Evidently, monomers which do not polymerize to completion on a particular catalyst system, reach higher degrees of functionalization. This might be caused by a gradual deactivation of the catalyst by complexation of the newly formed polymer chain. Catalyst **C1** was not tested for k_i/k_p values due to its expected low k_i/k_p and the ruthenium removal difficulties observed, resulting in limited synthetic relevance of this reaction.

Table 1. Thiol-Functionalized Polymers Synthesized Employing MT2 as a Sacrificial Monomer

entry	xNI	initiator	M_n/g mol^{-1}	PDI
1	**PNI**	**C1**	7300	1.24
2	**HNI**	**C1**	5600	1.27
3	**HNI**	**C1**	13800	1.28
4	**PNI**	**C2**	6900	1.13
5	**PNI**	**C2**	15200	1.16
6	**PNI**	**C2**	27300	1.13
7	**PNI**	**C2**	33000	1.15
8	**HNI**	**C2**	5900	1.11
9	**HNI**	**C2**	9500	1.09

A number of different polymers were synthesized by this method. The polymer characterization results are summarized in Table 1. The control over molecular weight and molecular weight distribution (PDI ~ 1.2 for catalyst **C1**, 1.1 for catalyst **C2**) is in full agreement with values typically obtained for the initiators used.

The well-known coating reaction of thiols on gold surfaces was used to further prove the presence of a thiol group on the polymer chains. For this, a gold nanoparticle solution obtained from the citrate nanoparticle synthesis[20] was added to a chloroform solution of the functionalized polymer. Upon shaking, the nanoparticles were drawn into the organic phase and stayed stable over months. UV/vis spectrometry of the phases proved quantitative phase transfer of the gold (spectra given in the Supporting Information, Figure SI-7). A transmission electron microscopy (TEM) image could verify the presence of a polymer layer that had forms around the nanoparticles (*cf.* Figure 7).

Conclusion

With the introduction of dithiepine **MT2** as a novel cleavable monomer, we have successfully achieved a valuable extension of sacrificial synthesis. The successful placement of an additional block of this thioacetal monomer was accomplished by two

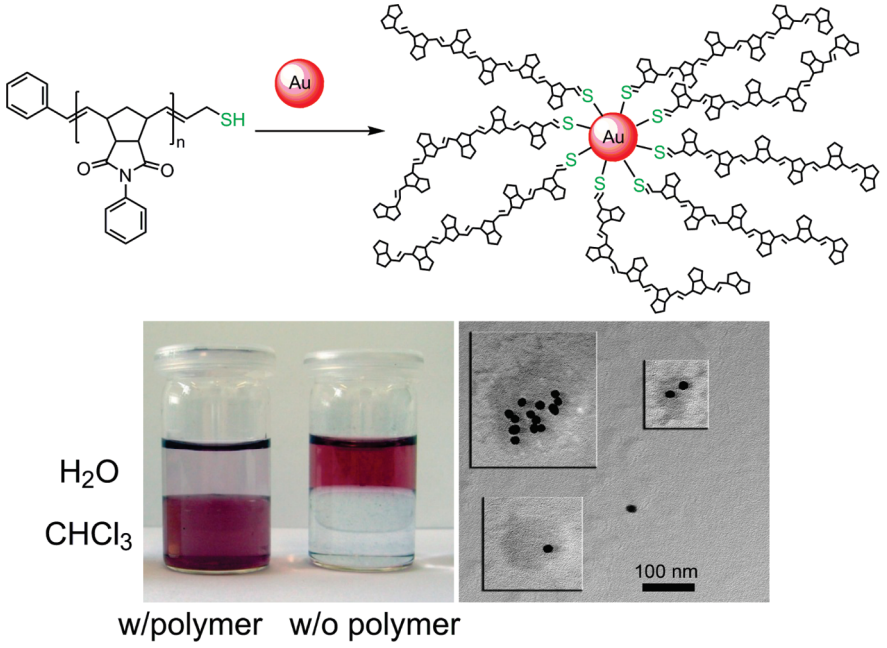


Figure 7. Top: Coating reaction of gold nanoparticles with poly(**PNI**)-SH. Bottom left: phase transfer of gold nanoparticles after addition of poly (**PNI**)-SH. Bottom right: The three insets show TEM images of polymer coated gold nanoparticles. One single nanoparticle (bottom right of the picture) is a nanoparticle reference sample that was not coated with the polymer.

different catalysts, **C1** and **C2**. While Grubbs first generation catalyst (**C1**) required a large excess of **MT2** in order to reach a high degree of functionalization, the bromopyridine complex **C2** required much smaller amounts of the sacrificial monomer in order to produce fully end-functionalized polymer chains. The precise and selective placement of the desired functional group was shown by MALDI−ToF MS giving no hint for falsely or nonfunctionalized polymer chains.

By a series of functionalization experiments and subsequent derivatizations, we have been able to determine the versatility of this method. Using the kinetic equation for the initiation efficiency of a living anionic polymerization, the k_i/k_p ratio of the key step for the functionalization by sacrificial synthesis has been determined which allowed us to establish the optimum conditions with the least amount of sacrificial monomer employed.

Furthermore, this new functional end group, which is of great importance to materials science and biochemical research, has been employed in a first application. By coating gold nanoparticles with the novel material, the reactivity of the thiol end groups was demonstrated. Considering the immense variety of functional polymers that can be synthesized by ruthenium-initiated ROMP using derivatized norbornene or other cycloolefin monomers, a number of different applications can be imagined ranging from electrode materials sensitive to complex stimuli to biomolecules bearing specially labeled polymer chains.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR and SEC data plots, and UV/vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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