Sacrificial Synthesis of Hydroxy-Telechelic Metathesis Polymers via Multiblock-Copolymers

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ABSTRACT: The synthesis of well-defined telechelic ring-opening metathesis polymers has been achieved by Sacrificial Synthesis. With the formation of cleavable triblock-copolymers, precise control over the molecular weight and the degree of functionalization was achieved. Introducing cleavable monomers that can be addressed separately, sequential deprotection was accomplished which opened the path to more sophisticated polymeric materials bearing different substituents at their respective chain ends. Sacrificial penta- and heptablock-copolymers are also presented which allow the synthesis of well-defined telechelic polymers in good yields and significantly improved initiator efficiency.

Introduction

Telechelic polymers represent a special class of chain-end functionalized polymers. In contrast to monofunctional polymers which are generally used for many applications such as surface functionalization[1] or drug immobilization,[2] they offer an additional functional group on the second chain end. They can be used to combine different molecules such as biomacromolecules with, e.g., dyes or inorganic tracers.[3] Therefore, they are particularly interesting for interdisciplinary applications. In polymer science, they have been applied in the formation of multiblock-copolymers by polycondensation of the telechelic prepolymers with other difunctional materials.[4]

Polymers bearing functional groups at both chain ends can be synthesized by a number of methods[5] reaching from step-growth[6] to chain growth polymerizations.[7] While step-growth polymerizations are easily accessible and typically give extremely high degrees of chain-end functionalization, they give broad molecular weight distributions and little control over the average chain length.

Chain growth polymerizations, on the other hand, can be used to synthesize telechelic polymers by the addition of functional chain transfer agents (CTA).[8] In this case, molecular weight control is given by the kinetic characteristics of the respective polymerization reaction, but narrow molecular weight distributions cannot be reached.

Only living polymerizations,[9] i.e., polymerizations without termination, chain transfer, or reinitiation processes, are able to form narrowly dispersed, highly bifunctional polymers. Furthermore, they involve difunctional initiators or initiators bearing a protected functional group.[10] However, these molecules are not available for all types of living polymerizations or have to be synthesized in numerous steps and need to be cautiously purified. All functionalization reactions involving classical living ionic or radical polymerizations involve a termination of the active species. Since termination of one chain end while maintaining the other chain end's activity is impossible, polymerizations involving difunctional initiators are limited to homotelechelics.

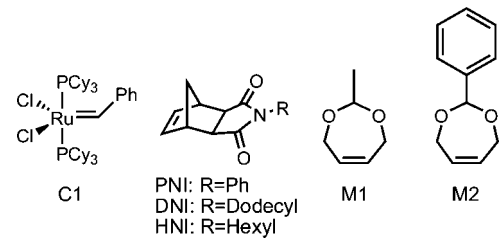
Telechelics from ring-opening metathesis polymerization (ROMP) have been realized by two different approaches. Acyclic, homobifunctional olefins have been used as CTA for the synthesis of various telechelic polymers.[11] The statistical copolymerization of monomers with a cyclic cleavable olefin also gave telechelics after hydrolysis.[12] Due to the low regioselectivity of ROMP, only homotelechelic polymers, bearing the same functional group on both chain ends, are available by these methods. Difunctional initiators have only been realized for molybdenum based catalysts, but were limited to nonfunctional monomers due to the high oxophilicity of the active species.

Prefunctionalized ruthenium alkylidene complexes[13] have been used to place functional end-groups at one chain end. However, bifunctional polymers were never prepared using this route. Also, this method requires complex organometallic transformations and purifications which can be carried out by specialists only.

Recently, we have reported a different strategy for the functionalization of ROMP polymers. In contrast to classical functionalizing termination reactions involving vinyl ethers[14] or vinyl lactones,[15] *sacrificial synthesis*[16] does not require a termination reaction for the placement of the desired functional group, but a macroinitiation step. Therefore, the active species is kept and can be used to polymerize additional polymer blocks. Cyclic acetals (*cf.* M1 and M2, scheme 1) were introduced for the formation of hydroxyl endgroups. The resulting polyacetal block could later be cleaved leaving exactly "half a dioxepine", i.e. a hydroxyl group at the chain-end. Such monofunctionalized polymers have already been used for the synthesis of graft[17] and block copolymers.[18] With the development of 2-methyl-1,3-dioxepine (M1) as sacrificial monomer was found that polymerized well and to high conversion.[19] For the first time, this allows the macroinitiation of a second monomer from a sacrificial block, thereby introducing a functional start-group.

Here, we present a new approach for the formation of telechelics based on the nonterminating functionalization prin-

Scheme 1. Initiator and the Monomers Used for the Synthesis of Telechelics



C1 PNI: R=Ph DNI: R=Dodecyl HNI: R=Hexyl M1 M2

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ciple of *sacrificial synthesis*. In contrast to the work of Fraser et al.[12] the cleavable sites are not introduced by statistical copolymerization, thereby scrambling the polymer chain into portions of statistically distributed sizes. Using blockwise polymerization of the hydrolyzable and the stable monomers, both polymer chain length and the order of cleavable and noncleavable blocks remain under full control.

In order to introduce two functional groups on every polymer chain, two cleavable blocks containing easily hydrolyzable acetal functions formed from dioxepines M1 or M2 (*cf.* Scheme 1) are introduced on each side of the desired polynorborneneimide (*x*NI). Grubbs' first generation catalyst (C1) was chosen as the initiator since it has proven sufficient functional group and long-term stability to be deployed on complex block-copolymer formations.

Furthermore, an advanced strategy is presented to cleave the two appending sacrificial blocks of an ABC triblock sequentially. Different conditions are used to cleave the two dioxepine blocks, thereby allowing for orthogonal derivatization of the two functional groups

An extension of this strategy to penta- and hepta-block-copolymers containing two or three nonhydrolyzable blocks leading to higher yields of telechelic polymer per molecule of initiator used is also described.

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. All spectra were referenced internally to residual proton 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 ($10^5/10^3/10^2$ 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 337nm.

exo-N-Phenyl-2,3-norbornene dicarboximide, *exo-N*-dodecyl-2,3-norbornene dicarboximide, and *exo-N*-hexyl-2,3-norbornene dicarboximide, as well as 2-phenyl-1,3-dioxepine, were synthesized as described in earlier publications.[16−18] 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. Dioxepine monomers were degassed by repeated freeze−pump−thaw−purge cycles using argon as the inert gas.

Synthesis of 2-Methyl-1,3-dioxepine. To 130 mL of toluene in a 250 mL flask were given 43 mL of *cis*-1,3-butenediol (0.5 mol), 29.5 mL of acetaldehyde (0.52 mol) and 50 mg of toluenesulfonic acid. The mixture was allowed to stand at room temperature for 30 min before it was connected to a Dean−Stark apparatus and refluxed until all produced water had been removed from mixture. After cooling, the content was washed with soda, water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was distilled over a short Vigreux column (bp = 135 °C) to give a colorless liquid in good yield (49.5 g, 87%).

^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 1.28 (3H, d, ^3J = 5.1 Hz, Me); 4.05−4.40 (4H, m, C═C−CH_2); 4.94 (1H, quart., ^3J = 5.2 Hz, O−CH−O); 5.66 (s, 2H, *C*═CH).

General Procedure for the Synthesis of ABA and ABC Triblock-Copolymers. To a stirred solution of Grubbs' first generation catalyst (164 mg in 3 mL of dichloromethane) was added 0.75 mL of 2-methyl-1,3-dioxepine. After 1 h, the solvent and all residual monomer was removed by high vacuum; the flask was evacuated for another 1 h. The living polymer was then redissolved in 10 mL dichloromethane and 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 1 h for 10 000 g/mol), 1 mL of the dioxepine monomer for the third block was added by syringe. After another 2 h, the polymerization was terminated by addition of 0.5 mL of ethyl vinyl ether in order to cleave the catalyst off the chain. 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 Hydrogenation of the M2-Block. The polymer bearing a poly(2-phenyl-dioxepine) block was dissolved in 50 mL of dichloromethane and placed in a 100 mL hydrogenation reactor. Then 1 mL of a Raney-Ni slurry dispersed in methanol was added, the reactor was sealed, evacuated, and flushed with nitrogen three times, and the mixture allowed to react under 8 bar pressure of hydrogen for 20 h with stirring. After the reaction time was completed, the mixture was filtered over a Celite pad, concentrated and precipitated in methanol. The polymer was obtained as an off-white solid in good yield (>75% typically).

Attachment of Pyrenebutyric Acid to One Hydroxyl-Group and Cleavage of the Second Dioxepine Block. Pyrenebutyric acid (100 mg), *N*,*N*′-dicyclohexyl carbodiimide (80 mg) and *N*,*N*-dimethylaminopyridine (100 mg) were added to a solution of 150 mg of poly(2-methyl-1,3-dioxepine-*b*-DNI)-OH in 15 mL of dichloromethane and stirred at room temperature for 14 h. The reaction mixture was then concentrated and precipitated in methanol. The polymer was collected, redissolved in chloroform, reprecipitated in methanol and dried in vacuo to give an off-white solid (135 mg, 92%). This polymer was then dissolved in dichloromethane (5 mL), 2 mL of 1 N HCl and 1 mL of methanol were added, and the reaction was stirred overnight. Then 20 mL of methanol was added to the mixture in order to precipitate the deprotected polymer. The collected solids were redissolved in chloroform, reprecipitated in methanol, collected, and dried in vacuo to give a colorless solid weighing 84 mg (61% of starting material).

^{1}H NMR (400 MHz, $CDCl_3$) δ[ppm]: 0.8−0.9 (m, 3H, $C_{11}-CH_3$); 1.1−1.4 (m, 18H, $C_3H_2-C_{11}H_2$); 1.5−2.2 (m, 4H, CH_2-bridge and N−C−CH_2); 2.6−2.7 (m, 2H, C_3CH); 2.9−3.1 (m, 2H, C(O)CH); 3.4−3.5 (m, 2H, N-CH_2); 4.07−4.14 (m, 2H, CH_2−OH endgroup); 4.58−4.67 (m, 2H, CH_2−O−PBA endgroup); 5.5−5.8 (m, 2H, double bonds); 7.7−8.3 (m, 9H, pyrene). GPC (chloroform): M_n = 20 200; PDI = 1.30.

General Procedure for the Synthesis of ABABA and ABABABA Multiblock-Copolymers. A solution of 82 mg of Grubbs' first generation catalyst in 2 mL dichloromethane was added 0.5 mL 2-methyl-1,3-dioxepine. The mixture was stirred for 2 h before a dichloromethane solution (5 mL) of the calculated amount of monomer (1 g for 10 000 g/mol) was added by syringe. After the polymerization of the second block had finished (ca. 1 h), the second portion of 2-methyl-1,3-dioxepine (0.5 mL) was added and allowed to react for 2 h. The monomer for the second polynorbornene block was added in the same manner as the first portion and was allowed to react for 1.5 h. The third dioxepine portion was added again by syringe (0.5 mL). For the pentablock copolymer, the reaction was terminated after 2 h by addition of 0.5 mL of ethyl vinyl ether. For the heptablock, another portion of the norbornenimide solution was added and allowed to react for 2 h before the final portion of the dioxepin was added and allowed to react overnight. Termination was conducted by addition of 0.5 mL of ethyl vinyl ether in order to cleave the catalyst off the chain ends and stabilize the polymer. Precipitation of the polymer by addition of excess methanol followed by redissolution of the collected solids in chloroform and reprecipitation in methanol afforded an off-white solid in 80−90% yield.

General Procedure for the Hydrolysis of All Cleavable Blocks. To 1 g of polymer dissolved in 15 mL of dichloromethane were given 5 mL of 1 N HCl and 2 mL of methanol. This mixture was vigorously stirred to allow for good phase mixing for 14 h

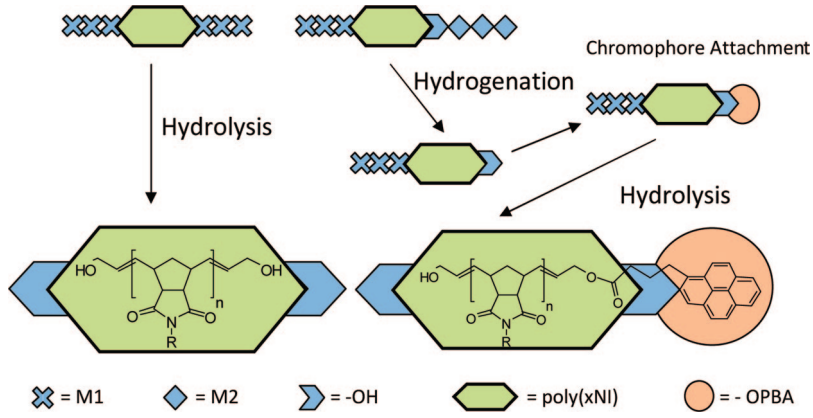
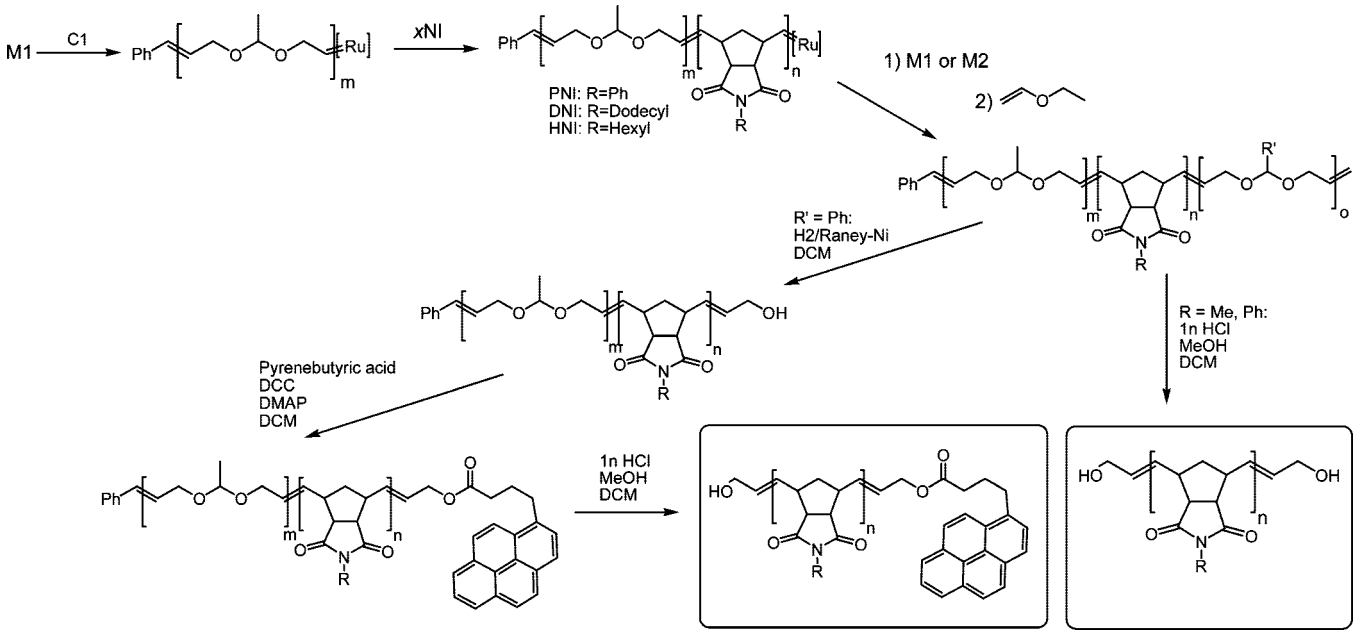


Figure 1. Principle of sacrificial ABA and ABC triblock-copolymers.

Scheme 2. Synthesis of Telechelic Polymers by *Sacrificial Synthesis*



before further methanol (50−100 mL) was added in order to precipitate the deprotected polymer. The resulting solids were collected, redissolved in chloroform, precipitated in methanol and dried overnight in a vacuum oven to give a colorless solid in >70% yield compared to the staring material (depending on polydioxepin content).

Results and Discussion

Telechelics form ABA and ABC Triblock Copolymers. The synthesis of telechelic ROMP polymers by a sacrificial approach involves the formation of triblock-copolymers. Two types of triblock copolymers can be prepared. The first type is a symmetric ABA-type (Figure 1 left) in which the stable polymer B-block is surrounded by hydrolyzable blocks made from monomer M1. The second type is a nonsymmetric ABC-type (Figure 1 right) in which A is poly-M1, B the stable polymer block and C poly-M2.

The latter approach involves two different dioxepines which can be addressed sequentially in subsequent cleaving reactions, allowing for precise placement of different substituents on the respective chain ends. For the synthesis of well-defined functionalized polymers by *sacrificial synthesis*, it is essential to ensure exact placement of the cleavable sites. Any infiltration of the stable polymer block with cleavable monomer units irrevocably leads to broad molecular weight distributions and loss of control over the average chain length. When cleavable monomers are polymerized prior to the stable block, it is therefore crucial to find a cleavable monomer that either polymerizes to completion or can be removed from the polymerization mixture without harming the living chain ends.

As outlined in Scheme 2, the synthesis of a polymer bearing hydroxyl-groups on each end of the polymer chain involves the polymerization of a polydioxepine homopolymer followed by the addition of the stable monomer and finally the second cleavable dioxepine block. Introducing monomer M2 as the second dioxepine, a different cleaving procedure can be utilized. Hydrogenation with Raney-nickel is known to remove phenyl-acetals cleanly and leave deprotected hydroxyl-groups behind.[20]

Previously used dioxepine M2 and its isopropyl-derivative only form oligomers and can not be removed under reduced pressure due to their high boiling points. Yet, both M1 and its parent compound 1,3-dioxepine, have proven to polymerize to completion and can be removed under reduced pressure. 1,3-dioxepine, however, can be cleaved under chemically harsh conditions only, which limits its applicability in *sacrificial synthesis*.

Preliminary polymerizations of M1 exhibited broad molecular weight distributions of the resulting homopolymer. However, the subsequent polymerization of a second monomer that is

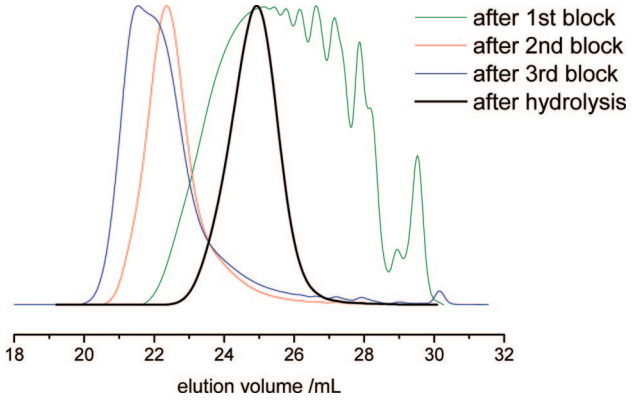


Figure 2. SEC-RI traces of poly(M1-*b*-PNI-*b*-M1) after each block and after hydrolysis of the polyacetal blocks.

known to polymerize in a living manner, gave a clean shift toward higher molecular weights, clearly showing that no termination reactions were induced by the polymerization of the first block. (cf. Figure 2) When initiating monomer M1 with initiator C1, the low k_i/k_p value of M1 requires the addition of a large excess of M1 to the initiator in order to achieve full functionalization. Typically, 50−75 equiv of M1 were applied in the first block.

After polymerization of the stable monomer block (*x*NI), the subsequent polymerization of the second M1 block performed in the same fashion as the first block. Similar amounts of M1 were applied as for the first block in order to ensure high functionalization. Interestingly, the low k_i/k_p-rate leads to the formation of a plateau-like maximum in the SEC trace. After hydrolysis of the polyacetal blocks, a polymer is retained that is well defined in is molecular weight and exhibits a Poisson-like molecular weight distribution as expected for a living polymerization (Figure 2).

When M2 is used as the second cleavable monomer, much smaller excesses of the dioxepine monomer are needed due to its lower k_i/k_p rate.[19] The respective SEC traces for the formation of a poly(M1-*b*-PNI-*b*-M2) triblock copolymer are given in the Supporting Information. It has to be noted at this point, that full conversion of the dioxepine monomer is needed in the case of subsequent addition of noncleavable, i.e., stable monomers only. Complete conversion of the second dioxepine monomer to form the third block is not needed as long as every diblock chain has reacted with the second dioxepine at least once. In order to label chains that had not initiated the final dioxepine block, additional termination with ethyl vinyl ether was performed after the polymerization had finished. This termination leads to terminal olefins which can be assigned and quantified in the ^{1}H NMR spectrum by their distinct signals.

Hydrolysis of all dioxepine blocks (M1 and M2) could be performed by addition of dilute acid. The reaction performed in the same manner as described for monofunctional polymers in earlier publications.[16,19] In addition, the poly(M2)-blocks were successfully removed by hydrogenation using Raney-Nickel as the catalyst. In this case, it is of outmost importance to remove the Ru-polymerization initiator as well as possible, as it can also act as a hydrogenation catalyst, thus hydrogenating the double bonds of the polymer backbone.

In order to prove the selective sacrificial decomposition of only one of the two polyacetal blocks of the triblock copolymer, the resulting OH-group was derivatized with a dye. Pyrenebutyric acid (PBA) was chosen since it had been successfully attached to a polynorbornene before.[16] PBA is an excellent UV dye typically used in labeling nanoparticles[21] and biomolecules such as amylopectin.[22] PBA was attached under mild coupling conditions using the classical DCC/DMAP (dicyclohexylcarbodiimide/4-dimethylaminopyridine) system.[23] These conditions were chosen in order to avoid the presence of free acid at any time since this could trigger cleavage of the methyl-acetal (M1) block. This remaining polyacetal (M1) block was then cautiously sacrificed by addition of dilute acid.

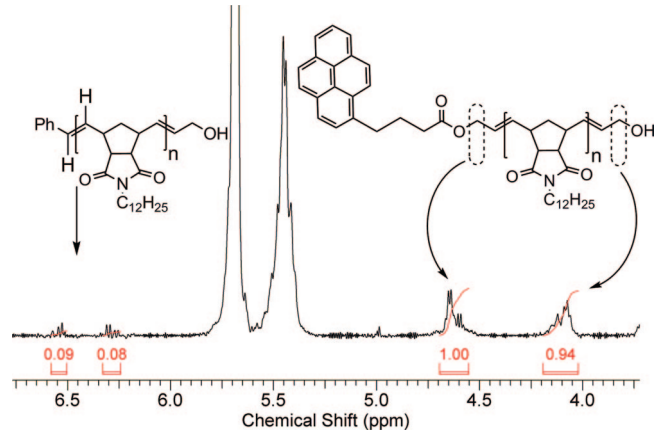


Figure 3. ^{1}H NMR spectrum of HO−(DNI)$_n$−PBA showing both functional endgroups at 4.1 ppm (OH) and 4.6 ppm (PBA).

The degree of functionalization was determined by ^{1}H NMR. Telechelics prepared by acidic cleavage of both acetal blocks exhibited one set of signals for the methylene group next to the hydroxyl-function (at δ = 4.1 ppm). The monoderivatized polymer showed two distinct endgroup signals (*cf.* Figure 3). The signals could be assigned to the polymer−CH_2−OH group (δ = 4.1 ppm) and the corresponding ester polymer−CH_2−O−PBA (δ = 4.6 ppm) in accordance with earlier publications.[16] Both NMR signals show similar integrals, and the integrals for residual styryl-endgroups induced by incomplete initiation of the first dioxepine block are minimal. This clearly shows the selectivity of both deprotection steps and the high degree of functionalization reached by the two dioxepine blocks. The presence of the pyrene moiety on the polymer chains was shown by SEC detecting a UV-signal at the maximum absorption wavelength of pyrene (340 nm). The respective SEC traces can be found in the Supporting Information.

Similarly high degrees of functionalization are reached when both dioxepine blocks are removed in one acidic hydrolysis. A ^{1}H NMR of the resulting polymer is given in the Supporting Information. In addition, the quality of the resulting materials could be shown by MALDI-ToF MS. The mass spectrum (Figure 4) shows no evidence at all for polymers bearing no functional group. The majority of signals observed correspond well to the calculated mass for the telechelic polymer (calc. 3785.01 *m/z*, observed 3787.1 *m/z*, both as Ag^+ adducts).

Comparison with previously prepared monofunctional and nonfunctional polymers of the same monomer and similar molecular weight showed that only a small amount of monofunctional impurity was present in the telechelic sample (Figure 4). These monofunctionalized polymer chains are probably due to incomplete initiation of the first dioxepine block since they are bearing styryl starting groups originating from the initiator C1. However, these chains represent <4% of the total polymer as shown by ^{1}H NMR experiments. It has to be noted, that the molecular weight of a polymer chain bearing two hydroxyl-endgroups is smaller than the monofunctional chain due to its lack of the styryl-endgroup generated by the initiator. The styryl group is removed during the cleavage of the first dioxepine block.

A number of different polymer materials were synthesized by this method, which are summarized in Table 1. Overall yields of this synthetic method ranged from 70−90% based on the norborneneimide monomer. As both dioxepine monomers are

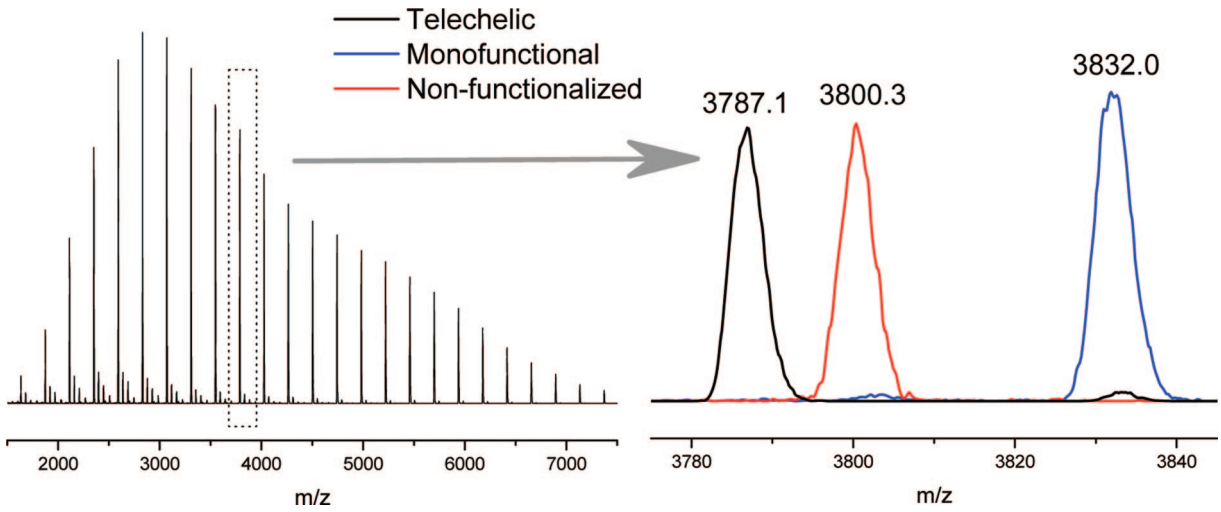


Figure 4. Left: MALDI-ToF MS spectrum of HO−(PNI)$_n$−OH. Right: Zoom of $n = 15$ region and comparison to reference material (red and blue curve).

Table 1. Characterization Data of Various Telechelic Polymers Synthesized from Triblock Copolymers

entry	1st dioxepine	*x*NI	2nd dioxepine	FG[a]	M_n[b]	PDI
1	M1	PNI	M1	OH/OH	2700	1.30
2	M1	HNI	M1	OH/OH	3700	1.33
3	M1	PNI	M1	OH/OH	5500	1.25
4	M1	DNI	M2	OH/OH	6700	1.32
5	M1	PNI	M2	OH/OH	9600	1.21
6	M1	PNI	M2	OH/PBA	7800	1.23
7	M1	DNI	M2	OH/PBA	9700	1.25
8	M1	DNI	M2	OH/PBA	20200	1.29

[a] Functional groups. [b] Molecular weights given in g mol^{-1}.

easy to synthesize even on large scale and workup and cleavage of the protective dioxepine blocks is versatile, this method can be expected to be very useful for many applications.

Polydispersity indices of all samples synthesized ranged from 1.2−1.3. They are a little higher than those obtained for monofunctional polymers by the *sacrificial synthesis* method using the same catalyst system, where PDI = 1.2−1.25 is typically reached. This small difference, however, can be explained considering the different initiation behavior of a polydisperse poly(M1)-macroinitiator compared to the neat Grubbs first generation catalyst.

Telechelics from Multiblock Copolymers. One drawback of the sacrificial triblock method for the synthesis of homotelechelic polymers is the consumption of one initiator molecule per telechelic chain. Since the characteristics of block copolymer formation between polynorborneneimides and dioxepine M1 had recently been established,[19] the question arose, as to what extent the addition of further alternating blocks of the two respective monomers would improve the yield of telechelic polymer chains per initiator molecule and thus lower cost of the desired material (Figure 5).

In order to test this concept, an ABABA pentablock-copolymer was synthesized and subsequently hydrolyzed by the same method as the triblocks (acidic hydrolysis). Figure 6 shows the GPC traces of the blockwise formation of the pentablock copolymer. A minor number of polymer chains can be found that were terminated during the polymerization of the second dioxepine block (3rd block) as these polymer chains did not reinitiate the fourth block (second polynorborneneimide block). However, hydrolysis of the final pentablock-copolymer resulted in cleavage of all dioxepine units and gave a polymer which showed a monomodal molecular weight distribution. In fact, the molar mass of the deprotected polymer is less than the masses of the individual multiblock samples, thus clearly showing the dioxepine separation between the two polynorborneneimide blocks. Any incomplete initiation at that point would have led to a bimodal mass distribution of the final telechelic polymer.

In analogy to telechelics synthesized from triblocks, the degree of functionalization was determined by ^{1}H NMR. (see Supporting InformationSI-6 top and SI-7 top for spectra) The total degree of functional endgroups was close to 100% in all cases. Minor signals could be found for styryl endgroups generated during the initiation of the first polynorborneneimide block (Supporting InformationFigure SI-6, peaks at 6.3−6.6 ppm). This shows that the efficiency of initiation of the first acetal monomer was greater than 95%. No signals could be found representing terminal olefin endgroups due to ethyl vinyl ether termination of the polynorborneneimide block.

The slightly higher total degree of functionalization is clearly a consequence of statistics: One initiator molecule forms two telechelic chains separated by a dioxepine segment. As this segment had been initiated in all chains, this could not create any nonfunctional groups. The probability of malformations at the beginning and the end of the pentablock copolymer due to incomplete initiation of the respective dioxepine blocks is the same as in the case of triblocks, however, these account for 50% of the functional groups in the case of sacrificial pentablocks only.

A further extension of the multiblock approach to a higher number of telechelics per initiator is especially interesting for short telechelics as their polymerization is fast and the amounts of polymer obtained per catalyst molecule are particularly low. This consideration prompted us to explore ABABABA heptablock copolymers as a source for low molecular weight telechelics. The synthesis of the heptablocks performed quite well, as the blockwise GPC analysis given in Figure 7 demonstrates.

After hydrolysis, a monomodal telechelic polymer was retained; however, the PDI's of the telechelics synthesized from heptablock-copolymers were higher than those obtained from pentablock-copolymers (PDI around 1.5). Overall yields of the telechelic polymer as well as the degree of functionalization were similar to those obtained from sacrificial pentablock-copolymers, thus a higher number of telechelic polymer chains per initiator molecule had been reached.

The average molecular weight of the telechelics is defined by the length of the polynorbornene blocks synthesized. It is of outmost importance to carefully tailor the amount of monomer

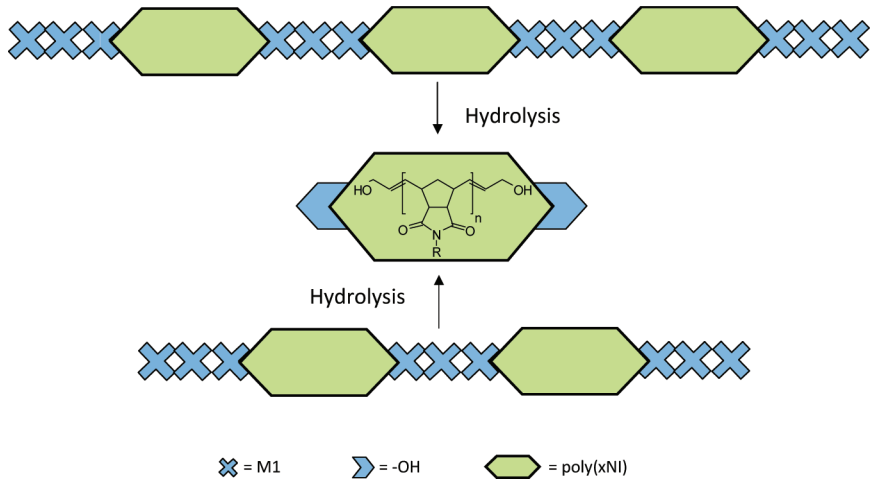


Figure 5. Formation of sacrificial multiblock copolymers and cleavage.

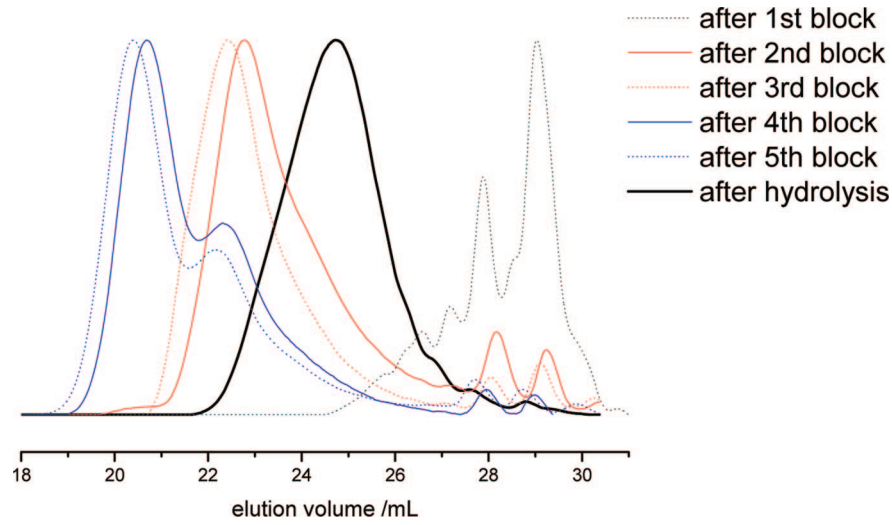


Figure 6. Formation of an ABABA pentablock-copolymer: SEC-RI traces of after each block (dotted lines after addition of acetal blocks, solid lines after stable blocks) and after hydrolysis of the polyacetal blocks (black solid line).

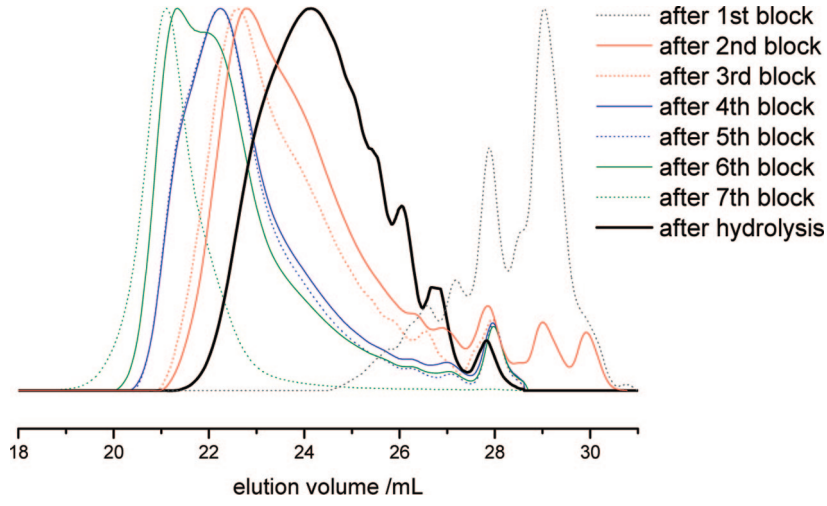


Figure 7. Formation of an ABABABA heptablock-copolymer: SEC-RI traces of each block (dotted lines after addition of acetal blocks, solid lines after stable blocks) and after hydrolysis of the polyacetal blocks (black solid line).

added as the second and consecutive norborneneimide block in order to avoid broadening of the molecular weight distribution.

By choosing different segment lengths for the different polynorbornenimides in a multiblock copolymer, multimodally distributed telechelic polymers can be synthesized on purpose. An example for a trimodal polymer and its synthesis as a heptablock-copolymer and subsequent hydrolysis are given in the Supporting Information. The characterization data for the bimodal pentablock equivalent is given in Table 2. Currently,

Table 2. SEC-RI Results of Various Telechelic Polymers Synthesized from Sacrificial Multiblock Copolymers

entry	*x*NI	no. of blocks	no. of modes	M_n	PDI
9	HNI	5	1	2300	1.35
10	HNI	5	1	3700	1.33
11	HNI	5	1	5700	1.32
12	PNI	5	1	4800	1.36
13	HNI	5	2	7000	1.87
14	HNI	7	1	6100	1.49
15	PNI	7	1	3800	1.50
16	HNI	7	3	4100	2.4

telechelics with orthogonally deprotectable hydroxyl groups can not yet be prepared from multiblock-copolymers.

Table 2 summarizes a number of different materials synthesized by the multiblock approach. As careful purification of the monomers is a key factor in the formation of multiblock-copolymers, HNI and PNI were chosen as the noncleavable monomer for this study since they can be obtained in excellent purity by high vacuum distillation or repeated recrystallization.

As expected, the degrees of functionalization that can be obtained by this heptablock approach lie close to 100%. The functionality of the synthesized polymer samples was confirmed by ^{1}H NMR in the same manner as for those materials generated from the aforementioned tri- and pentablock copolymers. Two representative ^{1}H NMR spectra can be found in the Supporting Information (Figures SI-6, bottom, and SI-7, bottom).

Polydispersity indices increase with the number of blocks synthesized for the sacrificial block-copolymer. Multiple reinitiation and block transfer reactions cause broadening of the molecular weight distribution, presumably due to increasingly worsening block transfer reactions. A general trend can be found in which the controlled sacrificial block copolymer synthesis gives telechelics with narrowly distributed molecular weight distributions for low numbers of blocks. With an increasing number of blocks, the polydispersity index approaches the statistical value of PDI = 2.

The synthesis of sacrificial heptablock-copolymers clearly increases the amount of telechelic polymer that can be obtained per initiator. However, increasing the number of blocks also leads to a steady bradening of the molecular weight distribution.

In comparison to the previously reported method for telechel synthesis involving chain transfer agents, the method described here allows for both, control over molecular weight and molecular weight distribution. The metathesis kinetics of acyclic molecules differ largely from those of cyclic olefins. Therefore the metathesis polymerization of a CTA−monomer mixture will inevitably lead to long polymer chains with the CTA remaining unreacted at first. Reversible cross-metathesis between the primary polymer chain and the acyclic functionalizing agent leads to molecular weight control and the introduction of the functional endgroups. Therefore, the CTA-method is applicable mainly to polymers bearing unhindered double bonds, i.e. monocyclic monomer structures such as cyclooctene.[11]

The same holds for the statistical copolymerizations of cyclic hydrolyzable monomers and stable monomers.[12] Since copolymerization parameters of such monomer combinations can not be expected to give aceotropic copolymerizations at all times. Therefore the average molecular weight of the telechelic molecules cannot be expected to follow the stoichiometric ratio of monomer and CTA concentration initially.[24]These kinetic problems were overcome in the present approach with the blockwise addition of the two respective monomers leaving the control over the molecular weight distribution largely in the hands of the chemist.

Conclusion

Well-defined ROMP-polymers with narrow molecular weight distribution bearing exactly one functional group on both chain ends can be synthesized by *sacrificial synthesis*. Two cleavable polyacetal blocks were polymerized on either side of the desired polymer segment. Subsequent sacrificial cleavage of these blocks yields telechelics with hydroxy end-groups. By choosing two different dioxepines, two cleavable blocks that could be removed sequentially under different conditions could be achieved. A telechelic polymer was synthesized, whose functional end-groups could be addressed orthogonally.

For sacrificial triblock copolymers, high degrees of functionalization of both chain ends and good definition of the polymer molecular weight could be achieved.

Sacrificial penta and hepta-blocks in which the sacrificial and the desired polymer blocks alternate were prepared. These multiblock copolymers yield well-defined telechelic polymers after hydrolysis. The advantage of the latter approach is the reduced amount of ruthenium initiator consumed per telechelic chain. In addition, the successful synthesis of sacrificial hepta block copolymers can be seen as proof for the strength of the synthetic method.

The extension of *sacrificial synthesis* to telechelic polymers has opened a new field of interesting materials. As well-defined homo- and heterotelechelic polymers are of interest for many scientific applications, this versatile method may attract a number of polymer scientists.

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Supporting Information Available: Figures showing further ^{1}H NMR results and SEC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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