Sacrificial Synthesis of Hydroxy-Functionalized ROMP Polymers: An Efficiency Study

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ABSTRACT: We present here a ^{1}H NMR spectroscopy study of the kinetics of the ROMP macroinitiation of poly(*exo-N*-phenyl-2,3-norbornene dicarboximide) with various dioxepine derivatives and Grubbs first generation ruthenium initiators. We have recently demonstrated that this so-called "sacrificial block copolymer" approach yields hydroxy-functionalized ROMP polymers with high end-group functionality. This study shows that the substituents on the dioxepine are important for functionalization efficiency, in the order phenyl > isopropyl > methyl. Addition of triphenylphosphine to the ruthenium carbene initiator resulted in lower k_i/k_p (rate of initiation/rate of propagation) values for the macroinitiation than in the absence of triphenylphosphine. We demonstrate that the value of k_i/k_p for macroinitiations can be estimated for new sacrificial monomers by analyzing one or two functionalization reactions. This provides an easy tool for the rapid screening and evaluation of new sacrificial monomers.

Introduction

Chain-end-functionalized polymers are of immense interest in polymer chemistry but also across the interdisciplinary borders. They offer interesting and quite modular pathways to novel hybrid materials such as bioactive[1,2] and ionic groups[3] or noncovalent binding motifs.[4] The need for polymers bearing exactly one functional group at one chain end requires the application of a living polymerization method, thus eliminating the possibility of reinitiation, termination, and chain transfer reactions.

Most living polymerization techniques, such as carbanionic polymerization,[5,6] RAFT,[7] ATRP,[8] or anionic ring-opening polymerization, offer straightforward routes to either functionalize the living polymer chain end or start the polymerization with a functional initiator.

Early well-defined catalyst systems based on titanium,[9] molybdenum, and tungsten[10] did not tolerate many functional groups in the monomer structure. While limiting the choice of monomer, this feature could be exploited in the introduction of functional end groups. The high oxophilicity of the metal carbenes allowed end-functionalization via addition of substituted aldehydes to the polymerization mixture.

As ruthenium-catalyzed ROMP is tolerant to most common organic functional groups, the functionalization reactions present in the literature mainly focus on olefins that deactivate the carbene species. The living end group of a ROMP polymer can be terminated using substituted vinyl ethers or vinyl lactones[11] which deactivate and remove the catalytic center from the chain end while leaving the desired functional group behind.[12] Applying specially functionalized ruthenium initiators[13] to place functional end groups at exactly one chain end also leads to monofunctionalized polymers, but involves challenging organometallic transformations which can be carried out by specialists to the field only.

Other groups have employed molecular oxygen,[14] which produces a terminal aldehyde. However, the functionalization reactions were often reported to be slow, gave low end-group conversions, or were not applicable in general.

End-functionalized telechelic polymers are also easily accessible using ruthenium carbene initiators in the presence of chain transfer agents. A number of functional groups such as hydroxyl groups[15] or amino and carboxylic acid groups[16] have been introduced in this manner; however, full control over the molecular weight distribution is lost. The necessity of precisely monofunctionalized polymer chains has limited the use of ruthenium-catalyzed olefin metathesis polymerization to polymers with highly functional pendant groups by employing functional monomers for a long period.[17]

Recently, we have reported a novel synthetic route to overcome many of the above-mentioned limitations by introducing a sacrificial block copolymer synthesis.[18,19] There, the living ROMP polymer to be functionalized was turned into a diblock copolymer by polymerizing dioxepine monomers onto the desired first polymer block (cf. Figure 1). The second (poly-

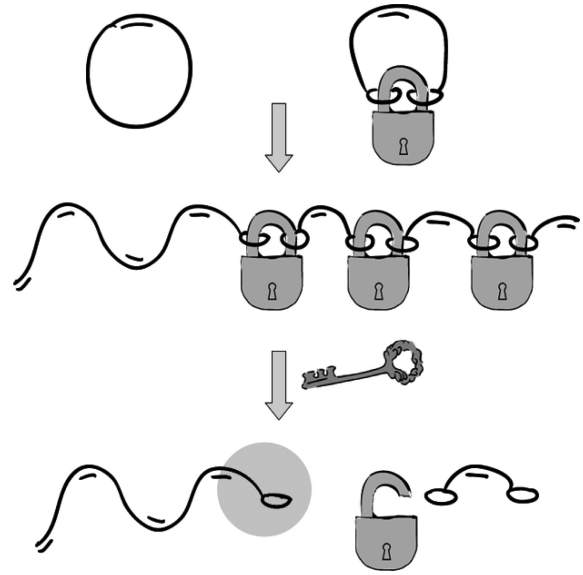

Figure 1. Concept of sacrificial synthesis.

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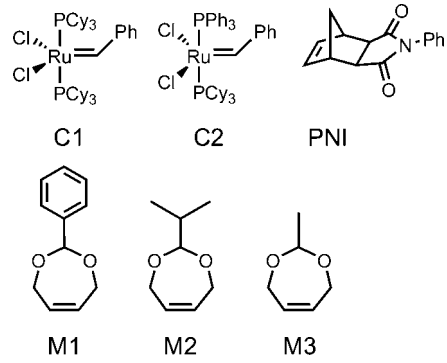
Scheme 1. Initiators and Sacrificial Dioxepine Monomers Studied



acetal) block could then later be cleaved, i.e., sacrificed, leaving exactly "half a dioxepine", i.e., a hydroxyl group, at the chain end.

In this case, no termination step is required for the functionalization. It can therefore be either omitted or conducted with a terminating agent, such as ethyl vinyl ether, that does not give a functional group at all. Hydroxy-end-functional polymers prepared via this route have already been used for the synthesis of graft[20] and amphiphilic diblock copolymers.[21]

In a first communication, which has drawn significant attention in the metathesis community,[19] we were able to demonstrate that extremely high degrees of functionalization (>97% typically) can be achieved. Yet, little was known about the amount of functionalizing agent necessary for a complete end-group conversion, and therefore the atom economy could not be determined.

Here, we report a sacrificial synthesis study exploring both efficiency and versatility of this novel functionalization strategy by analyzing the kinetics of the key step to functionalization, i.e., the initiation of the sacrificial block. The results are compared to classical initiation reactions of living polymerizations.

Three cleavable monomers and two catalyst systems were chosen for this study (cf. Scheme 1). The substituted 4,7-2*H*-dihydrodioxepine monomers **M1**−**M3** vary in both initiation and propagation behavior. In the presence of catalyst **C1** or **C2** the 2-phenyl-substituted dioxepine monomer **M1** and 2-isopropyl-substituted dioxepine **M2** do not form a homopolymer, but short oligomers. The 2-methyl-substituted derivative **M3** forms a homopolymer with a broad molecular weight distribution, when initiated with either catalyst **C1** or **C2**.

Experimental Section

General. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker AC300 or at 400 MHz on a Bruker AMX400. Kinetic ^{1}H NMR was conducted on a Varian Mercury 400 utilizing ACDLabs 10 for bulk processing. All spectra were referenced internally to residual solvent proton signals. Deuterated solvents were purchased from Deutero GmbH or Cambridge Isotopes. Size exclusion chromatography in 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 (10^4/500/50 Å). Signal detection occurred by use of a TSP Spectra System UV2000 (UV 254 nm) and a Wyatt Optilab DSP (refractive index). Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service.

exo-N-Phenyl-2,3-norbornene dicarboximide was synthesized as described in earlier publications.[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 solvent was dried by a Grubbs-type solvent system and stored under nitrogen.

Preparation of Kinetic ^{1}H NMR Samples. 15 mg (18 μmol) of Grubbs first generation catalyst was added to 0.3 mL of dichlormethane-d_2 under nitrogen. The solution was transferred into a nitrogen-filled NMR tube, which was sealed with a rubber septum. A solution of 43 mg (15 equiv) of PNI in 0.5 mL of dichlormethane-d_2 prepared under nitrogen was added by syringe. The polymerization mixture was allowed to stand for >30 min to allow for full polymerization. Upon measurement of a reference spectrum, the dioxepin monomer (29 mL of **M1**, 26 μL of **M2**, or 20 μL of **M3**) was added by microsyringe, and kinetic measurement was commenced immediately with four scans per measurement (44 s) and a 1 s pause incremented by 1 s after every measurement.

General Procedure for the Synthesis of Functionalization Series of Poly(PNI-*b*-dioxepin). Five 30 mL glass vials equipped with a silicone septum and a small stirbar were charged with 600 mg of PNI and degassed by passing a stream of purified Ar over the solid for 20 min. The samples were charged with 10 mL of dry, degassed dichloromethane each and allowed to dissolve. A 2 mL aliquot of a stock solution prepared from 690 mg of Grubbs first generation catalyst (and 1.035 g of PPh_3 (6.3 equiv) in cases where catalyst **C2** was used) dissolved in 10 mL of dry, degassed dichloromethane was added to the monomer solutions with stirring. After 30 min (6 h in cases where **C2** was used to initiate the polymerization), a 3 mL aliquot of the living polymerization mixtures was taken and terminated with 100 μL of ethyl vinyl ether. The appropriate amount of the respective dioxepin (14 μL for 1 equiv of Ph-dioxepin and Me-dioxepin or 18 μL for 1 equiv of iPr-dioxepin, doubled for every subsequent sample) was added to the polymerization mixture. Further 3 mL aliquots of the polymerization mixtures were taken after 15, 30, and 60 min (1, 2, and 12 h for polymerizations initiated with **C2**) and terminated by addition of 100 μL of ethyl vinyl ether each. All polymer samples were allowed to terminate for >1 h, precipitated in methanol, and dried overnight in vacuo to give virtually colorless solids, typically yielding >90%.

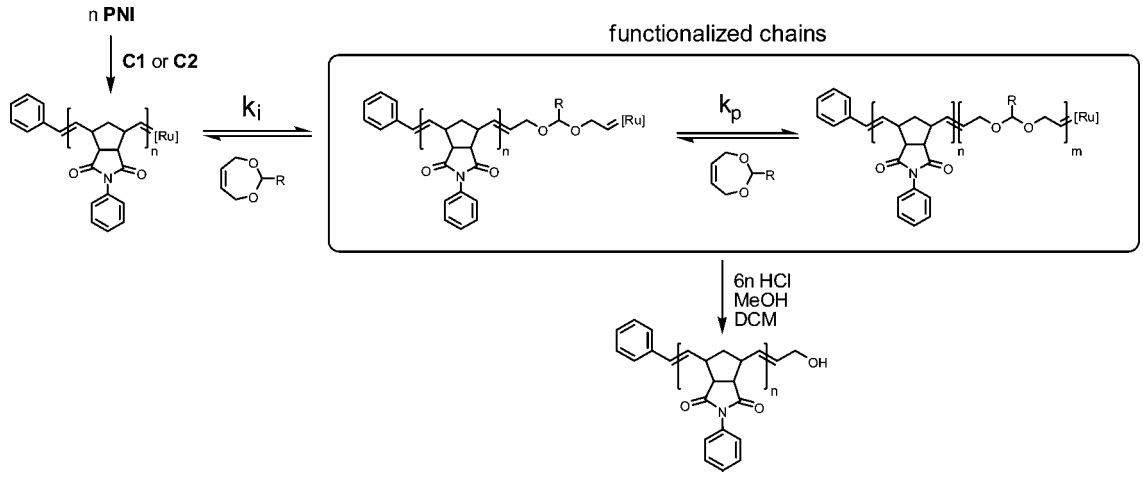
General Procedure for the Hydrolysis of Poly(PNI-*b*-dioxepin) Block Copolymers. The polymer samples were placed in a 12-vessel reaction carousel and dissolved in 5 mL of chloroform. 2 mL of methanol and 4 mL of 6 N HCl were added and stirred vigorously for 14 h. After the reaction time, the polymers were precipitated by addition of 15 mL of methanol, collected and redissolved in chloroform, and reprecipitated in methanol. The precipitate was filtered isolated by filtration and dried overnight in vacuo to give a colorless solid in 80−95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm]: 1.5−1.8, 2.1−2.3 (m, 2H, CH_2 bridge); 2.8−3.0 (m, 2H, C_3CH); 3.1−3.3 (m, 2H, C(O)CH); 4.16 (m, 2H, CH_2−O end group); 5.2−5.5 (m, 2H, olefin end group); 5.6−5.9 (m, 2H, double bonds polymer); 6.3−6.4 (m, 1H, double bond CH_2−OH end); 6.5−6.7 (m, 1H, double bond Ph end); 7.2−7.6 (m, 5H, Ph).

Results and Discussion

Sacrificial synthesis involves the polymerization of an additional block onto the desired polymer which is subsequently removed in order to set the terminal functionality free. The initiation kinetics of this cleavable block determine the efficiency of the entire synthetic strategy. The concurrent consumption of the sacrificial monomer during initiation and propagation of the sacrificial block limits the atom economy of this method because only chains bearing at least one unit of the cleavable monomer are functionalized, as depicted in Scheme 2. In cases where the initiation of the cleavable dioxepine monomer is much faster than its propagation, even low excesses of this monomer can be expected to lead to high degrees of functionalization. When the propagation is faster than the initiation, higher amounts of the sacrificial monomer have to be added.

In order to determine the efficiency of sacrificial synthesis, the optimum number of cleavable monomers per living chain

Scheme 2. Concurrent Reactions during Initiation of the Functionalizing Sacrificial Block



end had to be found. The polymerization of an additional block onto a living chain end is commonly classified as an initiation reaction involving the new monomer and a macroinitiator. Furthermore, ruthenium-catalyzed ring-opening metathesis polymerization represents a living polymerization, as termination and chain transfer reactions do not occur with most common ROMP monomers such as norbornene derivatives. Therefore, classical initiation kinetics of the living anionic polymerization can be applied to describe this reaction step.

The Grubbs first generation catalyst systems show rather slow initiation kinetics in comparison to many highly active living anionic polymerization initiators. However, the initiation kinetics of low-basicity intitiators[22] for the anionic polymerization can be applied to describe the concurrent reaction of initiation and propagation taking place during the macroinitiation step of the sacrificial block. As published by Szwarc et al.,[23,24] the initiation efficiency of an initiator can be calculated from the k_p/k_i factor and the equivalents of monomer applied to the initiator (cf. eq 1). In the case of sacrificial synthesis, M_{total}/C_{total} is defined by the number of equivalents of cleavable monomer per initiator (M_{total}: monomer concentration; C_{total}: initiator concentration) and the initiation efficiency f represents the degree of functionalization. However, as ROMP represents a theoretically reversible reaction, the values for k_i/k_p are apparent values.

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

The initiators chosen represent two readily available catalysts of the Grubbs first generation type. While catalyst **C1** is known for its commercial availability and good reactivity, the slower catalyst **C2** can be easily formed by addition of triphenylphosphine to **C1** and is known to give better control over molecular weight and PDI for lower molecular weight polymers.[25]

In order to determine the initiation kinetics of **M1**−**M3**, kinetic ^{1}H NMR spectroscopy was performed on catalyst **C1** initiated with 15 equiv of PNI. To ensure pseudo-first-order kinetics throughout the reactions, 10 equiv of the sacrificial monomer was added to the living polymerization. Figure 2 shows the time-resolved ^{1}H NMR spectra recorded for the reaction with **M2**. The signal at 19.2 ppm, representing the poly(PNI) carbene, vanishes over time, while a new signal at 19.5 ppm, which can be attributed to the newly formed dioxepine−carbene, develops at a similar rate. The benzylidene signal at 20.0 ppm is caused by noninitiated catalyst **C1**. It does not decrease noticeably owing to the lower reactivity of this carbene which has been reported previously.[26] By plotting the integrals of the carbene signals vs time, the progress of the reaction can be quantified. The reaction follows pseudo-first-order kinetics.

Reaction half-lifes were determined for all dioxepines **M1**−**M3** (see Supporting Information **S-1** and **S-2** for further kinetic measurements). Second-order initiation constants were calculated from the kinetic data which are summarized in Table 1.[27] Because of signal overlap of the dioxepine peaks with the poly(dioxepine) signals, the total monomer consumption could not be determined and no k_p values were calculated.

The obtained initiation constants correlate well with the general polymerization trend found for the three dioxepines, with **M3** giving broadly dispersed molecular weights and **M1** giving the best functionalization results. Similar kinetic results

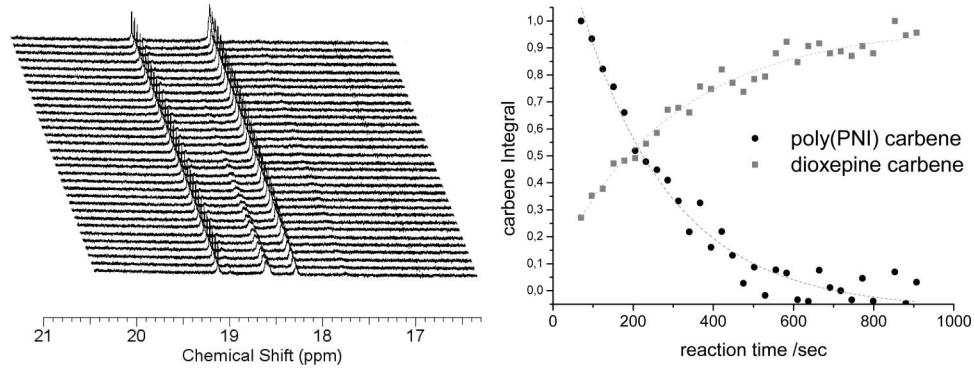


Figure 2. Left: time-resolved ^{1}H NMR spectrum of the reaction of **C1** initiated with 15 equiv of PNI after addition of 10 equiv of **M2** (top = start of reaction; the time (Δt) between spectra increases from top to bottom; for details see the Experimental Section). Right: development of carbene signal integrals over time.

Table 1. Half-Lifes and Initiation Constants for M1−M3 with PNI-Initiated Catalyst C1

dioxepine	$t_{1/2}$, s	k_i, L/(mol s)
M1	129	3.876
M2	237	1.596
M3	653	0.668

can be obtained when the formation of the new carbene is observed rather than the disappearance of the initial carbene. However, the signal of this carbene is broader and integration less exact. Generally, it has to be noted that quantitative evaluation of this active polymer end group is particularly tedious. The high rate of the reaction requires quick measurements, inevitably leading to a rather low signal-to-noise ratio.

In summary, kinetic ^{1}H NMR spectroscopy was insufficient to determine the k_p/k_i factor. However, this vital factor is needed in order to describe the overall efficiency of sacrificial synthesis. Alas, the k_i/k_p value could be determined using the total degree of functionalization. As eq 1 implies, with M_{total}/C_{total} set by the number of equivalents of the dioxepine monomer added and the degree of functionalization equaling the initiation efficiency f, the k_p/k_i factor can be calculated.

In order to obtain the total degree of functionalization, a series of sacrificial syntheses were carried out, employing poly(PNI) as the first block with either catalyst **C1** or **C2** and the three different dioxepines **M1**−**M3** to prepare the second block. A reference sample was collected before the cleavable dioxepine monomer was added. The reference sample was terminated with ethyl vinyl ether, thus forming a terminal olefin which could be distinguished from the desired functional end group by standard ^{1}H NMR spectroscopy. Upon addition of the cleavable dioxepine monomer, samples were taken at three representative reaction times (see Experimental Section) and treated with ethyl vinyl ether. All samples were subsequently hydrolyzed to liberate the terminal alcohol group.

The total degree of functionalization was determined by comparing the integral of the ^{1}H NMR signal of the functional end group (H_f) to the integrals of the styryl end group (H_{s1} and H_{s2}) introduced by the initiator (cf. Figure 3). The signal of the terminal olefin group (H_o) created by ethyl vinyl ether termination served as a reference.

As demonstrated in Figure 3, the degree of functionalization with catalyst **C1** and dioxepine **M1** reaches a maximum after ca. 1 h of reaction time, indicating that the reaction has been completed at this point. Using catalyst **C2** (Figure 4, right), the functionalization reaction is much slower, as expected, and takes 12 h to complete. A further increase of reaction time did not afford higher degrees of functionalization.

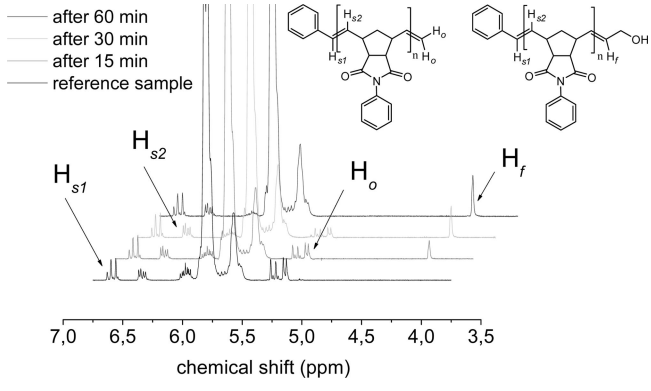


Figure 3. Determination of the degree of poly(PNI) end-functionalization by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra from bottom to top show the development of hydroxy-functionalization over time. 8 equiv of **M1** was added to the reaction.

The results of the end-functionalization series with the other two dioxepines (**M2** and **M3**) are given in the Supporting Information (**S-3** and **S-4**). It was found that full end-functionalization can be achieved by adding as little as 4 equiv of **M1** or 8 equiv of **M2** to polymers initiated with catalyst **C1**. 80% functionalization was achieved by addition of 16 equiv of the dioxepine **M3**.

When **C2** was used to initiate the polymerization of **PNI**, the degrees of end-functionalization were generally lower than with **C1**, but followed the same trend. Here, similar to the results presented above, dioxepine **M1** was the best functionalizing agent, giving nearly fully functionalized polymers (95%) employing 16 equiv of the dioxepine. **M2** and **M3** gave 67% and 50% end-functionalization under the same conditions, respectively.

In order to obtain the k_i/k_p factor, the degrees of functionalization after the polymerization reaction had come to completion were plotted against the number of equivalents of the dioxepine monomer added (cf. Figure 5). A function generated from eq 1 was then fitted to the raw data by varying k_p/k_i. For **M2** and **M3** (see **S-5** in the Supporting Information), adjusting the theoretical curve to the observed degrees of functionalization resulted in an excellent fit. When the functionalization results of **M1** were evaluated by the same method, a good agreement with theory could be found when catalyst **C1** was used. In the case of catalyst **C2**, however, the degrees of functionalization were underestimated for higher excesses of the dioxepine monomer. This effect can be explained taking into account that dioxepine **M1** cannot form a homopolymer due to steric and electronic reasons.[28] This means that the propagation of the monomer **M1** fades after a few monomer addition steps, and large excesses of **M1** are available for the macroinitiation step.

It has to be noted that the ability to calculate k_i/k_p values from functionalization results is extremely useful for future developments of sacrificial monomers. Determining the end-functionalization with one or two test reactions at different excesses of the cleavable monomer, the entire functionalization behavior of a monomer can be estimated using eq 1.

The k_i/k_p values found for all dioxepine monomers studied are summarized in Table 2. The difference in initiation behavior between the various monomer and catalyst systems is quite significant. The general trend of the k_i/k_p values resembles the functionalization results of earlier experiments, with **M1** giving the best results and **M3** giving the lowest degree of functionality. The effect of the addition of PPh_3 to catalyst **C1** (thus forming **C2**) on the k_i/k_p ratio is contrary to the findings of Bielawski et al.,[25] who saw a general increase of k_i/k_p when PPh_3 was added to the catalyst. However, the dioxepines **M1**−**M3** are rather low in polymerization reactivity, and steric effects might have a significant influence on the initiation of the sacrificial block. The poly(PNI)−carbene certainly represents a larger steric hindrance than the comparably small carbene of the ring-opened dioxepine. Therefore, much higher excesses of the dioxepine monomers have to be added in order to reach full functionalization of the polymer when using catalyst **C2**.

On the other hand, the addition of PPh_3 does have positive effects on the molecular weight distribution and the initiation efficiency of the first polymer block that is not sacrificed. As demonstrated by the SEC data given in Table 3, the polymers synthesized during the functionalization series with catalyst **C1** show a higher polydispersity index (typically ca. 0.1 higher than polymers synthesized with catalyst **C2**) and a significantly higher molecular weight, indicating incomplete initiation which is typical for **C1** when aiming for low molecular weights. Also, a slight broadening of the molecular weight distribution can be monitored during the long reaction times required for quantitative functionalization with catalyst **C2**. However, the function-

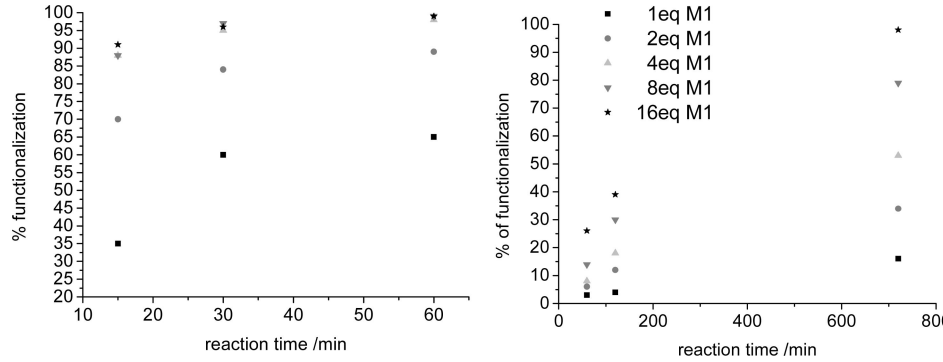


Figure 4. Degrees of poly(PNI) end-functionalization with different amounts of **M1**. Left: polymerization initiated with **C1**. Right: polymerization initiated with **C2**.

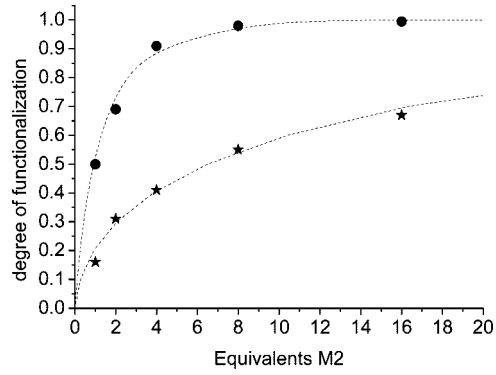


Figure 5. Degrees of end-functionalization vs excess of dioxepine monomer **M2** and fitted theoretical values (dashed lines, according to eq 1) for poly(PNI) initiated with catalyst **C1** (squares) and catalyst **C2** (stars).

Table 2. k_i/k_p Values Determined for the Macroinitiation/ Propagation of Poly(PNI) and the Dioxepine Monomers M1−M3

dioxepine	initiator	equiv of PPh_3 added	k_i/k_p
M1	**C1**	0	0.625
M1	**C2**	6.3	0.065
M2	**C1**	0	0.472
M2	**C2**	6.3	0.032
M3	**C1**	0	0.040
M3	**C2**	6.3	0.012

alization time can be reduced by addition of larger excesses of the respective dioxepine. The SEC characterization data for **M1** and **M3** can be found in the Supporting Information (**S-6** and **S-7**).

The need to apply an excess of the functionalizing agent applies to most other functionalization methods such as for example the use of substituted vinyl ethers.[12] However, it is particularly pronounced in sacrificial synthesis when catalyst **C2** is used. Nonetheless, this is a small price to pay for obtaining well-defined and fully functionalized polymers, especially with commercially available or conveniently accessible dioxepine monomers and catalyst systems.

Conclusions

Sacrificial synthesis using the ring-opening metathesis polymerization (ROMP) is an extremely useful and versatile functionalization method. The concept is unique in the sense that a macroinitiation step rather than a termination reaction is used to attach a desired functional group to the polymer chain end.

The efficiency of this functionalization concept was demonstrated by a series of functionalization reactions applying different amounts of the cleavable monomer and varying

Table 3. SEC Results (RI Detection) for the End-Functionalization of Poly(PNI) Using Either Catalyst C1 or C2 and Employing Different Amounts of Dioxepine Monomer M2

	catalyst **C1**			catalyst **C2**		
excess **M2**	time (min)	M_n	PDI	time (h)	M_n	PDI
1	reference	6400	1.23	reference	2500	1.08
	15	6500	1.20	1	2400	1.15
	30	6700	1.15	2	2800	1.09
	60	6400	1.16	12	3100	1.10
2	reference	6100	1.16	reference	2600	1.08
	15	5800	1.15	1	2600	1.08
	30	6100	1.17	2	2800	1.10
	60	5900	1.17	12	3200	1.13
4	reference	5900	1.16	reference	2600	1.09
	15	5700	1.16	1	2500	1.07
	30	5900	1.17	2	2700	1.09
	60	6100	1.17	12	2900	1.16
8	reference	6900	1.12	reference	2300	1.09
	15	6000	1.16	1	2500	1.09
	30	5900	1.17	2	2600	1.10
	60	6000	1.17	12	2600	1.15
16	reference	6000	1.16	reference	2400	1.08
	15	5900	1.15	1	2500	1.10
	30	5600	1.19	2	2300	1.12
	60	5900	1.15	12	2500	1.13

reaction times. Moreover, the functionalization results were found to be in good agreement with theoretically derived degrees of initiation on low-basicity initiators of the living anionic polymerization.

With the examination of the macroinitiation behavior of the dioxepine monomers involved in this study, the basis has been established to combine the characteristics of this functionalization reaction with the kinetic equation describing the initiation reaction of classical living polymerizations. This theoretical basis will aid future developments of new sacrificial monomers as it could be shown that the key factor to the efficiency of sacrificial synthesis, the value of k_i/k_p, can be estimated for each cleavable monomer by as little as one or two functionalization reactions.

Therefore, this study will be of major importance to further functionalization strategies applying sacrificial strategies and will simplify the comprehension of essential factors such as atom economy and reaction times.

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Supporting Information Available: Further kinetic ^1H NMR results and kinetic plots, results of additional functionalization series,

and SEC data thereof. This material is available free of charge via the Internet at http://pubs.acs.org.

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