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Mechanical Activation of a Latent Olefin Metathesis Catalyst and Persistence of its Active Species in ROMP

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Supporting Information

ABSTRACT: Preparation, substrate scope, and activity of a previously reported mechanically activated metathesis catalyst were investigated. Scission of the catalyst under ultrasound irradiation was followed by GPC, which showed a first-order scission rate constant of 0.011 min⁻¹. The resulting active species was shown to have catalytic reactivity in ring closing metathesis (RCM) of various (un)hindered substrates. Further investigations of the active species showed that it was not influenced by radicals formed during ultrasound and that the most effective method to increase its lifetime was an increase in the substrate concentration. In ring-opening metathesis polymerization



(ROMP), the lifetime of the active species was shown to be several hours, in contrast to the short lifetimes found in RCM. ROMP experiments also showed that all of the latent precatalyst broken leads to active catalyst species.

INTRODUCTION

Controlling the activity of a catalyst by an external trigger creates opportunities in applications ranging from alternative production methods of polymeric materials (e.g., reaction injection molding) to self-healing materials. Latent catalysts are the subject of numerous studies because the inactive state, most often, is also a stable state, making it possible to create a *catalyst that lives forever*.¹ Ideally, a latent catalyst can be stored together with the substrate for a prolonged period, only initiating the reaction after the appropriate stimulus.² Traditionally, this stimulus consists of an increase in temperature,^{3–5} addition of a chemical agent,^{6,7} or irradiation with light.⁸ Activation is often based on breakage of a metal–ligand bond; the resulting coordinatively unsaturated species can bind to a substrate.

An alternative way to break metal—ligand bonds is the application of mechanical force.^{9,10} Mechanochemical scission of covalent bonds in polymers is well-studied; in these large molecules, forces on the molecule accumulate in the center of the chain to result in preferential scission midchain.^{11–13} However, when one of the bonds in the chain is weaker, it selectively breaks at this weaker bond; examples found in literature include azo¹⁴ and peroxide¹⁵ bonds. Recently, we demonstrated that this principle also holds for coordination bonds.^{16,17}

Combining the work of latent catalysts with mechanical scission of coordination bonds recently led us to develop latent catalysts that can be activated by mechanical force, i.e., mechanocatalysts.^{17–20} The newly defined field of mechanocatalysis opens ways to signal high stresses in materials or to reinforce materials that tend to fail (e.g., self-healing materials).²¹ One of the catalysts reported by us (complex **1a**, Chart 1) is a modification of the Grubbs-type olefin metathesis catalyst¹⁸ with two carbene ligands.²²





Grubbs catalysts catalyze various olefin metathesis reactions, including ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), cross metathesis (CM), and ene-yne metathesis.²³ These ruthenium alkylidene complexes are known for their tolerance to most functional groups.^{24,25} Their versatility and functional group tolerance makes them into an increasingly important tool for organic and polymer chemists. The generally accepted activation mechanism for Grubbs type of catalysts is a dissociative one, where one of the ligands decoordinates to induce catalyst activation.^{26,27}

Ruthenium alkylidene complexes containing two N-heterocyclic carbene (NHC) ligands are known latent catalysts.^{22,28,29} The lack of activity at room temperature is ascribed to the strong NHC–Ru bond, which dissociates only at elevated temperatures. Modification of the facile one-step synthesis of bis NHC complexes reported by Verpoort et al.²² by attaching polymer chains onto the NHC ligands (Chart 1) led to a latent

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metathesis catalyst that was activated by application of ultrasound. $^{18}\,$

Ultrasound is one of the most efficient ways to apply mechanical forces in solution. Upon sonication, strong shear gradients arise around collapsing cavitation bubbles. In these gradients, polymers of sufficient length are stretched, and they eventually break midchain due to accumulation of stress.³⁰ For ultrasonic activation of complex **1a**, the rate of activation was dependent on the molecular weight of the polymer. As expected, lower molecular weight polymer chains led to lower activity, and an analogue containing only butyl chains was not activated at all. Switching off the ultrasound led to an immediate stop of the catalytic reaction; this was ascribed to fast decomposition of the active species.

In the article by Piermattei et al.,¹⁸ the mechanochemical activation of complex 1a was established; however, fundamental questions still remained. Here, we describe a thorough investigation of the earlier described mechanically activated metathesis catalyst. We show that mechanochemical scission of the complex follows first-order reaction kinetics and that the activated catalyst performs ring-closing metathesis of various (un)hindered substrates. The limited lifetime of the active catalyst in RCM is extended at higher substrate concentration. In ring-opening metathesis polymerization, the lifetime of the active catalyst lifetime is increased to at least several hours. The concentration of active catalyst is estimated using a ROMP substrate, which indicates that all broken complex leads to an active catalyst.



RESULTS AND DISCUSSION

Synthesis and Characterization. In order to build a catalyst that can be activated by mechanical force, a latent catalyst should be incorporated into a polymer chain which transfers macroscopic forces to the individual molecular bonds. More specifically, polymer chains should be attached to the ligands that have to dissociate in order to activate the latent catalyst. Complex 1a was synthesized (Scheme 1) following the original report by Piermattei et al.¹⁸ and analyzed by gel permeation chromatography (GPC) in dimethylformamide (DMF) as the eluent. The GPC trace shows a shoulder at the molecular weight of the uncoordinated pTHF chain (Figure 1, red line). Attempts to minimize the amount of unfunctionalized pTHF chains were not successful (Supporting Information). However, thermal activity at 75 °C of complex 1a and model complex 1b were exactly the same when the concentration of complex 1a was corrected for the presence of unfunctionalized pTHF chains (Supporting Information). This suggests that these chains do not influence the catalytic activity. From the absence of a signal of an imidazolium proton around 10 ppm in ¹H NMR spectroscopy, we concluded that product **1a** did not contain original 2a, and analysis using hexafluoroacetone^{31–33} showed that the amount of OH end groups is <1% (Supporting Information). Therefore, we speculate that the shoulder in GPC is caused by pTHF chains with decomposed NHC ligands.³⁴ The fraction of these unfunctionalized pTHF chains varies from batch to batch and was estimated using ¹H NMR in order to allow determination of catalyst concentration.

Scission by Sonication in Solution. Further investigations focused on scission and activation of complex 1a. Upon sonication of a toluene solution of 1a, the weak NHC–Ru bond is broken, leading to products 5a and 6a (Scheme 2). Previously, this was demonstrated¹⁸ in an experiment in which the adduct of 5a with tricyclohexylphosphine was obtained when sonication was performed in the presence of PCy₃. Since 1a has twice the molecular weight of 5a and 6a and rebinding of the ligand was shown not to occur, the extent of scission could be followed by GPC.

During sonication, the higher molecular weight peak decreased and the lower molecular weight peak increased (Figure 1). By fitting two Gaussian peaks with similar peak width to the data, scission of complex **1a** could be followed quantitatively.



Figure 1. (a) GPC traces in DMF of solution containing 0.2 mM 1a (batch 2), 200 mM diethyldiallyl malonate 7, and 136 mM hexadecane in toluene before and during sonication. GPC trace of ligand 2a. (b) First-order kinetic plot of relative area of fitted Gaussian curve belonging to complex 1a. Data points and error bars based on average and standard deviation of experiments in triplicate (2 experiments with 200 mM 7, 1 experiment with 200 mM 9).

Scheme 2. Scission of 1a under Ultrasound



The reaction was shown to follow first-order reaction kinetics, with a rate constant of $(1.12 \pm 0.03) \times 10^{-2} \text{ min}^{-1}$ (Figure 1). The rate constant was found to be independent of substrate (7, 8, and 9, *vide infra*) and substrate concentration (20 and 200 mM, *vide infra*), indicating that the measurement indeed probes the primary scission process independent of rebinding or substrate (Supporting Information). When low molecular weight analogue **1b** was used, ¹H NMR showed no visible decrease in the alkylidene signal (19.2 ppm) over 80 min of sonication under similar conditions (Supporting Information), confirming the mechanical origin of the scission process.

Compound 5 is believed to be the active species in the dissociative mechanism of ruthenium-type olefin metathesis catalysts.^{26,35} Therefore, we tested catalytic activity against different substrates for ring-closing metathesis. As can be seen in Figure 2,



Figure 2. (a) Structures of substrates 7–9. (b) Time-conversion of ring-closing metathesis of diethyldiallyl malonate 7 (\blacksquare), diethyldilylmethallyl malonate 8 (\bullet), or methyl-*N*,*N*-bis(methylallyl)benzenesulfonamide 9 (\blacktriangle) using 0.2 mM 1a (batch 2) and 200 mM substrate. Conversion determined by GC-FID, using hexadecane as an internal standard; data points and error bars based on average and standard deviation of experiments in duplicate.

1000 equivalents of diethyldiallyl malonate (DEDAM) 7 is converted by more than 40% after 75 min of sonication in the presence of polymeric complex 1a (batch 2), resulting in a turnover number (TON) of 440. Sonication with low molecular weight analogue 1b results in conversion below 1% (Supporting Information), proving the necessity of polymer chains and the mechanical nature of activation. Increasing the steric demand of the substrate by using diethylallylmethallyl malonate **8** leads to a significant decrease in activity, with only 15% conversion after 75 min. RCM of **8** is known to be more challenging, and the observed decrease in reaction rate by a factor of 2.8 is well in agreement with the reduction observed in literature by a factor of 2 to $3.^{36,37}$ The even more challenging substrate methyl-*N*,*N*-bis(methylallyl)-benzenesulfonamide **9** is only 6% converted after 75 min of sonication.

Increasing the Lifetime of the Active Species. In our earlier report,¹⁸ it was shown that upon discontinuation of ultrasound, conversion via ring-closing metathesis immediately stopped. The most likely cause for this effect was a limited lifetime of the active species. After confirming this on/off cycle (Supporting Information), we attempted to increase the lifetime of the active catalyst, in order to increase the conversion during ultrasound.

One of the known effects of ultrasound is the formation of radicals due to the high temperatures and pressures reached in the cavitation bubble.³⁸ Sonication experiments in the presence of known radical scavengers (2,6-bis(1,1-dimethylethyl)-4-methylphenol and 1,4-benzoquinone), however, showed that that radical species do not limit the lifetime of the active species under the current conditions (Supporting Information).

Decomposition is thought to occur mainly through a 14electron species generated upon activation.³⁹ The addition of pyridine and isopropoxystyrene, both coordinating species, however, led to a decrease in activity in the RCM of DEDAM 7 (Supporting Information). Possibly, competition between substrate and these species plays a role. When triphenylphosphine was added, a shape change in the time conversion plot suggests initial coordination of PPh₃ toward the catalyst, followed by activation of the resulting species by dissociation of PPh₃. This, however, did not lead to persistent catalytic activity in an on-off experiment with added PPh₃. For ruthenium– methylidenes, which are the propagating species in RCM, it is known³⁹ that adding coordinating phosphine ligands does not influence their decomposition, in contrast to other ruthenium– alkylidene complexes.

In a final attempt to increase the lifetime of the active species, we varied the concentration of substrate. Figure 3 shows that decreasing the concentration of 7 from 200 mM to 20 mM led



Figure 3. Time-conversion plots of RCM of DEDAM 7 upon sonication of a 0.2 mM solution of 1a (batch 2) and 20 mM (\blacksquare), 200 mM (\bullet), or 1 M (\blacktriangle) of 7 in toluene. Conversions determined by GC-FID, using hexadecane as an internal standard; data points and error bars based on average and standard deviation of experiments in duplicate.



Figure 4. (a) Ring-opening metathesis polymerization of **15** (100 mM) using **1a** (batch 3) (0.2 mM) under ultrasonic activation in toluene and subsequent quenching with ethyl vinyl ether. (b) Time-conversion plot for ROMP of **15** under continuous sonication (\blacksquare) and 10 min sonication on, then sonication off (\blacktriangle); gray area indicates sonication period for on-off experiment. Conversion determined by ¹H NMR for continuous experiment and GPC peak area for on-off experiment (for the on-off measurement, points at *t* = 0, 10, 20, and 33 min are in triplicate; *t* = 5, 12, 15, 26, and 45 min are in duplicate; *t* = 60, 90, 120, 180, and 240 min are single experiments; error bars indicate standard deviation). (c) Typical resulting GPC traces (in THF, 254 nm UV detector) of an on-off experiment taking 100 μ L aliquots at different time intervals. Molecular weights were corrected to correspond to actual molecular weights for this polymer by multiplication by a factor of 1.32.

to a decrease in conversion after 75 min of 44% to 36%. The calculated TON after the same time period decreased from 440 to 36. On the other hand, increasing DEDAM concentration to 1 M led to a higher conversion of 53% and a TON of 2657 after 75 min. Apparently, the higher substrate concentration stabilizes the active species and leads to increased conversion, similar to what was observed for ring-closing metathesis with Ru-alkylidene catalysts when bulk substrates were used.⁴⁰ Since olefin binding to the activated species is rate determining,^{26,27} it is likely that the reaction rate can be enhanced by increasing the substrate concentration further. In an attempt to push the catalyst to its limit, sonication in pure DEDAM was attempted. However, no conversion was observed, most likely due to the absence of cavitation bubbles in DEDAM, due to its high viscosity and low vapor pressure.⁴¹ It should be noted that at all concentrations conversion using catalyst 1b was found to be below 1% (GC-FID or GC-MS) upon applying ultrasound, providing additional evidence for the mechanical nature of the activation step (Supporting Information).

Persistence of Active Species in ROMP. Conversion and lifetime of the active species were further investigated in ringopening metathesis polymerization. In this reaction, the catalyst acts as initiator, and one active species leads to a single growing chain under the conditions that the polymerization can be considered "living".²³ Therefore, product molecular weight, combined with conversion, provides information on the concentration and lifetime of the active species.

Polymerizations were performed with bis-biphenyl-functionalized norbornene monomer **15**, with a UV absorption band at 250 nm ($\varepsilon = 3.4 \times 10^4$ L mol⁻¹ cm⁻¹), which allows distinguishing its ROMP product from the polymeric complex **1a** $(\varepsilon = 1.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \text{ at } 250 \text{ nm})$ by GPC using a UV detector. Continuous sonication of monomer 15 led to a conversion of 20% after 75 min (Figure 4). Sonication of control catalyst 1b resulted in a conversion below 0.2% (Supporting Information). However, the molecular weight of the product could not be used to analyze the polymerization rate, because it was established in a separate experiment that sonication of a solution of high molecular weight poly-15 results in a reduction of its molecular weight (Supporting Information).

In further experiments, ultrasound was therefore stopped after 10 min, and conversion and $M_{\rm n}$ were then followed by GPC or ¹H NMR. Figure 4 shows that conversion continued to increase for hours after sonication was stopped, albeit at an approximately 4 times lower rate than under continuous sonication. A significant part of the reduced rate can be ascribed to the decrease in temperature from \sim 35 to 14 °C when sonication is stopped. When the data were fitted to a model assuming that the active catalyst decomposed following first-order kinetics, a half-life of 4 ± 1 h and a polymerization rate of 1.1×10^{-4} M min⁻¹ were found (Supporting Information). The long lifetime is in strong contrast with the behavior of the latent catalyst with DEDAM.¹⁸ It is known from literature that the ruthenium-methylidene intermediate formed in RCM (Chart 2) is a slow propagating, fast decomposing species.^{27,39,42} The propagating species in ROMP is much more stable, with a typical half-life of several hours.³⁹

The concentration of growing chains, and hence the concentration of active catalyst, was calculated from the ratio of increase in degree of polymerization (DP) and conversion (Supporting Information). During the first 50 min after sonication is stopped, the calculated concentration is approximately 3×10^{-2} mM, or 15% of the initial catalyst concentration.

Chart 2. Structures of Ruthenium–Methylidene (left) and Ruthenium–Alkylidene (right) as the Propagating Species in RCM and ROMP, Respectively



The batch of **1a** used for ROMP has a slightly higher molecular weight than the batch that was used in scission rate determination. Therefore, 15% activation is nicely in line with the 11% scission after 10 min of sonication calculated from scission rate data and indicates that many, if not all, chain scission events give rise to active catalyst species.

Finally, the concentration of active species was used to calculate the second-order rate constant of its reaction with monomer. The value obtained is $35 \text{ min}^{-1} \text{ M}^{-1}$, approximately 20 times lower than for third-generation Grubbs catalyst $((H_2\text{IMes})(\text{py})_2(\text{Cl})_2\text{Ru}=\text{CHPh})$ at 14 °C (Supporting Information). The lower activity is most likely due to a combination of steric and electronic differences between the active species.²⁷ These differences include the presence of a polymer chain and one instead of two aryl groups on the NHC ligand of catalyst 1a.

CONCLUSION

The work presented here establishes polymeric complex 1a as a useful latent catalyst that is activated by mechanical force, as opposed to a low molecular weight analogue 1b. GPC experiments demonstrated that scission of 1a by ultrasound follows first-order reaction kinetics, whereas for low molecular weight analogue 1b, no scission was observed. The activated complex is active in ring-closing metathesis for various substrates. In these reactions, the lifetime of the active species is limited, but it is not affected by radicals formed by ultrasound. The addition of triphenylphosphine leads to delayed initiation, but increases the lifetime of the active species. Lifetime is increased more effectively by increasing substrate concentration. In contrast to RCM, the active species in ring-opening metathesis polymerization has a lifetime of several hours, opening opportunities for catalysis in the solid state, where diffusion is low and, hence, reaction times are longer. Data obtained with ROMP also make it plausible that most scission events lead to an active catalyst. However, its activity is estimated to be more than an order of magnitude lower than for the active species formed from a third-generation Grubbs catalyst.

ASSOCIATED CONTENT

S Supporting Information

Experimental procedures and characterization data, fitting procedure, estimation of active catalyst concentration and lifetime, additional catalytic tests, and control experiments. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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