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Highly controllable poly(*N*-vinylimidazole)-supported ruthenium catalysts for olefin metathesis reactions in aqueous media

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In this study, we reported a novel poly(*N*-vinylimidazole) (PVI)-supported latent ruthenium catalyst for olefin metathesis applications in aqueous media. The catalysts were synthesized using direct immobilization of first- and second-generation Grubbs catalysts on poly(*N*-vinylimidazole). The immobilized catalysts were characterized using FT-IR, SEM and EDX. The catalysts are metathesis inactive in both organic and aqueous media but can be activated via the introduction of acid to the reaction medium. The activity of the catalysts was tested on ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP) reactions. It was shown that the molecular weight of the ROMP polymers can be controlled by initiating the reaction with varying HCl/Ru ratios. Additionally, the reusability of the catalysts for RCM of diethyldiallylmalonate was studied. In addition, the RCM reaction of diethyldiallylmalonate can be switched on and off via the introduction of acids and bases to the reaction media using PVI-supported ruthenium catalysts.

1. Introduction

Olefin metathesis is a useful synthetic method to construct carbon–carbon double bonds with high atom efficiencies [1]. Many applications of metathesis reactions were developed parallel to the development of ruthenium-based metathesis catalysts with high tolerance to air, moisture and functional groups [2]. Among these applications, ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) reactions have gained widespread interest in both academia and industry. Polymers with various functional groups can be synthesized via ROMP reactions with advanced architectures and narrow PDI values [3]. Ring-closing metathesis reactions are used to form challenging heterocyclic compounds, as well as to form polycyclic compounds in combination with enyne metathesis and other reactions [4]. Due to the increasing demand for more environment-friendly catalytic applications, many researchers are focused on the design of olefin metathesis catalysts that can function in aqueous media [5]. To date, the reported olefin metathesis catalysts that are designed to work in aqueous media are based on two strategies: the first is to use an insoluble catalyst dispersed in the reaction medium via ultrasound or surfactant [6], and the other one involves the functionalization of the catalysts with water-soluble ligands [7]. Water-soluble ruthenium catalysts are commonly based on hydrophilic tags, such as poly(ethylene glycol) chains [8]. Another approach is to modify ruthenium catalysts with quaternary ammonium groups [9].

The direct application of a Grubbs-type catalyst in homogenous mixtures of water and water-miscible organic solvents was reported by Connon and Blechert [10]. Using this approach, cross-metathesis (CM) and RCM reactions were carried out using Grubbs-type catalysts in pure MeOH or binary mixtures of water–DMF or water–MeOH. In addition to Grubbs first-generation catalyst, other well-known ruthenium catalysts, such as Hoveyda–Grubbs-type catalysts, were employed under similar reaction conditions by several research groups [11]. Additionally, microwave- and ultrasound-assisted olefin metathesis reactions in water were reported, where the metathesis reactions of water-insoluble substrates were catalyzed by hydrophobic ruthenium catalysts [12]. Hydrophobic polymer-tagged ligands in combination with ruthenium catalysts were also employed for olefin metathesis reactions in water [10]. Amphiphilic poly(2-oxazoline)-derived block copolymers tagged on Hoveyda–Grubbs-type catalysts were reported by Buchmeiser and co-workers [13]. Phosphine ligands, modified with polyethyleneglycol (PEG) polymers, were coordinated to Hoveyda–Grubbs second-generation catalysts. These catalysts were used in ROMP of norbornene derivatives in aqueous media,

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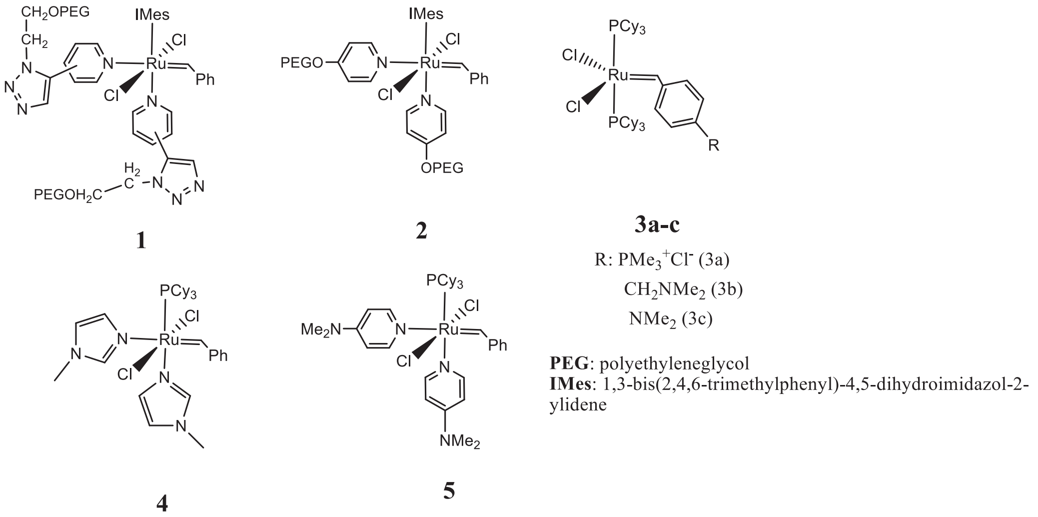


1 2 3a-c 4 5

R: $PMe_3^+Cl^-$ (3a)
CH_2NMe_2 (3b)
NMe_2 (3c)

PEG: polyethyleneglycol
IMes: 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene

Scheme 1. Various ruthenium-based metathesis catalysts bearing N-donor ligands.

resulting in a highly *trans*-polynorbornene with a lower PDI [14]. Hexa-coordinated ruthenium alkylidene complexes with modified pyridine ligands were reported by Breitenkamp and Emrick [15]. Pyridine ligands were modified by PEG and PEG-triazole polymers and coordinated to Grubbs second-generation catalyst. The activity of **1** and **2** were tested on ROMP of norbornene derivatives bearing PEG groups (Scheme 1). The ROMP reactions in aqueous media proceeded in acidic conditions (pH < 2) without any molecular weight control. The catalyst was activated by the protonation of the pyridine tags by Bronsted acids, initiating the ROMP reactions under acidic conditions. Phosphoryl choline modified the quaternary ammonium, and triazole groups were used instead of PEG [16]. This catalyst is also soluble in water and exhibits high biocompatibility.

Schanz et al. modified Grubbs first-generation catalyst by the addition of ionically tagged groups, such as $PMe_3^+Cl^-$ (**3a**), CH_2NMe_2 (**3b**) and NMe_2 (**3c**), at the para position of the benzylidene ligand. Exo-7-oxanorbornene derivatives were polymerized under acidic, aqueous media, yielding ROMP polymers with very low polydispersities [17,18]. Grubbs first-generation catalyst was modified in situ with N-donor ligands, such as 1-methylimidazole (**4**) and bis-*N*,*N*′-di-methylaminopyridine (**5**) to have latent and controllable catalyst systems [19].

In this contribution, poly(*N*-vinylimidazole)-supported first- and second-generation latent Grubbs catalyst systems are developed for olefin metathesis applications in aqueous media. The activities of the catalysts are tested on RCM and ROMP reactions in aqueous media. In addition, the switching ability and reusability of the catalyst for RCM of diethyldiallylmalonate are investigated in detail.

2. Experimental

2.1. Materials

Grubbs first- and second-generation catalysts and other chemicals were obtained from Sigma-Aldrich and used as-received. Toluene and dichloromethane were dried under Na wire/benzophenone and P_2O_5 and stored under an inert nitrogen atmosphere. Poly(*N*-vinylimidazole) (**PVI**) was synthesized according to [20].

2.2. Instrumentation

GC–MS analyses were performed with a Shimadzu GC-MS QP5050A using an Optima column-5, 10 μm (50 m × 0.32 mm), a temperature range of 50–300 °C and a heating rate of 15 °C/min. The carrier gas was helium with an elution rate of 1 mL/min. The surface morphology of the polymers was examined using field emission scanning electron microscopy (FESEM-Carl Zeiss, Supra 40 VP) with an accelerating voltage of 10 kV. The samples were sputter-coated with gold (Qourum Q 150 R ES DC Sputter).

2.3. Immobilization of the Grubbs first-generation catalyst on poly(N-vinylimidazole) [Ru-I]

0.6 g of **PVI** was dissolved in 10 mL of dimethylformamide under a nitrogen atmosphere, and a dichloromethane solution of a first-generation Grubbs catalyst (0.40 g, 0.486 mmol) was added dropwise to the reaction medium, which was then stirred at room temperature for 30 min. After 30 min, the resulting bright greenish viscous solution was poured into a mold and dried at room temperature for 24 h. After drying, the resulting bright greenish solid was washed with dichloromethane (10 mL × 3), toluene (10 mL × 3) and water (10 mL × 3) and dried under high vacuum. The resulting catalysts were characterized using FT-IR, EDX, SEM and ICP-MS.

2.4. Immobilization of Grubbs second-generation catalyst on poly(N-vinylimidazole) [Ru-II]

0.6 g of **PVI** was dissolved in 10 mL of dimethylformamide under nitrogen atmosphere and a dichloromethane solution of a second-generation Grubbs catalyst (0.40 g, 0.486 mmol) was added dropwise to the reaction medium, which was then stirred at room temperature for 5 min, followed by the addition of CuCl (0.059 g, 0.600 mmol) and stirring for an additional 30 min at room temperature. After 30 min, the dark green, viscous solution was poured into a mold and dried at room temperature for 24 h. After drying, the resulting dark green solid was washed with dichloromethane (10 mL × 3), toluene (10 mL × 3) and water (10 mL × 3) and dried under high vacuum. The resulting catalysts were characterized using FT-IR, EDX, SEM and ICP-MS.

2.5. General procedure for the ring-closing metathesis (RCM) of diethyldiallylmalonate with Ru-I and Ru-II

A reactor was charged with 0.025 g of **Ru-I** (0.471 mmol Ru/g), diethyldiallylmalonate (57 μL, 0.235 mmol) and 2 mL of water and was stirred at room temperature for 5 min. After 5 min, the reaction was initiated by the introduction of 1 M HCl (294 μL) to the reaction medium. Aliquots taken from the reaction mixture were extracted with diethyl ether, dried under $MgSO_4$, diluted with dichloromethane and analyzed using GC–MS.

2.6. General procedure for the ring-opening metathesis polymerization (ROMP) of 5-norbornene-2yl-acetate with Ru-I and Ru-II

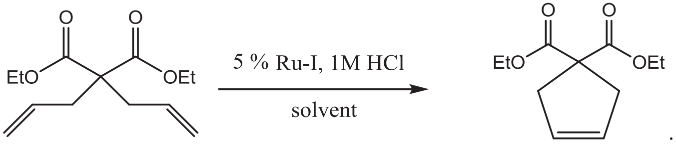
A reactor was charged with 7 mL of water and Tween-20 (1 mL) and stirred for 10 min. 5-Norbornene-2-yl-acetate (2 mL, 13.72 mmol) was added dropwise to this solution and stirred for an additional 10 min. **Ru-I** or **Ru-II** (0.025 g) was introduced into the solution and stirred for 30 min. The reaction was initiated by the introduction of 1 M HCl to the reaction medium. The reaction mixture was stirred for 24 h at room temperature. The reaction was quenched through the addition of ethylvinyl ether and then the catalyst, and the ROMP polymer was separated by extracting the reaction mixture with an excess of THF. The organic THF phase was filtrated, and the resulting ROMP polymer was isolated by precipitating in cold methanol.

3. Results and discussion

In this study, we use poly(*N*-vinylimidazole) (**PVI**) (Mn = 10,000) instead of 1-methylimidazole for modification of first- and second-generation Grubbs catalysts. Grubbs-type catalysts can be easily immobilized on **PVI** via neutral ligand exchange in a binary mixture of DMF/dichloromethane. For this purpose, a dichloromethane solution of first-generation Grubbs catalyst is added dropwise to a dimethylformamide (DMF) solution of poly(*N*-vinylimidazole) at room temperature (Scheme 2); following this addition, the color of the solution turned bright green in the case of the first-generation catalyst. After stirring the resulting solution at room temperature for 30 min, a gel-like solution was formed. The resulting gel-like solution was poured into a mold and allowed to dry in an air atmosphere for 24 h. The dried films were cut into small fractions, dried at 50 °C and washed with dichloromethane and acetone. The second-generation Grubbs catalyst was immobilized on **PVI** using a similar procedure. In this case, Cu(I)Cl is used to promote the dissociation of the phosphine ligand to further increase the ligand exchange rate. The resulting polymer-supported catalysts, **Ru-I** and **Ru-II**, were characterized using EDX, ICP-MS, SEM and FT-IR methods. **Ru-I** and **Ru-II** were insoluble in common solvents, such as dichloromethane, toluene and THF, but swell in water and methanol to an extent.

The immobilization of the first- and second-generation Grubbs catalysts on PVI was achieved using 40% catalyst by weight, relative to PVI. The immobilization of the ruthenium catalyst (97% for **Ru-I** and 95% for **Ru-II**) on PVI was determined gravimetrically and using ICP-MS. **Ru-I** has a ruthenium content of 0.471 mmol Ru/g, and **Ru-II** has 0.430 mmol Ru/g. The catalytic activity of the immobilized catalysts **Ru-I** and **Ru-II** were tested on ring-closing metathesis (RCM) of diethyldiallylmalonate (**S1**). The initial tests were carried out in common organic solvents, dichloromethane and toluene, with a catalytic loading of 5% (relative to the Ru content of the catalysts) at room temperature. Both **Ru-I** and **Ru-II** were metathesis inactive at room temperature and even at high temperatures. At both 25 and 80 °C, no conversion to the desired metathesis product was observed in dichloromethane, toluene or water. These observations are in good agreement with the results obtained using 1-methylimidazole-modified Grubbs-type catalysts. A chemical activation step is needed to produce metathesis-active species. Activation will be achieved through the protonation of imidazole groups on the polymer chain, which will form a coordination hole on ruthenium via the decoordination of the bonded imidazole groups. **Ru-I** was activated via the introduction of 1 M HCl (HCl:Ru, 2:1) in dichloromethane at room temperature (Table 1, Run 3). Although the catalyst can be activated via the addition of HCl (HCl:Ru, 2:1), complete conversion to the desired product could not be observed. Conversions of 10, 30 and 50% for RCM of diethyldiallylmalonate were achieved in dichloromethane, toluene and water, respectively. These observations indicate that only a small portion of the catalyst is activated; thus, an excess of HCl is needed to protonate the available nitrogen atoms of the imidazole ring on the polymer chain to promote the complete activation of the catalyst.

Table 1
RCM of diethyldiallylmalonate in the presence of **Ru-I** under various reaction conditions.



Run[a]	Solvent	HCl/Ru	Temperature (°C)	Time	Conversion[b] %
1	CH_2Cl_2	–	25	24	0
2	CH_2Cl_2	–	25		0
3	$C_6H_5CH_3$	–	25	24	0
4	Toluene	–	80		0
5	Water	–	80	24	0
6	Water	–	80		0
7	CH_2Cl_2	2	25	24	1
8	Toluene	2	25	24	2
9	Water	2	25	24	5
10	CH_2Cl_2	25	25	24	80
11	Toluene	25	25	24	60
12	Water	25	25	24	100

[a] All reactions were carried out using **Ru-I** (0.025 g) and diethyldiallylmalonate (57 μL, 0.235 mmol) in 2 mL of water at indicated temperatures.
[b] Determined by GC–MS.

The introduction of excess (500-fold excess relative to the ruthenium content) 1 M HCl to the reaction medium activated the catalyst completely, yielding the desired RCM product quantitatively in dichloromethane, toluene and water. Among the tested solvents, water shows the best performance for RCM of diethyldiallylmalonate, giving complete conversion to the RCM product without any side products, such as oligomeric by-products. Considering the environmental impact of the common organic solvents, water is an environmentally friendly and universal solvent, so further olefin metathesis reactions were performed in water.

The effect of the concentration of HCl on the activation of the catalyst was investigated in detail. To illustrate this effect, RCM of diethyldiallylmalonate was performed by initiating the reaction with 0.5, 1, 2, 3 and 4 M HCl solutions under pre-determined reaction conditions (Table 1, entry 12, and Fig. 1). The 0.5-M HCl addition led to incomplete catalyst activation, giving a 70% conversion for RCM of diethyldiallylmalonate. The quantitative formation of RCM products was observed by increasing the concentration of the HCl solution to 1 M. The conversion of diethyldiallylmalonate

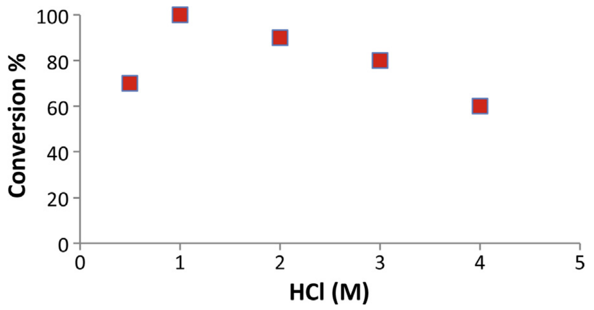
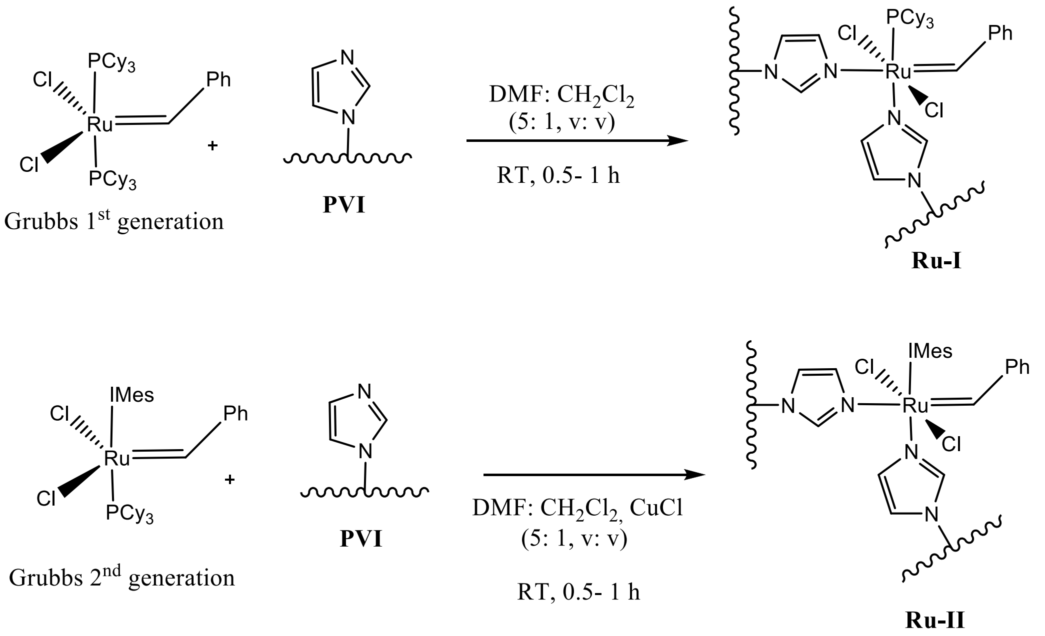


Fig. 1. RCM of diethyldiallylmalonate in the presence of 1% **Ru-I**, initiated by different concentrations of HCl.



Scheme 2. Immobilization of Grubbs first- and second-generation catalysts on PVI.

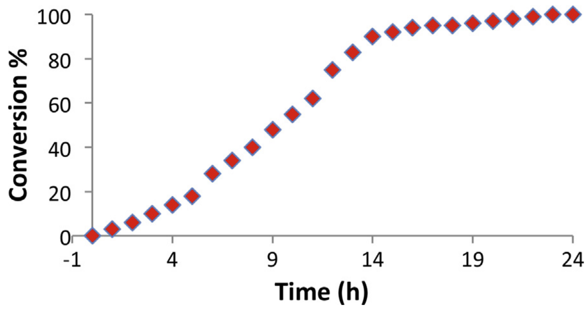


Fig. 2. RCM kinetics of **Ru-I**.

Table 2
RCM of diethyldiallylmalonate in the presence of various acids.

Run[a]	Acid (1 M)	Acid:Ru (mol:mol)	Time (h)	Conversion %
1	HCl	25	24	100
2	H_3PO_4	25	48	73
3	H_2SO_4	25	48	43
4	CH_3COOH	25	96	0
5	CCl_3COOH	25	96	0

[a] All reactions were carried out with a catalytic loading of 1% **Ru-I** (0.025 g) or **Ru-II** (0.025 g) and diethyldiallylmalonate (57 μL, 0.235 mmol) in 2 mL of H_2O. The reaction was initiated by addition of 1 M acid solutions (294 μL).

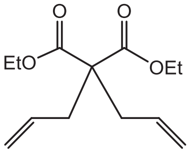
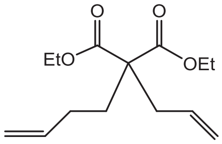
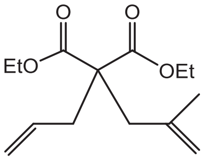
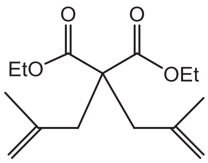
gradually decreased with further increases in the HCl concentration. This observation can be related to the fast catalyst initiation, followed by a fast decomposition step. Although the initiation rate of the catalyst is increased with an increase in the acid concentration, the propagating species are not stable enough to catalyze the reaction for more than a few cycles. These results indicate that a slow and controlled initiation step is needed for quantitative conversion of diethyldiallylmalonate to the desired product. To support these observations, the kinetics of the RCM were monitored using ^{1}H NMR and **Ru-I** as the metathesis initiator, and the results are given in Fig. 2. In the case of 1 M HCl, the reaction initiates slowly and small portions of catalyst are activated at a time, as shown in Fig. 2. After a few cycles, the initiated species decomposes and another portion of the catalyst is activated.

Ru-I was activated using various acids to predict the effect of the acid structure on the catalytic activity (Table 2). Among the chosen acids, HCl (1 M) initiates the catalyst better for the RCM of diethyldiallylmalonate. H_3PO_4 and H_2SO_4 give relatively lower conversion values. Conversely, no conversion is observed in the trials performed using organic acids.

Next, more sterically hindered RCM substrates were tested in pre-determined reaction conditions, and the results are listed in Table 3. The full conversions of diethyldiallylmalonate (**S1)** and diethyl-2-allyl-2-butenylmalonate (**S2)** were observed using **Ru-I** and **Ru-II**. More challenging and sterically hindered substrates, i.e., diethyl 2-allyl-2-(2-methylallyl)malonate (**S3**) and diethyl 2,2-bis(2-methylallyl)malonate (**S4**), were tested in the RCM reactions to make a distinct comparison between the RCM activity of **Ru-I** and **Ru-II**. Only a 20% conversion of diethyl 2-allyl-2-(2-methylallyl)malonate (**S3**) was observed with **Ru-I**. **Ru-II** is more active towards the RCM of sterically hindered substrates; a 65% conversion of **S3** was observed using **Ru-II** under the same reaction conditions. To further monitor the catalytic activity of **Ru-I** and **Ru-II**, diethyl 2,2-bis(2-methylallyl)malonate (**S4**) was tested, and only traces of the RCM product were observed using **Ru-I** (conversion < 0.5%) and **Ru-II** (conversion < 10%).

The RCM reactions proved that **Ru-I** and **Ru-II** are metathesis inactive in the absence of acids, and the activity of the catalysts can be controlled via the addition of acids. This strategy was employed in ROMP reactions of 5-norbornene-2-yl-acetate to give ROMP processes that can be both controlled and performed in aqueous media (Table 4). The first reaction was carried out in water without any surfactant and a catalytic loading of 0.5% using **Ru-I**. No conversion to the desired ROMP product was observed in the absence of HCl; after the addition of HCl, the ROMP reaction started, yielding a polymer with a molecular weight of 440 kDa and a PDI of 2.94. As a direct result of the comparatively slower initiation of **Ru-II** under the same reaction conditions, a polymer with a molecular weight of 640 kDa and a PDI of 2.80 was obtained in 98% yield. The second experiment was performed using the surfactant Tween-20 in a 10% (v:v) ratio and **Ru-I** with an HCl/Ru ratio of 500. After 24 h, a polymer was isolated in 92% yield with an MW of 370 kDa with a more reasonable PDI value of 1.30. The HCl/Ru ratio was increased to determine the effect of the initiation rate on the polymer molecular

Table 3
RCM of diethyldiallylmalonate derivatives in the presence of 5% **Ru-I**.

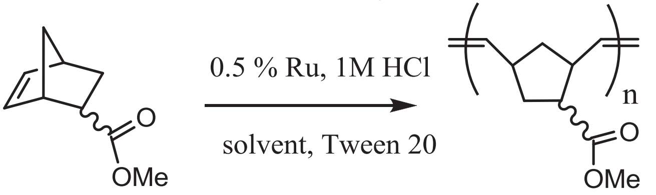
Run	Substrate	Catalyst	Time	Conversion[b] %
1[a]	 S1	Ru-I	24 h	100
2[a]		Ru-II	24 h	100
4[a]	 S2	Ru-I	24 h	100
		Ru-II	24 h	100
5[a]	 S3	Ru-I	24 h	20
		Ru-II	24 h	65
6[a]	 S4	Ru-I	24 h	<0.5
		Ru-II	24 h	10

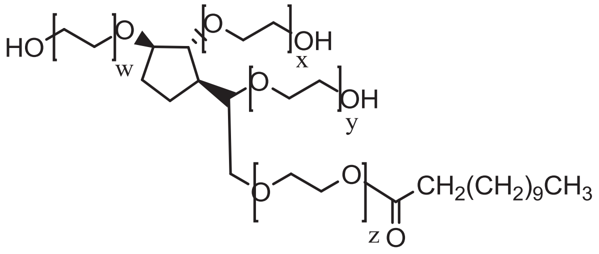
[a] All reactions were carried out with **Ru-I** (0.025 g) or **Ru-II** (0.025 g) and substrate in 1 mL of H_2O. The reaction was initiated by addition of 1 M HCl (294 μL).
[b] Determined by GC–MS.

weight and the PDI value. As we have seen before, the molecular weight decreased with increases in the HCl/Ru ratio from 500 to 1000. The molecular weight of the polymer was decreased to 288 kDa (PDI: 1.40) from 370 kDa. Further increases in the HCl/Ru ratio led to a decrease in the molecular weight, as expected. The molecular weight of the polymer was decreased to 200 kDa by using a 1500:1 HCl:Ru ratio and to 170 kDa with an HCl:Ru ratio of 2500:1. In contrast, **Ru-II** exhibits greater control over the ROMP reaction of 5-norbornene-2-yl-acetate. A wide molecular weight range of 102–640 kDa was observed when using **Ru-II** instead of **Ru-I** (170–440 kDa) in the ROMP reactions of 5-norbornene-2-yl-acetate.

The switching ability of the **Ru-I** catalyst was investigated in detail. The results are summarized in Fig. 3. It has been reported that the first-generation Grubbs catalyst can be switched on and off through the introduction of both 1-methylimidazole and acid. In this current approach, we chose the RCM of diethyldiallylmalonate to monitor the switching ability of the catalyst, based on the conversion of diethyldiallylmalonate. The RCM of diethyldiallylmalonate was initiated through the introduction of HCl and 1% **Ru-I** to the reaction medium. After 2 h and a 26% conversion of diethyldiallylmalonate, the reaction was switched off via the introduction of an equimolar amount of 1 M KOH. The reaction was stirred for 1 h to prove that reaction stopped completely. A slight increase in the conversion (27%) of diethyldiallylmalonate was observed. The reaction was turned on via the introduction of 1 M HCl, and a 45% conversion of diethyldiallylmalonate was obtained. The reaction was again turned off via the introduction of 1 M KOH, followed by turning on again via the introduction of 1 M HCl. This process was repeated until a plateau in the conversion of diethyldiallylmalonate was reached after activation by HCl.

Table 4
Controlled ROMP reactions of 5-norbornene-2yl-acetate.





Tween 20 .

Run[a]	Catalyst	Surfactant	HCl/Ru	Yield %	M^b_n	PDI[b]
1	Ru-I	–	25	90	440	2.94
2	Ru-I	T20	25	92	370	1.30
3	Ru-I	T20	50	96	288	1.40
4	Ru-I	T20	75	95	200	1.30
5	Ru-I	T20	125	90	170	1.13
6	Ru-II	–	25	98	640	2.80
7	Ru-II	T20	25	97	268	1.75
8	Ru-II	T20	50	100	218	1.31
9	Ru-II	T20	75	98	160	1.46
10	Ru-II	T20	125	94	102	1.26

[a] A reactor was charged with Tween-20 (1 mL), 5-norbornene-2yl-acetate (2 mL, 13.72 mmol), **Ru-I** or **Ru-II** (0.025 g) and 7 mL of water. The reaction was stirred at room temperature for 30 min before introduction of 1 M HCl.
[b] Determined by GPC using poly(methylmethacrylate) standards.

Next, the reusability of **Ru-I** and **Ru-II** was tested on RCM of diethyldiallylmalonate (Fig. 4). For this purpose, the RCM reactions were run under predetermined reaction conditions. After the full conversion of diethyldiallylmalonate was observed, the catalysts were deactivated by the addition of 1 M KOH and filtered, washed with water, acetone and toluene, respectively, then immediately placed into other reaction vessels containing both diethyldiallylmalonate and water, and then the reaction was initiated via the addition of 1 M HCl. On the second run, a 68% conversion was

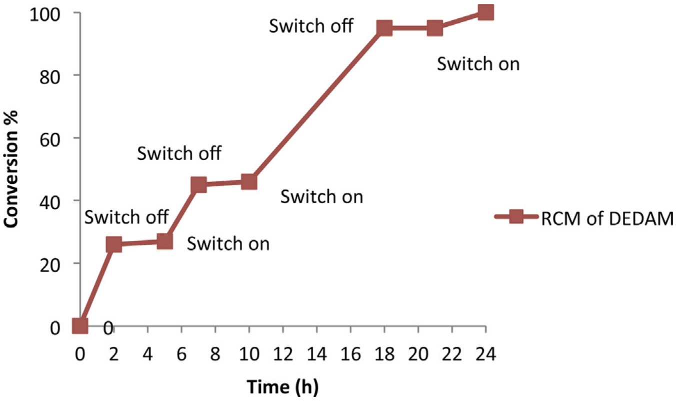


Fig. 3. Switch on/off studies on RCM reactions of diethyldiallylmalonate catalyzed by **Ru-I**.

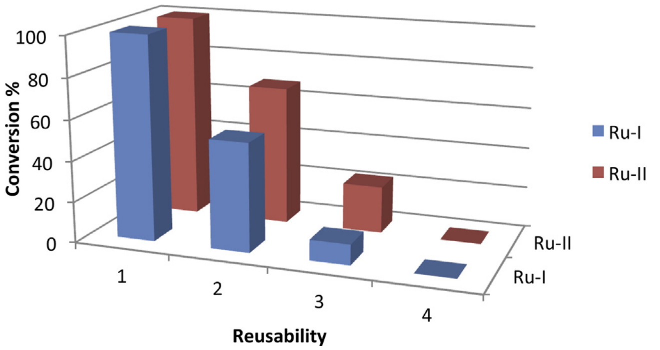


Fig. 4. Reusability studies of **Ru-I** and **Ru-II** in RCM of diethyldiallylmalonate.

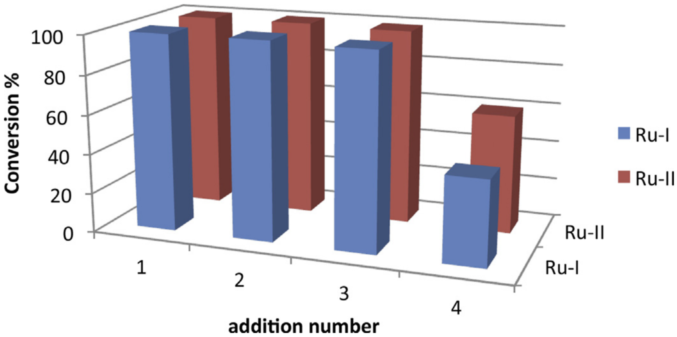


Fig. 5. RCM of diethyldiallylmalonate in the presence of **Ru-I** and **Ru-II** under continuous flow conditions.

achieved using **Ru-I**, but **Ru-II** only yielded the desired product in 53% yield. On the third run, a sharp decrease in the catalyst activity was observed for both **Ru-I** and **Ru-II**: 23 and 10% conversion values were observed in the third run with **Ru-I** and **Ru-II**, respectively.

Another important application area of supported catalysts is their usability under continuous flow conditions. Therefore, the activity of the catalysts under continuous flow conditions was investigated in detail. For this purpose, a reactor was charged with diethyldiallylmalonate and 1% **Ru-I** or **Ru-II** in water (Fig. 5). The reaction was initiated via the introduction of 1 M HCl. When the full conversion of diethyldiallylmalonate was obtained after 24 h, another equivalent portion of diethyldiallylmalonate was introduced into the reaction solution. The reaction mixture was reacted until full conversion was observed. A second portion of diethyldiallylmalonate was added to the reaction medium. The reaction completed within 24 h. After the addition of the third portion, a 99% conversion rate was observed within 36 h for **Ru-II** and 96% for **Ru-I**. The activity of the catalyst began to decrease after the addition of the fourth portion. After the addition of the fourth portion, a 60% conversion of diethyldiallylmalonate was observed for **Ru-II**, whereas only a 43% conversion was obtained with **Ru-I** after 48 h.

4. Conclusion

In this study, latent and switchable ruthenium metathesis catalysts were developed for olefin metathesis applications in water via the direct immobilization of first- and second-generation Grubbs catalysts on **PVI**. The catalysts perform RCM and ROMP reactions in aqueous media with a high degree of control for olefin metathesis reactions by varying the HCl/Ru ratio. ROMP polymers with molecular weights in the range of 170–440 kDa for **Ru-I** and 102–650 kDa for **Ru-II** were obtained by varying the HCl/Ru ratios. The reusability of **Ru-I** and **Ru-II** were tested in the RCM of diethyldiallylmalonate. The **Ru-I** and **Ru-II** catalysts are reusable and they can catalyze RCM reactions for three runs. Additionally, the RCM of diethyldiallylmalonate, catalyzed by **Ru-I** and **Ru-II**, can be turned on and off by initiating the reaction with HCl and turning off the reaction via the addition of KOH.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.06.024.

References

[1] R.H. Grubbs, Handbook of Metathesis, vol. 1, 1st ed., Wiley-VCH, Weinheim, 2003.
[2] R.H. Grubbs, Tetrahedron 60 (2004) 7117.
[3] (a) A.B. Lowe, C.L. McCormick, Prog. Polym. Sci. 32 (2007) 283;
(b) C. Slugovc, Macromol. Rapid Commun. 25 (2004) 1283.
[4] (a) R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413–4450;
(b) J.M. Berlin, S.D. Goldberg, R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 45 (2006) 7591;
(c) M. Rosillo, G. Dominguez, L. Casarrubios, U. Amador, J. Perez-Castells, J. Org. Chem. 69 (2004) 2084;
M.W. Grafton, L.J. Farrugia, H.M. Senn, A. Sutherland, Chem. Commun. 48 (2012) 7994.
[5] (a) D. Burtscher, K. Grela (Eds.), Angew. Chem. Int. 48 (2009) 442;
(b) J. Tomasek, J. Schatz, Green Chem. 15 (2013) 2317.
[6] (a) C. Torborg, C. Samojowicz, K. Grela, Metathesis reactions, in: S. Kobayashi (Ed.), Science of Synthesis: Methods of Molecular Transformations. Vol. 2011/5: Water Organic Synthesis, Georg Thieme Verlag KG, 2012, pp. 225–256 (Section 3.6);
(b) Ł. Gułajski, P. Śledź, A. Lupa, K. Grela, Green Chem. 10 (2008) 271.
[7] (a) D. Burtscher, K. Grela (Eds.), Angew. Chem. Int. 48 (2009) 442;
(b) K. Grela, Ł. Gułajski, K. Skowerski, Alkene metathesis in water, in: P.H. Water, V. Dixneuf, Cadierno (Eds.), Metal-Catalyzed Reactions, Wiley-VCH, Weinheim, 2013, pp. 291–336.
[8] (a) S.H. Hong, R.H. Grubbs, J. Am. Chem. Soc. 128 (2006) 3508;
(b) J.P. Gallivan, J.P. Jordan, R.H. Grubbs, Tetrahedron Lett. 46 (2005) 2577.
[9] (a) Ł. Gułajski, A. Michrowska, J. Naroznik, Z. Kaczmarska, L. Rupnicki, K. Grela, ChemSusChem 1 (2008) 103;
(b) J.P. Jordan, R.H. Grubbs (Eds.), Angew. Chem. Int. 46 (2007) 5152.
[10] S.J. Connon, S. Blechert, Bioorg. Med. Chem. Lett. 12 (2002) 1873.
[11] S.J. Connon, M. Rivard, M. Zaja, S. Blechert, Adv. Synth. Catal. 345 (2003) 572.
[12] (a) R.S. Varma, Green Chem. 10 (2008) 1129;
(b) C.O. Kappe (Ed.), Angew. Chem. Int. 43 (2004) 6250;
(c) G. Cravotto, P. Cintas, Chem. Soc. Rev. 35 (2006) 180;
(d) G. Cravotto, P. Cintas, Chem. Eur. J. 13 (2007), 1902;
(e) T. Dwars, E. Paetzhold, G. Oehme (Eds.), Angew Chem. Int. 44 (2005) 7174.
[13] J.O. Krause, M.T. Zarka, U. Anders, R. Weberskirch, O. Nuyken, M.R. Buchmeiser (Eds.), Angew. Chem. Int. 42 (2003) 5965.
[14] S. Elias, A. Vigalok, Adv. Synth. Catal. 351 (2009) 1499.
[15] K. Breitenkamp, T. Emrick, J. Polym. Sci. A: Polym. Chem. 43 (2005) 5715.
[16] D. Samanta, K. Kratz, X. Zhang, T. Emrick, Macromolecules 41 (2008) 530.
[17] A.N. Roberts, A.C. Cochran, D.A. Rankin, A.L. Lowe, H.-J. Schanz, Organometallics 26 (2007) 6515.
[18] M.A. Dunbar, S.L. Balof, L.J. LaBelaud, B. Yu, A.B. Lowe, E.J. Valente, H.J. Schanz, Chem. Eur. J. 15 (2009) 12435.
[19] M.A. Dunbar, S.L. Balof, A.N. Roberts, E.J. Valente, H.J. Schanz, Organometallics 30 (2011) 199.
[20] X. Li, S.H. Goh, Y.H. Lai, A.T.S. Wee, Polymer 42 (2001) 5463.