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

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ABSTRACT

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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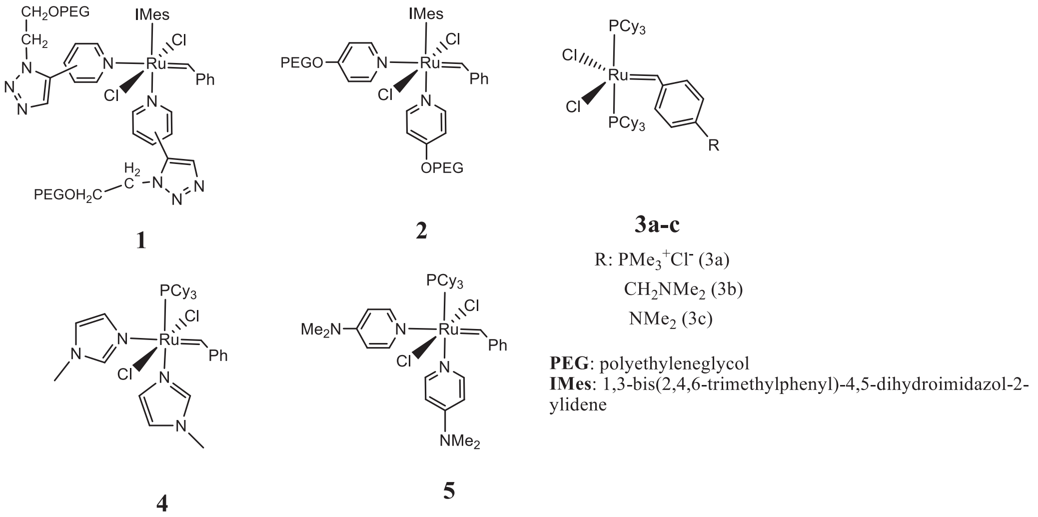

R: $PMe_3^+Cl^-$ (3a)
CH_2NMe_2 (3b)
NMe_2 (3c)

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