



Note

Immobilization of ruthenium benzylidene on thermoresponsive polymer: Methodology and application



Nagaraju Pentela^{a, b}, P. Murugan^a, Sellamuthu N. Jaisankar^a, Debasis Samanta^{a, *}, Asit Baran Mandal^{b, c, **}

^a Polymer Division, Council of Scientific and Industrial Research (CSIR), Central Leather Research Institute (CLRI), Adyar, Chennai 600020, India

^b Academy of Scientific and Innovative Research (AcSIR), Rafi Marg, New Delhi, India

^c Chemical Lab, CSIR-CLRI, Chennai 600020, India

ARTICLE INFO

Article history:

Received 16 July 2014

Received in revised form

6 December 2014

Accepted 8 December 2014

Available online 16 December 2014

Keywords:

Ruthenium benzylidene

Thermoresponsive

Metathesis

Recyclable catalyst

ABSTRACT

Attachment of metal complex on polymer has direct implication for the development of novel catalyst with recyclability, reusability and water solubility in the context environmental concern. In this paper, we illustrate a simple strategy to immobilize ruthenium benzylidene organometallic complex on thermoresponsive polymer. For this, pyridine-substituted poly (N-isopropylacrylamide) has been synthesized by atom transfer radical polymerization from a suitable initiator. Then, ruthenium benzylidene has been conjugated by binding with pyridine part of the polymer. Polymer conjugated ruthenium benzylidene is shown to have thermoresponsive characteristic in water (soluble below lower critical solution temperature (LCST) but precipitates out above LCST in water). Hence it can act as smart catalyst for metathesis reaction in water. For instance, it can be used as homogeneous metathesis catalyst for allyl alcohol in aqueous medium below lower critical solution temperature (LCST), that can be recovered as heterogeneous catalyst above LCST and recycled again as homogeneous catalyst. This is the first example of water-soluble recyclable metathesis catalyst. It is further demonstrated that steric crowding in the ligand play an important role in the superior performance of the catalyst.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Ruthenium benzylidene complexes are important as catalysts for the metathesis reaction [1–3]. Attachment of ruthenium benzylidene on different polymers [4,5] is an integral part of research for the development of environmentally benign catalyst with water solubility and recyclability [6,7].

Various polymers can be used to render water solubility [8]. For example, polyethylene glycols were conjugated with ruthenium benzylidene independently by Grubbs [9–11], Emrick [12,13] and Raines [14]. Some of those compounds showed excellent catalytic activity for self metathesis, cross metathesis or ring opening metathesis polymerization reactions in water medium. Those developments paved the way to eliminate the usage of toxic organic

solvents: an important parameter for green chemistry approach, successful biochemical reactions and cost effectiveness.

In most cases, recyclable metathesis catalysts were prepared by immobilizing them on polymer support. Recently we reported various methods of covalent or non covalent bond formation on flat or curved surfaces [15–17]. Hoveyda and others prepared recyclable ruthenium benzylidene by immobilizing it on porous sol–gel glass [18]. Yang et al. [19] prepared recyclable supported catalyst by immobilizing it on mesoporous material, Kirschning and others anchored Grubbs III type catalyst onto polyvinyl pyridine [20], while Lee et al. prepared silica-supported Hoveyda type catalyst [21]. Many of them are either not soluble in organic or aqueous medium; hence homogeneous catalysis – a prerequisite for high efficacy – still remains a challenge in either media with recyclable polymer supported catalyst [22]. In a recent review article, several aspects of homogeneous catalysis particularly resolving of heterogeneity problems have been discussed by Robert H. Crabtree [23].

It was recognized that, Poly(N-isopropylacrylamide) poly (NIPAM) is thermoresponsive in nature [24,25]. Hence, contrary to the behaviour of most compounds in water, poly (NIPAM) becomes less soluble in water at elevated temperature. The temperature

* Corresponding author. Tel.: +91 44 24422059; fax: +91 44 24911589.

** Corresponding author. Chemical Lab, CSIR-CLRI, Chennai 600020, India. Tel.: +91 44 24910846; fax: +91 44 24912150.

E-mail addresses: debasis@clri.res.in (D. Samanta), abmandal@clri.res.in (A.B. Mandal).

above which poly (NIPAM) undergoes from soluble to insoluble state in water is called Lower Critical Solution Temperature (LCST). By exploiting thermoresponsive nature of poly(NIPAM), several groups have prepared smart protein [26] or smart surface [27] after suitable conjugation. Those types of thermoresponsive polymers or conjugates have been also used for targeted drug delivery [28,29], nanotechnology [30], etc. However, to the best of our knowledge, there is no example of ruthenium benzylidene with thermoresponsive tag, to use as homogeneous as well as recyclable metathesis catalyst in water.

We report in this paper a clear cut demonstration that ruthenium benzylidene complexes with poly (NIPAM) tag can be prepared in four simple steps to show thermoresponsive characteristics. Hence, it can be used as “smart” catalyst for metathesis reaction of allyl alcohol in aqueous medium with the advantages of both homogeneous and heterogeneous metathesis reaction.

Results and discussions

Scheme 1 depicts the synthesis of thermoresponsive ruthenium benzylidene compounds from azido alcohol. First, azidoethanol or azidohexanol was reacted with 2-ethynylpyridine or 3-ethynylpyridine, respectively to obtain the triazole **3a** or **3b** respectively. The products were purified by column chromatography using a mixture of methanol and dichloromethane. Disappearance of peak at $\sim 2090\text{ cm}^{-1}$ in IR and appearance of triazole ring proton signal at 7.7–7.8 ppm in both cases confirmed the success of this “click” reaction. The triazole compounds were esterified with 2-bromoisobutyrylbromide to form the suitable initiator for Atom Transfer Radical Polymerization (ATRP) **5a** or **5b**.

Both the compounds **5a** or **5b** were purified by column chromatography to obtain pale yellow solid compounds. In ^1H NMR spectra, two methyl groups ($2 \times \text{CH}_3$) appeared as singlet in the region 1–2 ppm and the carbonyl carbon appeared at around 170 ppm, in ^{13}C NMR spectroscopy. The carbonyl stretching absorption appears as a sharp peak at $\sim 1730\text{ cm}^{-1}$ in IR.

Our initial attempts to perform the ATRP reaction of N-isopropylacrylamide (NIPAM) using either initiators in common solvents like toluene, methanol or DMSO were not successful. The successful ATRP reaction was achieved by using a solvent mixture of methanol and water along with a catalyst system of copper (I) bromide and bipyridine. Thorough degassing of the solvent with nitrogen prior to the polymerization reaction is also crucial for its success. The degree of polymerization was controlled by changing the initiator to monomer ratio. A higher degree of polymerization

for *ortho*-substituted compound was desirable to impart the steric crowding close to the metal centre (*vide supra*). An initial purification of the polymer was achieved by reprecipitation from diethyl ether and tetrahydrofuran mixture. The trace amount of copper was removed by the quick filtering of the polymer through a pad of silica gel using methanol as solvent. The disappearance of peak at 5–6 ppm confirmed the absence of monomer while the appearance of new broad peaks between 1 and 2 ppm confirmed the success of polymerization to obtain pyridine-poly(NIPAM) compounds **7a** or **7b**. In ^{13}C NMR (ESI), the characteristic signal for amide carbon was observed at 170–180 ppm. The degree of polymerization (**Scheme 1**) was confirmed from the end group analysis by ^1H NMR and GPC traces.

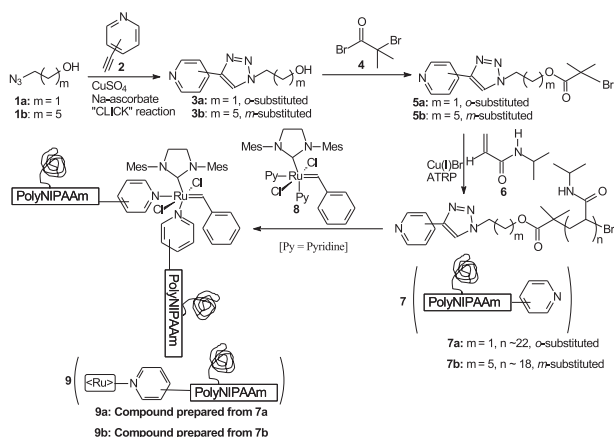
The pyridine-poly(NIPAM) compound **7a** or **7b** was reacted with $[(\text{H}_2\text{IMes})_2(\text{pyridine})_2(\text{Cl})_2\text{Ru}=\text{CHPh}]$ (**8**) to obtain the poly(NIPAM)-tagged ruthenium benzylidene compound **9a** or **9b**. We presumed that, two units of pyridine are attached to provide a more stable 18 electron species as reported by Grubbs and Emrick [12,31] separately for pyridine-based ruthenium benzylidene complexes. ^1H NMR spectra further indicated an attachment of multiple pyridine units.

The compounds were purified by flash column chromatography under nitrogen to obtain deep green colour compound. Complete removal of starting material (**8**) was achieved by repeated removal of solvent, under high vacuum in three cycles. Complete disappearance of starting material **8** was also confirmed by TLC and ^1H NMR. A characteristic new singlet for benzylidene proton at ~ 19 ppm in ^1H NMR for **9a** or **9b** further confirmed the success of the reaction. The ruthenium loading in comparison to pyridine moieties were calculated by comparing the ratio of integration of benzylidene proton (one proton) at ~ 19 ppm and methyl protons (6 protons) of N-isopropyl groups at ~ 1 ppm.

Both compounds **9a** and **9b** showed thermoresponsive characteristics in water. While both the compounds were soluble in water below $36\text{ }^\circ\text{C}$, a rapid phase separation and precipitation occurs upon heating above $38\text{ }^\circ\text{C}$ from water medium. This specific property was exploited to perform the homogeneous catalysis below $36\text{ }^\circ\text{C}$ in water and heterogeneous catalytic recovery from water above $38\text{ }^\circ\text{C}$.

Our initial attempt to perform metathesis reaction using catalyst **9b** was not successful. However, metathesis reaction in acidified D_2O for various substrates using catalyst **9a** was successful. In this case, 95%, 73% and 60% conversion was observed for self metathesis of allyl alcohol, 3-buten-1-ol, and Ring Opening Metathesis Polymerization (ROMP) of PEGylated oxanorbornene in acidified D_2O respectively.

Scheme 2 summarizes the strategy of recycle of catalysts in deuterated water medium using a model substrate allyl alcohol. We have chosen allyl alcohol particularly because the substrate is usually challenging for metathesis reaction in water and very few reports along the line existed [11]. First, allyl alcohol and catalyst **9a** was dissolved in degassed D_2O at pH 1.0 below $36\text{ }^\circ\text{C}$ and stirred under nitrogen atmosphere for 24 h. The reaction mixture was heated above $38\text{ }^\circ\text{C}$ to get the green colour precipitation (**Scheme 2**, picture on the right). The product, which is in solution and the catalyst (mod), which is in the precipitation, was separated and the catalyst was recycled again by dissolving in D_2O for the catalytic reaction of allyl alcohol. **Scheme 2**, highlighted table, summarises the result of % of conversion of allyl alcohol in different cycles. Reduction in the conversion of the metathesis reaction was also observed with the increase in the number of cycles. This may be attributed to the leaching out of some of the metal complex after reaction or slight change in catalytic structures. Inductively Coupled Plasma (ICP) experiments were performed to study the leaching phenomenon. In this case, ruthenium metal content of



Scheme 1. Synthesis of thermoresponsive ruthenium benzylidene compounds.

Download English Version:

<https://daneshyari.com/en/article/1321008>

Download Persian Version:

<https://daneshyari.com/article/1321008>

[Daneshyari.com](https://daneshyari.com)