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Tuning the molecular weight of ROMP polymers by using Grubbs type catalysts and terminal alkynes

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ABSTRACT

In this study, ruthenium vinyl carbene derivatives were obtained in situ by reacting Grubbs 1st and 2nd generation catalysts with terminal alkynes in toluene at 85 °C. These active species were used in ROMP of norbornene derivatives. The effect of alkyne/Ru (mol/mol) ratio and alkyne substituent on number average molecular weights (M_n) of ROMP polymers were investigated in detail. ROMP polymers with M_n values between 75 and 680 kDa were synthesized by varying alkyne/Ru (mol/mol) ratio in the presence of Grubbs type catalysts. The mechanism of the reaction and the role of alkyne in ROMP reactions were investigated in detail by ^{1}H NMR.

1. Introduction

Ring Opening Metathesis Polymerization (ROMP) is an efficient method to build advanced macromolecular structures [1]. ROMP polymers have been widely used for high-tech applications such as polymeric supports, column materials, drug carriers and self-healing materials [2]. With the invention and commercialization of Grubbs 1st (G1), 2nd (G2) and 3rd (G3) generation catalysts (Scheme 1), a tremendous increase in ROMP applications was observed. Following this progress, novel catalytic systems were developed for tuning the molecular weight of ROMP polymers [3]. The earliest examples of molecular weight control in ROMP reaction utilize various bisallylic ruthenium (IV) complexes along in combination with diazoalkanes [4]. In this strategy, number average molecular weight (M_n) of polymers can be controlled in a wide range by varying solvent content. Another strategy for tuning the molecular weight (M_n) of ROMP polymer is to use latent ruthenium metathesis catalysts [5]. Verpoort et al. used bidentate (N, O) Schiff bases to synthesize latent ruthenium alkylidene and indenylidene complexes [6]. Later on, a practical in situ modification method for Grubbs type catalysts was developed by Schanz et al. [7]. Grubbs type catalysts were inhibited by addition of 1-methylimidazole and activated by introduction of acids to reaction media. Later on, same research group reported a highly controllable ROMP catalysts bearing dimethylamino tagged *N*-heterocyclic carbene ligand [8] and systematically investigated the effect of protonation degree on the initiation-propagation rates. Another strategy for tuning the molecular weight of polymers is to use chain-transfer agents (CTA) in ROMP reactions [9]. Terminal and internal olefins were used as CTA in ROMP of cyclic olefins [10,11]. Although ruthenium alkylidene derivatives have been extensively used in ROMP reactions, rather less attention has been paid to synthesize ruthenium vinyl carbene derivatives from carbene sources [12]. Ruthenium vinyl carbene derivatives can be synthesized from non-carbene and carbene sources. Although considerable research has been devoted to synthesize vinyl carbene derivatives from non-carbene sources [13], only a few efficient protocol was reported for the generation of ruthenium vinyl carbene derivatives from carbene sources [14]. The main problem in synthesis of ruthenium vinyl carbenes from acetylene derivatives is to stop the reaction at the vinyl carbene stage.

Herein, we demonstrated that ruthenium vinyl carbene derivatives can be synthesized in-situ by reaction of Grubbs 1st and 2nd generation catalyst with an excess terminal alkyne. The activity of metathesis active intermediates was tuned by varying alkyne/Ru ratio and alkyne substituent. In addition, linear dependence of Mn of the polynorbornene on the alkyne/Ru (mol/mol) ratio was

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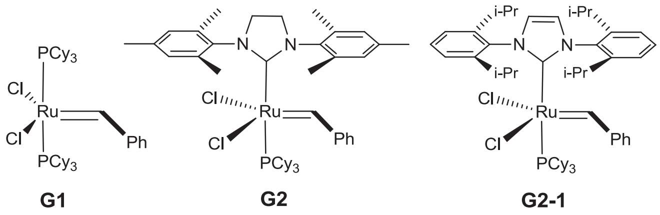


Scheme 1. Grubbs type olefin metathesis catalysts.

demonstrated, indicating that acetylenes can act as chain-transfer agents in ROMP of norbornene derivatives.

2. Results and discussion

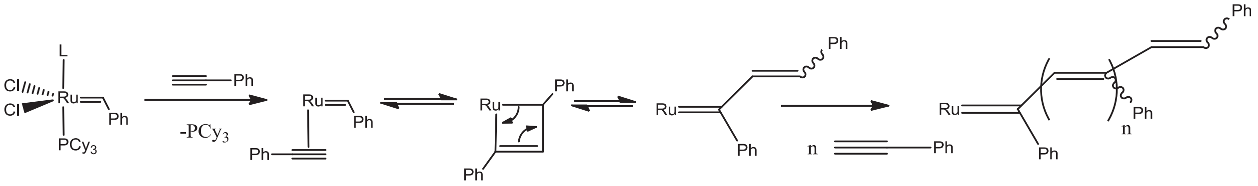
Enyne metathesis is an efficient method to form conjugated dienes by reaction of alkene and alkyne moieties [15]. The reaction involves the formation of a ruthenacyclobutene intermediate and transformation of this intermediate to ruthenium vinyl carbenes (Scheme 2). If excess alkyne is present in the reaction media, the conjugation in ruthenium vinyl carbene increases and conjugated polyenes can be obtained through the formation of ruthenacyclobutene intermediates. From this starting point, we envisioned that novel ruthenium vinyl carbenes with different reactivity can be synthesized in-situ by reacting Grubbs 1st and 2nd generation catalyst with terminal alkynes prior to ROMP reactions. In order to get more insight into the proposed reaction mechanism, a key-control experiment was carried out by reacting Grubbs 2nd generation analog; **G2-1** (Scheme 3), with phenylacetylene in toluene at 85 °C with a phenylacetylene/Ru (mol/mol) ratio of 4/1 for 30 min. The reaction was terminated by addition of excess ethyl vinyl ether. As it can be seen in Scheme 3, 1,3-conjugated vinyl derivatives; **1a** ([M$^+$] = 206 when R: Ph) and **1b** ([M$^+$] = 308 when R: Ph), were liberated when the active ruthenium vinyl carbene intermediates**, Ru-1a** and **Ru-1b**, were treated with ethyl vinyl ether. The reaction mixture was analyzed by GC-MS. GC-MS analysis showed that reaction mixture consisted of **1a**, **1b**, unreacted phenylacetylene and trace amounts of alkyne dimerization ([M$^+$] = 204) product. The reaction was repeated by using phenylacetylene/Ru ratios of 2/1, 4/1 and 8/1 to determine the ratio of **1a** and **1b** in each case. The results were given in Table 1. As it can be seen in Table 1, the amount of **1b** was increased with an increment in alkyne/Ru ratio. The reaction time was increased to 2 h in order to achieve full conversion of phenylacetylene. Phenylacetylene was totally consumed after 2 h and alkyne dimerization ([M$^+$] = 204) and [2 + 2+2] cyclotrimerization products ([M$^+$] = 306) were observed in GC-MS analysis. On the next trial, the reactivity of tert-butylacetylene with **G1** and **G2-1** was tested under identical reaction conditions (Table 1). The reaction of G1 with tert-butylacetylene under pre-determined reaction conditions yielded desired products **1a** ([M$^+$] = 186 when R: t-Bu) and **1b** ([M$^+$] = 268 when R: t-Bu) These preliminary results showed that tert-butylacetylene is less reactive than phenylacetylene towards G1. However, relatively higher amounts of dimerization and cyclotrimerization products were formed when alkyne/Ru ratio was chosen as 8/1. A similar trend was also observed for reaction of

Table 1
Formation of 1a and 1b.

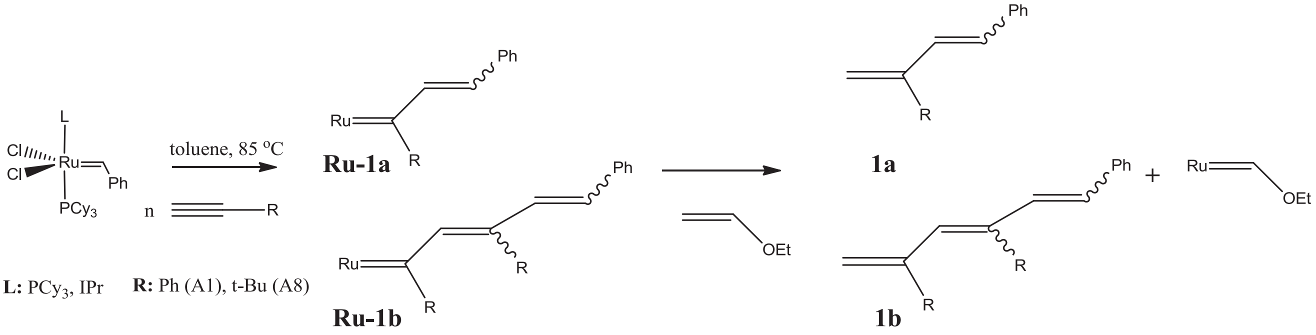
Run[a]	Catalyst	Alkyne	Alkyne/Ru (mol/mol)	**1a** %[b]	**1b** %[b]
1	G1	A1	1	99	–
2	G1	A1	2	90	5
3	G1	A1	4	85	6
4	G1	A1	8	70	10
5	G2-1	A1	1	99	–
6	G2-1	A1	2	92	5
7	G2-1	A1	4	88	10
8	G2-1	A1	8	70	20
9	G1	A8	1	85	2
10	G1	A8	2	80	5
11	G1	A8	4	78	7
12	G1	A8	8	60	7
13	G2-1	A8	1	99	–
14	G2-1	A8	2	80	10
15	G2-1	A8	4	75	15
16	G2-1	A8	8	70	15

[a] A Schlenk reactor was charged with G1 or G2 (0.024 mmol), phenylacetylene (0.098 mmol) in toluene (2 ml) and reacted for 30 min at 85 °C. The reaction was quenched with addition of excess ethyl vinyl ether. The reaction mixture was analysed by GC-MS.

[b] Determined by GC-MS by using n-tetradecane as internal standart.



Scheme 2. Enyne metathesis mechanism.



Scheme 3. Reaction of G2-1 with phenylacetylene.