



# Polymerization of hydroxyacetylenes by ruthenium alkylidene complexes

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## ABSTRACT

Polymerization of a series of acetylenes with a hydroxy functional group was investigated by using modified 2nd generation Grubbs (**A**) and Grubbs–Hoveyda (**B**) initiators. Owing to excellent tolerance for polar functional groups, catalysts **A** and **B** polymerized 3-butyn-2-ol (**1**), 2-methyl-3-butyn-2-ol (**2**) and 3-butyn-1-ol (**3**). The catalytic activities of catalyst **B** were greater than those of initiator **A** for these polymerizations. The steric bulk and the position of hydroxyl group of the monomer had an influence on the rate of polymerization. In order to investigate the role of hydroxyl group of monomers in the polymerization, the reaction between hydroxyacetylenes and the ruthenium complexes were monitored by <sup>1</sup>H NMR spectroscopy. The results revealed the formation of new alkylidene species via  $\alpha$ -insertion. The calculated relative energies of propagating species formed in the reaction of **A** with monomer **1** suggested the formation of oxygen-chelated species. The structures of resulting polymers were characterized by various methods such as NMR, IR and UV–Vis spectroscopies. The ruthenium initiators gave polymers with different geometric structure of main chain than conventional catalysts.

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## 1. Introduction

Polymerization of substituted acetylenes provides a useful tool for synthesis of various poly(acetylene) derivatives which have potential utility as electrical and optoelectronic materials, materials for gas or liquid-mixture separation and so on [1–8]. The substituted poly(acetylene)s are practically more useful because of their higher stability towards air and their solubility in organic solvents compared to non-substituted poly(acetylene) [9–12]. The polymerization of substituted alkynes has been carried out with a number ill-defined Mo-, W-, Ru-, Rh- etc. compounds as well as well-defined tungsten and molybdenum carbene initiators [10–17]. However, the sensitivity of the well-defined tungsten and molybdenum catalysts to oxygen, water and heteroatom functionalized substrates prevents the well controlled metathesis polymerization of highly functionalized monomers. Although, the tolerance of ruthenium based catalysts towards various functional organic compounds has been well known [18], attempts to initiate the polymerization of various acetylenes with 1st generation Grubbs catalyst failed [13]. Buchmeiser and coworkers developed polymerization systems by using 1,6-heptadiynes bearing different polar groups as monomers and mainly ruthenium carbenes containing trifluoroacetate ligands as catalysts [19–22]. The 2nd generation Grubbs catalyst reportedly reacts with disubstituted alkynes to afford  $\eta^3$ -vinylcarbene complexes with an unusual metallacycle structure, which is regarded as an intermediate of

the polymerization of acetylenes [23]. However, the catalytic reactivity of that Grubbs catalyst in the polymerization of diphenylacetylene is low. Although Sponsler and coworkers reported the polymerization of acetylene and its derivatives in the presence of more active 2nd generation catalysts modified with 3-bromopyridine, the substituted polyacetylenes formed have not been mentioned in detail [24]. The 2nd generation Grubbs–Hoveyda complex has been reported as catalyst capable of polymerizing mono- and disubstituted acetylenes bearing non-polar and polar groups such as ester, amide etc. [25,26]. However, polymerization of acetylenes containing polar hydroxyl groups in the presence of well-defined complexes was not examined. Many advantages of Grubbs catalysts, especially their tolerance to impurities and organic functionality prompted us to examine polymerization of hydroxyacetylenes by modified 2nd generation Grubbs and Grubbs–Hoveyda initiators. Due to the substantial lack of information concerning the influence of OH functional group on polymerization initiated with ruthenium carbenes, we were also interested in obtaining more information about the active species formed during the alkyne polymerization.

## 2. Results and discussion

### 2.1. Polymerization of hydroxyacetylenes

Polymerization of various hydroxyacetylenes (**1–4**) was examined by using 2nd generation Grubbs catalyst modified with 3-bromopyridine (**A**) and Grubbs–Hoveyda catalyst (**B**) (Fig. 1).

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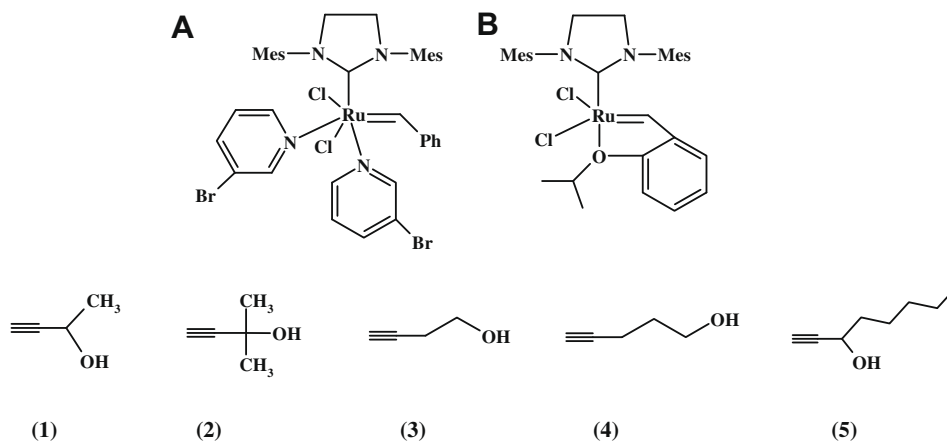


Fig. 1. Structures of catalysts (A–B) and hydroxyacetylenes (1–5).

The polymerization reactions of 3-butyn-2-ol (**1**) in various solvents were at first studied in detail (Table 1). The initiators **A** and **B** showed similar catalytic activity only in chlorobenzene as solvent, 16% of polymer yield in 24 h. Attempts to polymerize **1** by initiator **A** in  $\text{CH}_2\text{Cl}_2$  failed even at longer reaction time. No heptane-insoluble polymer was obtained. In contrast, the polymerization initiated by **A** showed reaction activity in toluene (26% of polymer yield in 24 h). Although the catalyst's solubility in both solvents is comparable, lack of polymerization in  $\text{CH}_2\text{Cl}_2$  could be attributed to slight decomposition of the catalyst in this solvent. In contrast to **A**, initiator **B** polymerized **1** in  $\text{CH}_2\text{Cl}_2$  to give 44% yield of polymer in 24 h. Moreover, the yield of polymer obtained in toluene after 24 h of reaction time is higher than this obtained in the presence of **A**. The polymerization by both initiators in toluene seems to level off after a certain period of time, because the polymer yield did not obviously increase after 48 h. The  $M_n$  of polymers prepared by both initiators slightly increased in 48 h, while no difference of polymers polydispersity was observed. In the case of **B**, with extending reaction time to 72 h the  $M_n$  of polymer significantly decreased and its polydispersity increased. The effect of polymerization temperature was examined only in the case of catalyst **B** because of its good stability at higher temperature. Raising the reaction temperature to 60 °C resulted in slightly lower polymer yield than this obtained at room temperature, while the  $M_n$  of polymer decreased and its polydispersity increased. This suggests that the reactions could be accompanied by backbiting and other secondary reactions. Next, the hydroxyacetylene-to-**B** molar ratio was varied while keeping the polymerization temperature at 25 °C. Decreases in the  $[1]/[B]$  ratio resulted in higher polymer yields. When  $[1]/[B] = 25$ , polymer was obtained in 59%, while in the case of  $[1]/$

**B**] of 100 polymerization proceeded to give only 18% yield. With increasing the monomer-to-catalysts ratio decreasing of the  $M_n$  was also observed.

Both initiators, **A** and **B**, were found to be less effective for the polymerization of 2-methyl-3-butyn-2-ol (**2**) (Table 2). However, in contrast to polymerization of **1** monomer **2** was polymerized by **A** in  $\text{CH}_2\text{Cl}_2$  as a solvent. Moreover, the polymer yield as well as  $M_n$  of polymer is comparable with that obtained in the presence of initiator **B** in the same reaction conditions. In the case of polymerization with initiator **B**, higher polymer yield and the  $M_n$  were achieved in toluene as a polymerization solvent than in  $\text{CH}_2\text{Cl}_2$ . With increasing the temperature to 60 °C the polymer yield and  $M_n$  slightly increased, in contrast to monomer **1**. The GPC chromatograms of obtained poly(**2**) showed the presence of two peaks. The low-molecular-weight peak had similar retention time in all chromatograms while the higher-molecular-weight peak varied with initiator used and reaction conditions. Retention time earlier peak corresponds to molecular weight of ca. 250, suggesting the occurrence of cyclization process. The  $^1\text{H}$  NMR spectrum of the product also showed additional signals that might be confirmed the formation of this type of products. The cyclodimerization of alkynes with phosphine-free ruthenium alkyldiene complexes was previously observed by Diver and coworkers [27]. Unfortunately, separation of poly(**2**) from the cyclic products by reprecipitation was not feasible due to the similar solubility of the compounds.

Attempts to polymerize 3-butyn-1-ol (**3**) proceeded to low conversion, below 25% regardless of solvent and initiator. However, higher catalytic activity of **B** (18–23%) than **A** (9–10%) was observed. Since poly(**3**) was insoluble in common organic solvents, its molecular weights were not able to be determined.

Table 1  
Polymerization of 3-butyn-2-ol (**1**) by catalysts **A** and **B**.

Catalyst	$[1]/[Cat]$	Solvent	Time (h)	Yield (%)	$M_n$	$M_w$	PDI
A	50/1	$\text{CH}_2\text{Cl}_2$	4 days	0	–	–	–
	50/1	PhCl	24	16	408	537	1.32
	50/1	PhMe	24	26	320	434	1.35
			48	30	347	481	1.39
B	50/1	$\text{CH}_2\text{Cl}_2$	24	42	473	699	1.48
	50/1	PhCl	24	16	530	737	1.39
	100/1	PhMe	24	18	570	844	1.48
	50/1	PhMe	24	48	658	936	1.42
			48	45	670	944	1.41
			72	40	555	858	1.55
	25/1	PhMe	24	59	727	1134	1.56
	50/1	PhMe <sup>a</sup>	24	43	511	869	1.70

<sup>a</sup> Polymerization temperature of 60 °C.

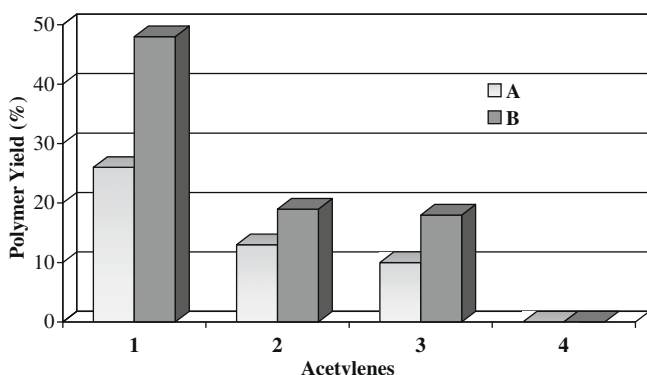
**Table 2**  
Polymerization of 2-methyl-3-butyn-2-ol (**2**) by catalysts A and B.

Catalyst	[BO]/[Cat]	Solvent	Yield (%)	$M_n$	$M_w$	PDI
A	50/1	CH <sub>2</sub> Cl <sub>2</sub>	12	492	531	1.10
		PhMe	13	320	402	1.26
B	50/1	CH <sub>2</sub> Cl <sub>2</sub>	12	467	591	1.27
		PhMe	19	557	707	1.27
		PhMe <sup>a</sup>	21	609	676	1.11

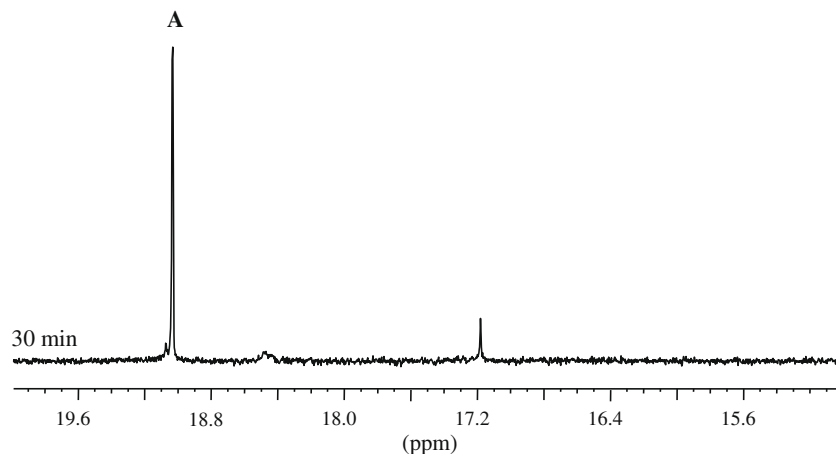
<sup>a</sup> Polymerization temperature of 60 °C.

Attempts to polymerize 4-pentyn-1-ol (**4**) by both initiators failed. No heptane-insoluble polymer was obtained.

The effect of monomer type and initiator on the polymer yield is shown in Fig. 2. In general, the decreasing tendency of polymer yield with increasing number and/or bulkiness of substituents in the polymerization of hydroxyacetylenes is observed in the case of polymerization by both initiators. However, the initiator **B** exhibited a higher activity than **A**, which might be related to better stability of **B** in the reaction conditions. Better reactivity of monomer **1** in comparison for **2** could be explained by steric hindrance effect of monomer in the reaction. Similar tendency of polymer yield with increasing bulkiness of the substituent in the polymerization of 2-propyn-1-ol and its derivatives by Mo-based initiators was observed by Gal et al. [11] Unexpectedly low catalysts activity in polymerization of linear monomer **3** can be attributable to the precipitation of polymer during the reaction. From a comparison of reactivity of monomers **3** and **4**, it might follow that polymer



**Fig. 2.** The effect of monomer type (**1–4**) and initiator (**A** and **B**) on the polymer yield obtained in the polymerization in PhMe.



**Fig. 3.** Alkylidene region of <sup>1</sup>H NMR spectrum (300 MHz) of the reaction of **A** with 20 equiv. of **1** in CDCl<sub>3</sub>.

yields drastically decreased as the number of methylene units between the hydroxyl and acetylene functional groups increased. The same tendency was observed in the polymerization of various hydroxyalkylacetylenes by Mo-based catalyst systems [12].

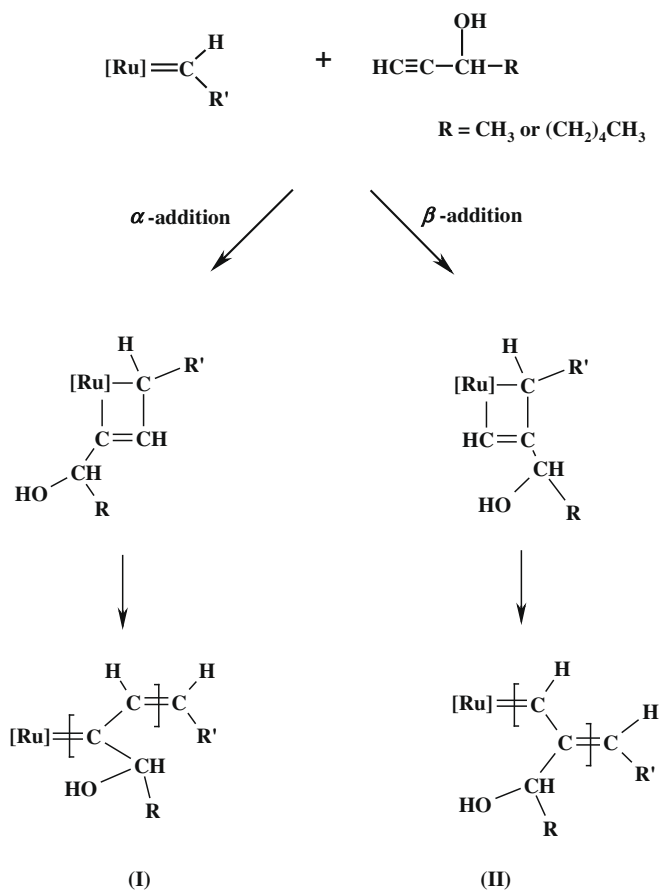
## 2.2. Polymerization of hydroxyacetylenes in NMR tube

The different influences of the monomers on the polymerization of hydroxyacetylenes using alkylidene ruthenium catalysts in order to provide a better understanding the stability of the propagating species, could be rationalized by an evaluation of the carbene peaks in the <sup>1</sup>H NMR spectra. Although analysis of the <sup>1</sup>H NMR spectra for the kinetic studies of the ROMP reactions initiated by well-defined ruthenium catalysts was extensively discussed in many publications [28–32], there are only few reports concerning analogous research of alkyne polymerization reactions [19–21]. Investigation of polymerization of 1,6-heptadiynes containing hydroxymethyl and ester groups with well-defined Ru-based initiators, i.e. 2nd generation Hoveyda–Grubbs catalyst (**B**) showed that cyclopolymerization of 1,6-heptadiynes bearing ester group with those initiators proceed selectively via  $\alpha$ -insertion [19].

During the reaction of initiator **A** with monomer **1** a new signals appeared at 18.49 and 17.18 ppm alongside residual **A** at 19.03 ppm (Fig. 3). The presence of new signals in the alkylidene region (25–16 ppm) rather excludes the formation of  $\eta^3$ -vinylcarbene complex [23] or ruthenium alkylidyne [33,34]. The new peaks can be assigned to hydrogen atoms in the  $\beta$ -position to the ruthenium of the propagating species **I** (Scheme 1) than new carbene protons of **II**.

When monomer **1** was subjected to polymerization mediated by initiator **B**, the alkylidene region of the <sup>1</sup>H NMR spectra showed mainly a resonance for the alkylidene proton of residual **B** at 16.95 ppm (Fig. 4). Besides, the small broad signals could be seen at 18.10, 16.69 and 16.60 ppm. The chemical shift of new alkylidene protons of the first, second etc. insertion products indicates that the insertion of the monomer moieties proceeds via  $\alpha$ -insertion (Scheme 1).

The reaction of more bulky 1-octyn-3-ol (**5** in Fig. 1) with initiator **B** proceed much more slowly than that of monomer **1**, and the alkylidene region of the <sup>1</sup>H NMR spectra exhibited well-resolved signals besides peak for the proton of residual **B** (Fig. 5). The chemical shift of appeared signals ( $\delta_H = 18.14, 16.69$  ppm) is almost identical with those of propagating species seen in the case of the polymerization of **1**. In addition, the very low-intensity signals at 16.61, 16.26 and 15.89 ppm in the <sup>1</sup>H NMR spectrum recorded after 15 min were detected. Those new signals could be also due



**Scheme 1.** Possible propagating species formed in the polymerization of **1** and **5** by initiator **A** and **B**.

to the insertion products. This suggests analogous structure of propagating species **I**, as was proposed in the case of polymerization of **1** (Scheme 1).

To get some insight into the steric effects of the hydroxyacetylenes on the polymerization mediated by **B**, the reaction of less bulky monomer **3** with **B** was followed by  $^1\text{H}$  NMR spectra. Unfortunately, due to insolubility of polymer, a precipitate formed immediately after adding **3** in solution of **B** in the NMR tube and consequently no more  $^1\text{H}$  NMR spectra were obtained.

When initiator **B** was used to mediate the polymerization of monomer **4**, 89% of **B** was consumed in 30 min. However, no propagating alkylidene resonances were observed during the reaction followed by  $^1\text{H}$  NMR spectra and no polymer was recovered.

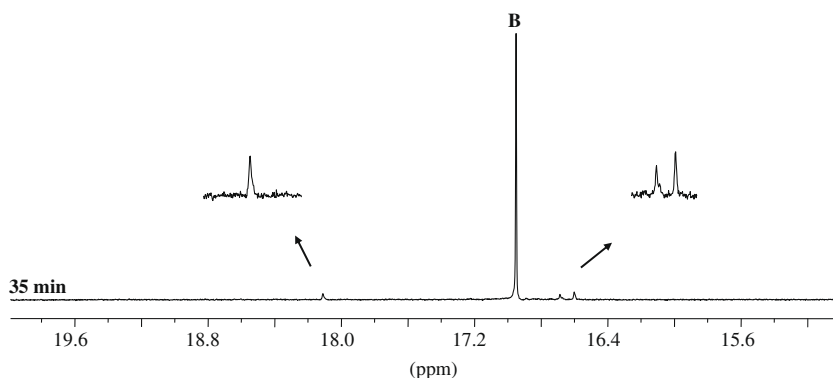
In all these reactions a resonance for the alkylidene proton of residual initiator **A** or **B** was observed. However, in reaction of monomer **1** 92% of initiator **A** was consumed in 30 min, whereas with complex **B** only 52% of the initiator was consumed. This observation is consistent with much higher values of  $k_i$  relative to  $k_p$  of the initiator **A** observed in the ROMP reactions [28,29,35]. In the case of polymerization of **5** mediated by **B**, the amount of initiator consumed (53% in 30 min) was similar to that observed the reaction of **1**. Thus, initial consumption of initiator **B** rather depends on the location of hydroxyl group in monomer. Although the reason of this observation is not fully understood, it might be due to the formation of oxygen-chelated propagating species. The complexation of monomers containing OH group to the ruthenium centre observed in the ROMP reactions initiated by Grubbs first generation initiators has been documented [31]. The formation of oxygen-chelated propagating alkylidene species could be form by chelation of an oxygen further down the polymer chain as well as oxygen of the monomer closest to the ruthenium centre [30,32]. Moreover, Slugovc et al. showed that increase of chelation abilities of different groups in disubstituted norbornenes results in the decrease of the polymerization rate constants of ROMP [29]. In the case of metathesis polymerization of various acetylenes mediated by Schrock-type molybdenum initiators, the ether functions of 4-oxa-1-octyne decreased its reactivity with respect to the overall rate [13]. Thus, the oxygen-chelation of propagating species could slow if not prevented further polymerization, and hence the low polymers yield obtained in the polymerization reactions initiated by **A** and **B** were observed (Tables 1 and 2).

Generally, analysis of the  $^1\text{H}$  NMR spectra indicates that the rate of propagation is greater than the rate of initiation. This can be directly related to the broad molecular weight distribution of polymers calculated from GPC chromatograms [36].

Finally, it is interesting to note that both ruthenium initiators were stable in the presence of acetylenes with OH groups. In contrast to reactions of ruthenium complexes with primary and allylic alcohols [37,38], no signals of hydride of the decomposition compounds were detected in the  $^1\text{H}$  NMR spectra recorded during all investigated reactions.

### 2.3. DFT calculations of propagating species formed in reaction of **A** with monomer **1**

In an effort to confirm all these experimental data theoretically, the stability of propagating species formed in reaction of alkylidene ruthenium catalyst (**A**) with monomer **1** was investigated by density functional theory (DFT) methods (Scheme 2). For each type of the Ru complexes, the geometry of various conformations has been optimized. In Fig. 6 the selected most stable conformers of the reactant (**A**) and five possible products (**A1–A5**) are



**Fig. 4.** Alkylidene region of the  $^1\text{H}$  NMR spectrum (300 MHz) of the reaction of **B** with 20 equiv. of **1** in benzene- $d_6$ .

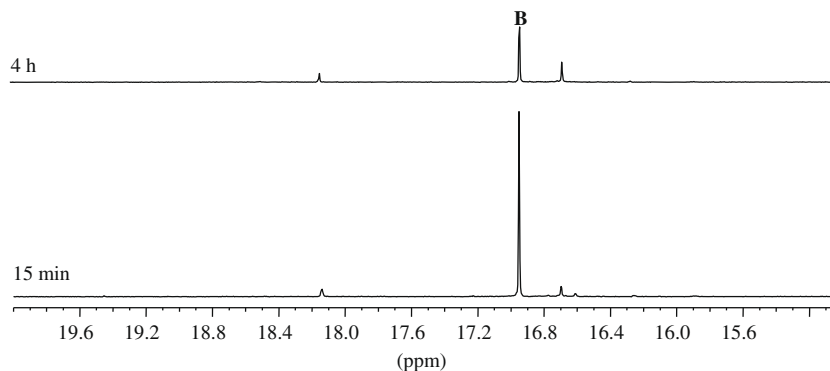
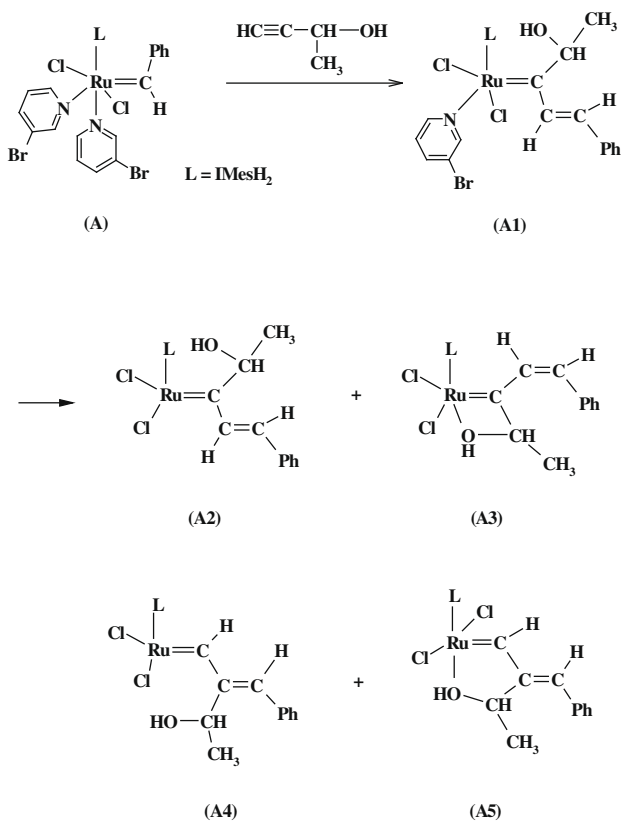


Fig. 5. Alkylidene region of the  $^1\text{H}$  NMR spectra (300 MHz) of the reaction of **B** with 20 equiv. of **5** in benzene- $d_6$ .

presented. A common feature of the ruthenium complexes **A1**–**A5** is a presence of hydrogen bond, involving the hydroxyl group and one of the chlorine atoms. The calculated O–H...Cl contacts of presented products are similar to the O–H...Cl distance of 2.32 Å found in ruthenium–NHC complex bearing unprotected hydroxyl group in the side-chain [39].

Formation of the compound **A1**, which retains one bromopyridyne ligand, is a clearly exothermic and irreversible reaction ( $\Delta H = -137 \text{ kJ mol}^{-1}$ ,  $\Delta G = -135 \text{ kJ mol}^{-1}$ ). Further dissociation of the bromopyridyne ligand, leading to the Ru complex **A2**, requires moderate energy ( $\Delta H = 59 \text{ kJ mol}^{-1}$ ), according to our gas phase calculations. Although, the previous theoretical studies dealt with mechanism of olefin metathesis initiated with 2nd generation Grubbs catalyst of the type  $[\text{RuCl}_2(\text{PR}_3)(\text{IMesH}_2)(=\text{CHR}')] (R'=\text{H}, \text{Ph})$  [40,41], the comparison of the calculated ligand dissociation energies of previous data with ours reveals the lowest bromopyridyne dissociation energy. The predicted Gibbs free energy for the bromopyridyne dissociation ( $-2 \text{ kJ mol}^{-1}$ ) indicates a possible thermodynamic equilibrium between the compounds **A1** and **A2**. However, the structure **A3**, in which oxygen in inserted monomer chelates to the ruthenium centre, reveals higher stability than **A2**, by 21  $\text{kJ mol}^{-1}$  ( $\Delta G$ ).

On the other hand, the structure **A4**, which differs from **A2** by the position of the  $\{-\text{CH}(\text{OH})\text{CH}_3\}$  group, is more stable than **A2**, by 30  $\text{kJ mol}^{-1}$  ( $\Delta G$ ). In addition, an agostic interaction, between the respective C–H bond and the ruthenium centre takes place. It is confirmed by the relatively small Ru–H distance (2.09 Å) and the elongated C–H bond (1.15 Å, compared to typical calculated value of 1.11 Å). Although, that agostic interaction can not be supported by our experiment, these parameters, as well as the agostic Ru–C distance (2.88 Å) are consistent with other experimental [42–47] and theoretical [47–49] data reported for the three-centre C–H...Ru interaction. The complexation of oxygen to the ruthenium centre via 5-membered ring causes an increase of the thermodynamic stability of **A4** by 36  $\text{kJ mol}^{-1}$  (**A5** in Fig. 6). Thus, the oxygen-chelation to the ruthenium centre via 5-membered ring leads to formation of more stable species (**A5**) than oxygen-complexation via 4-membered ring (**A3**). Intuitively complex **A3** with more strained 4-membered ring might be more active than **A5**. The proton NMR studies show that monomer **1** reacts with **A** via  $\alpha$ -insertion. Although, the thermodynamic stability alone is not so strong support for concluding about the kinetic information, on the basis of our theoretical calculations  $\alpha$ -insertion product, **A3** might be capable to polymerize **1**. In addition, the obtained theoretical results suggest the formation of oxygen-chelated propagating species in the reaction between initiator **A** and the hydroxyacetylene, as suggested above.



Scheme 2. Possible propagating species formed in the reaction of **A** with **1** (the computationally studied system).

#### 2.4. Structure and properties of polymers

It has been reported that hydroxyacetylenes **1**–**3** can be polymerized by ill-defined Mo-, W- and Pd- catalyst systems [11,12]. However, the geometric structure of those polymers has not been discussed in detail. In general, it is known that the polymerization of monosubstituted acetylenes by Mo-based catalytic systems provide polyacetylenes with rather low cis contents [10,13,50]. Therefore, polymers of **1** and **2** were prepared by  $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$  to compare the geometric structure with that obtained with Ru initiators. The  $[\text{MoCl}(\text{SnCl}_3)(\text{CO})_3(\text{NCMe})_2]$  was chosen since this heterobimetallic complex was found as a very efficient initiator for polymerization reaction of terminal alkynes such as, phenylacetylene or *tert*-butylacetylene [50,51].

All of poly(**1**) and poly(**2**) samples were soluble in halogenated solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{PhCl}$ ), toluene, methanol and insoluble in hexane. However, the Ru-based polymers were completely soluble

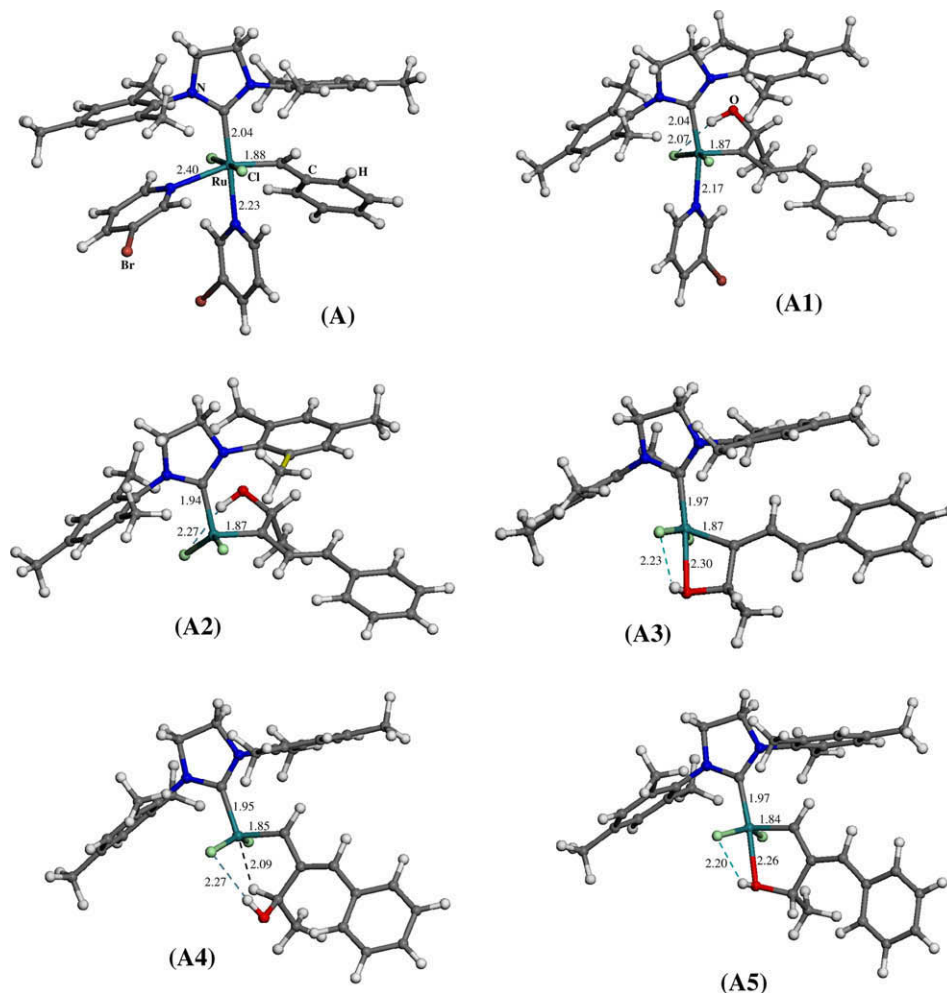


Fig. 6. The calculated structures of the initiator **A** and potential products (**A1**–**A5**) formed in the reaction of **A** with **1**.

while Mo-based ones only partially soluble. Some differences of colors of these polymers have been observed as well. Polymers prepared by Mo-based initiator were usually black while these obtained by Ru catalysts were light brown.

The infrared spectra of poly(**1**)s obtained with Ru and Mo catalysts showed the stretching vibration of conjugated double bond at 1633(vs)  $\text{cm}^{-1}$ . The OH groups peaks were observed at ca. 3337(br,s) and 1071  $\text{cm}^{-1}$ . The differences between infrared spectra of the Ru- and Mo-based polymers were seen in the range of 1300–600  $\text{cm}^{-1}$ . The spectrum of poly(**1**) obtained by Ru initiator showed peaks characteristic of *trans* structure [52] at 1266(s) and 900(m)  $\text{cm}^{-1}$ , while those of *cis* structure [52] (870 and 740  $\text{cm}^{-1}$ ) were absent. In contrast, peaks due to *trans* and *cis* structure were seen in the IR spectrum of Mo-based polymer. Therefore, it is evident that poly(**1**)s obtained by Ru initiators have a rich *trans* structure, while that prepared by Mo initiator rather has comparable amounts of *trans* and *cis* structures. Comparison of the  $^1\text{H}$  NMR spectra of Ru- and Mo-based poly(**1**)s also indicated different structure of both polymers. The  $^1\text{H}$  NMR spectrum of Ru-based polymer showed sharp peaks. The strong signal at 6.94 ppm which can be assigned to *trans* polyenic protons [53] was observed. In contrast, the spectrum of Mo-based polymer showed broad signals and was similar to those of polymers prepared in the presence of other ill-defined Mo-based catalytic systems.[11] This suggests high stereoregularity of the Ru-based poly(**1**)s, while the polymer produced with Mo catalyst have geometrically irregular structure. A rich-*trans* structure of poly(phenylacetylene) obtained by trifluo-

roacetate-based Ru alkylidene initiator was also reported by Buchmeiser et al. [54].

The infrared spectrum of poly(**2**)s produced with Ru catalysts besides of signals characteristic of *trans* structure [52] (1266(s) and 959(m)  $\text{cm}^{-1}$ ) showed also signal at 854(m)  $\text{cm}^{-1}$ , which could be due to *cis* structure [52]. However, the IR spectrum of the Mo-based poly(**2**) was quite different in the range of 1500–1000  $\text{cm}^{-1}$ , which appeared to reflect differences in the structure of the polymers. The UV–Vis spectra of poly(**2**)s also showed different structure of polymers depending on used initiators. Whereas the spectrum of polymer obtained with ill-defined Mo initiator displayed two peaks at ca. 244 and 292 nm, the polymers with ruthenium catalysts possessed only one peak at 248 nm. This indicates that the conjugation length of the polymers prepared in the presence of Ru catalysts is much shorter than those of the polymers obtained in the Mo-based one. Analogous tendency was observed by Masuda et al. for the Ta- and Ru-based polymers of diphenylacetylene derivatives bearing silyl and siloxy groups [25,26].

Although the poly(**3**)s were not characterized by NMR and UV–VIS spectroscopies due to their insolubility in halogenated and polar solvents regardless of the polymerization conditions, the polymers were characterized by the infrared spectroscopy. Besides of the peaks characteristic of hydroxyl group (ca. 3320 and 1044  $\text{cm}^{-1}$ ), the carbon–carbon double bond stretching frequencies were observed at 1654  $\text{cm}^{-1}$ . However, those IR spectra did not enable the determination of the geometric structure of the main chain.

The thermal properties of polymers were determined by TGA. All measured polymers lost weight steeply with increasing temperature. The slight weight loss at the initial temperatures might be due to the emission of absorbed moisture and residual organic solvents. Among Ru-based polymers of **1–3**, the poly(**3**) is the most and the poly(**1**) is the least stable. The poly(**1**) prepared with Ru initiator are more stable than that with Mo-based one.

### 3. Summary

The reactivity of the well-defined ruthenium alkylidene complexes: 2nd generation Grubbs catalyst modified with 3-bromopyridine (**A**) and 2nd generation Grubbs–Hoveyda catalyst (**B**) towards metathesis polymerization of acetylenes having hydroxy functional polar group has been investigated. To the best of our knowledge, this is the first example of the polymerization of acetylene derivatives carrying such a polar group by well-defined Ru catalysts. Up to now those hydroxyalkynes were polymerized only by ill-defined catalytic systems. In general, the catalytic activities of catalyst **B** were greater than those of initiator **A**. The rates of polymerization of hydroxyacetylenes by Ru initiators depend on the structure of hydroxyacetylene and the location of hydroxyl group in the substrate.

The proton NMR studies of polymerization reaction mediated by the ruthenium complexes show that hydroxyacetylenes **1** and **5** react with initiators **A** and **B** via  $\alpha$ -insertion. Our initial theoretical results suggest that the oxygen-chelated propagating species are more stable than the species without the chelation of oxygen to the ruthenium. Thus, relatively low yields of prepared polymers might be explained by formation of oxygen-chelated propagating complexes. Further investigations concerning the mechanism of the formation of propagating species formed in reaction of ruthenium alkylidene compounds with hydroxyacetylenes are in progress.

The geometric structure and properties of the polymers obtained with the Ru catalysts were different from those of Mo-based ones. The Ru-based polymers, except poly(**3**s), were completely soluble while Mo-based ones only partially soluble. The NMR, IR and UV–Vis analysis indicates different geometric structure of the main chain of polymers prepared with the Ru and Mo catalysts.

## 4. Experimental

### 4.1. General

The metathesis polymerizations were carried out under nitrogen using the conventional vacuum/nitrogen line or glove-box techniques. NMR spectra were recorded using a Bruker AMX-300 and 500 spectrometer. Gel Permeation Chromatography (GPC) data were obtained using a Hewlett-Packard 1090II equipped with a refractive index detector HP 1047A and Plgel 5  $\mu$ m mixed C column. Chloroform was used as the eluent at a flow rate of 1 ml/min at 40 °C. Polystyrene standards were used for calibration. A polydispersity (PDI) was calculated by the non-commercial computer program examine the peaks at high molecular weight in GPC. Thermogravimetric analyses (TGA) were conducted in nitrogen with Perkin Elmer TMA-7 thermal analyzer. Ultraviolet–Visible (UV–Vis) and infrared (IR) spectra were measured on Hewlett-Packard 8452A spectrophotometer and Nicolet 400 FT-IR instrument, respectively.

### 4.2. Materials

[RuCl<sub>2</sub>(=CHPh)(3-Br-py)<sub>2</sub>(IMesH<sub>2</sub>)] (**A**) (modified 2nd generation Grubbs catalyst) [55] and [MoCl(SnCl<sub>3</sub>)(CO)<sub>3</sub>(NCMe)<sub>2</sub>] [50]

were prepared according to literature procedure. 3-butyn-2-ol (**1**) (97% Aldrich) was vacuum distilled prior use. [RuCl<sub>2</sub>(=CH-*o*-OiPrC<sub>6</sub>H<sub>4</sub>)(IMesH<sub>2</sub>)] (Grubbs–Hoveyda initiator) (**B**) (Aldrich) and hydroxyacetylenes: 2-methyl-3-butyn-2-ol (**2**) (99% Fluka), 3-butyn-1-ol (**3**) (97% Fluka), 4-pentyn-1-ol (**4**) (99% Alfa Aesar) and 1-octyn-3-ol (**5**) (98% Fluka) were purchased from Aldrich and used as received. Solvents: dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) toluene (PhMe), chlorobenzene (PhCl), dichloromethane-*d*<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>), benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) and chloroform-*d* (CDCl<sub>3</sub>) were dried under CaH<sub>2</sub> and distilled prior to use. Heptane (HPLC grade) and methanol (HPLC grade) was used without further purification.

### 4.3. General procedure for metathesis polymerization of hydroxyacetylenes at RT

The hydroxyacetylenes were polymerized in a glove-box under an atmosphere of N<sub>2</sub>. The initiator (**A** or **B**) dissolved in 0.5 ml of solvent (CH<sub>2</sub>Cl<sub>2</sub>, PhMe, PhCl or CH<sub>2</sub>Cl<sub>2</sub>) was added to the hydroxyacetylene (0.5 M) dissolved in the same solvent. Unless otherwise specified, the reaction was allowed to run for 24 h at room temperature. Next, the reaction was removed from the glove-box, and ethyl vinyl ether (0.5 ml) was added. The polymers of **1** and **2** were precipitated into an excess of heptane, isolated by filtration, dried, and then reprecipitated in CH<sub>2</sub>Cl<sub>2</sub>/heptane and dried under vacuum. The polymer of **3** was precipitated into CH<sub>2</sub>Cl<sub>2</sub> and then reprecipitated in methanol/CH<sub>2</sub>Cl<sub>2</sub>.

### 4.4. General procedure for metathesis polymerization of hydroxyacetylenes at 60 °C

In the glove-box solution of hydroxyacetylene (0.5 M) in PhMe was added to initiator **B** dissolved in 0.5 ml of PhMe and placed in a Schlenk tube. The reaction was stirred at 60 °C under nitrogen for 24 h. The formed polymer was isolated and reprecipitated as specified above.

### 4.5. General procedure for metathesis polymerization of hydroxyacetylenes in NMR tube

In the glove-box the initiator **A** or **B** (ca. 14 mg) was dissolved in 0.5 ml of CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> and transferred into a NMR tube. Next, the relevant hydroxyacetylene (10 or 20 equiv.) was added to the NMR tube. The reactions were monitored by <sup>1</sup>H NMR spectroscopy at room temperature.

### 4.6. Computational details

Density functional theory calculations were carried out with the generalized gradient approximation using Becke exchange functional [56] combined with Perdew correlation functional [57] (BP86). A good performance of this method in reproducing geometries and relative energies of organometallics compounds, among others, ruthenium complexes, was proved [41,58–63]. The split-valence def2-SVP basis set [64] was applied for the geometry optimization, whereas the further single point calculations were performed using the triple- $\zeta$  valence def2-TZVP basis set [64]. The latter was recommended for quantitative DFT calculations [64]. The 28 innermost electrons of Ru were replaced by the Stuttgart effective core potential [65].

All structures were fully optimized with the Berny algorithm with redundant internal coordinates [66]. Harmonic vibrational frequencies were calculated for each structure to confirm the potential energy minimum. Thermochemical quantities were estimated by treating the systems studied as ideal gas molecules at  $T = 298.15$  K and under  $p = 1$  atm.

The calculations were done with the GAUSSIAN 03 suite of programs [67]. For the graphic presentation of the structures, Materials Studio 4.2 software was used [68].

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