Acetylene polymerization by titanocene alkyne complexes

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Abstract

Efficient polymerization of acetylene is achieved by using titanocene alkyne complexes as precatalysts. The in situ generated titanocene 'Cp$_2$Ti' is the catalytically active species which induces acetylene polymerization. A mechanism including an exo-allylidene metallacyclobutene complex for the catalytic formation of polyacetylene is proposed.

Keywords: Polymerization; Acetylene; Titanocene; Alkyne complexes

1. Introduction

Since the recognition of electrically conducting polyacetylene (PA) considerable effort has been made by several research groups using different catalytically active systems to efficiently polymerize acetylene [1]. In the group 4 metallocene chemistry as a classical example [Cp$_2$Ti(PMe$_3$)$_2$] was used as a precatalyst in the polymerization of acetylene [2]. It was suggested, that an η^2-acetylene complex [Cp$_2$Ti(PMe$_3$)(HC≡CH)] is converted into a titanocene vinylidene complex [Cp$_2$Ti=C=CH$_2$(PMe$_3$)] which gives after replacement of PMe$_3$ the corresponding acetylene complex [Cp$_2$Ti=C=CH$_2$(HC≡CH)]. Such a vinylidene compound is assumed to be an active catalyst in the polymerization of acetylene.

A recent paper describes the polymerization of acetylene by using the heterobimetallic titanocene aluminium complex Cp$_2$Ti(μ-H)$_2$AlH$_2$ as catalyst [3].

During the polymerization of acetylene the crystallization of a black polymer is observed. In a side reaction a small portion of acetylene is cyclotrimerized to benzene. Dependent upon the reaction temperature at $T \leq 255$ K mainly *cis-*, at $T \geq 350$ K exclusively *trans*-PA is obtained. In between initially a mixture of both isomers is formed, followed by gradual conversion of the *cis*-PA, at temperatures above 0°C, into the thermodynamically more stable *trans*-isomer [4]. PA is characterized by means of IR spectroscopy. A typical absorption at about 1015 cm^{-1} in the IR spectrum is given by *trans*-PA, whereas the IR spectrum of the *cis*-PA exhibits characteristic absorptions at 445 cm^{-1}, 740 cm^{-1} and 1329 cm^{-1} [1]. Unfortunately, polyacetylene is insoluble in conventional solvents and sensitive to oxygen. This characteristic restricts possible applications and the subsequent treatment of polyacetylene.

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2. Results and discussion

In the polymerization experiments using metallocene alkyne complexes the catalyst was tested in several solvents in an acetylene atmosphere. Upon steady supply of acetylene (normal pressure) an intense exothermic reaction, following a short incubation time of 2–5 min, with high acetylene consume took place. The gas consumption was observed by a bubble counter and the reaction was stopped 10 min after the last acetylene provision after a reaction time of about 2–3 h. The furnished PA was isolated and subsequently characterized as described in the experimental part.

The conducted experiments revealed no polymerization activity for zirconocene alkyne complexes, like $[Cp_2Zr(L)(Me_3SiC\equiv CSiMe_3)]$ (L = THF [5](a), py [5](b)). A probable explanation is the preferential formation of a zirconacyclopentadiene [6], which owing to its stability is then unsuitable as catalyst.

In addition to various titanocene alkyne complexes $[Cp_2Ti(RC\equiv CSiMe_3)]$ (R = Ph [7](a), SiMe$_3$ [7](b), ^tBu [7](c)), the permethyltitanocene alkyne complexes $[Cp_2^* Ti(RC\equiv CSiMe_3)]$ (R = SiMe$_3$, Ph [7](d)) and the dinuclear vinyl carboxylate complex

$$[Cp_2Ti\text{-}C(SiMe_3)=C(SiMe_3)\text{-}COOTiCp_2]$$
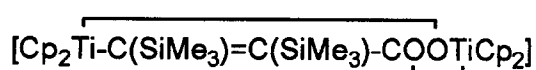
[7](e) were used as well. These catalyst complexes revealed distinct activities. The highest yields of PA were found for the bis(trimethylsilyl)acetylene complex $[Cp_2Ti(Me_3SiC\equiv CSiMe_3)]$ [7](b) and the vinyl carboxylate complex. Results of both catalysts are summarized in Table 1.

As previously described for the olefin isomerization by titanocene and zirconocene alkyne complexes [8], the compound $[Cp_2Ti(Me_3SiC\equiv CSiMe_3)]$ was most reactive,
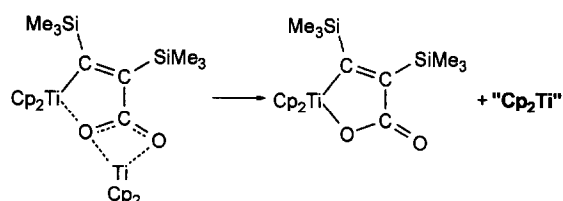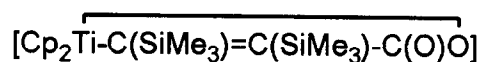
which can be attributed to the facile dissociation of the alkyne generating the 'Cp$_2$Ti' fragment:
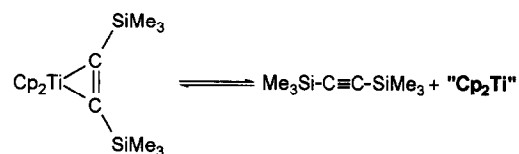
Likewise the titanocene vinyl carboxylate

$$[Cp_2Ti\text{-}C(SiMe_3)=C(SiMe_3)\text{-}COOTiCp_2]$$
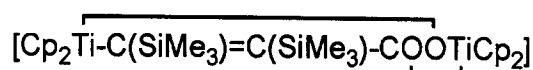
gave high yields of PA per mole titanocene, which may lie in the rapid release of a Cp$_2$Ti unit and the formation of a titanafuranone

$$[Cp_2Ti\text{-}C(SiMe_3)=C(SiMe_3)\text{-}C(O)O]$$

The data of Table 1 show that the yields of PA depend on the used solvent. So, in n-hexane rather poor results were found with all catalysts tested. The differing acetylene turnover can be related to the varying solubility of acetylene in the solvents employed (pyridine > THF > hexane, e.g. solubility of acetylene at 25°C, 1 atm acetylene pressure: 2.4 ml C_2H_2 in 1 ml n-hexane; 21.0 ml C_2H_2 in 1 ml THF [9]), which should determine the rate of the monomer supply in the intense reaction. Confirmation of this is seen by the significant improvement of yield PA when the volume of solvent is increased and therefore a greater amount of dissolved acetylene is accessible (higher substrate-to-catalyst ratio in solution).

In contrast, the higher substrate excess in solution and strongly coordinating solvents like THF or pyridine should favour the dissociation of the silylalkyne and stabilize the Cp_2Ti fragment.

The velocity of polymerization is also affected by changing the temperature. Below 0°C, polymerization rarely occurs, when it does it is slight, while at room temperature significant turnover of acetylene is observed. In toluene and pyridine at 60°C highest yields of PA are achieved, notwithstanding the solubility of acetylene decreases with increasing temperature. Obviously a higher temperature is necessary to generate a sufficient amount of catalytically active 'Cp$_2$Ti' in order to start the reaction.

Little is known about the mechanism of the acetylene polymerization. A plausible description (Scheme 1) assumes a metal vinylidene intermediate as the active polymerization catalyst as postulated by a number of authors [10]. It differs from the alternative mechanism of the dimerization of terminal alkynes which is based on an oxidative addition to metallocene–acetylide–hydride species as catalytic centers [11].

In our case the complexed silylalkyne is substituted by acetylene, forming the not isolated titanocene acetylene complex a (Scheme 1). Subsequently a hydrogen shift [12] could take place whereby the η^2-acetylene complex rearranges into the titanocene vinylidene [$Cp_2Ti=C=CH_2$] (b [13]). This alkyne-to-vinylidene rearrangement is a key step in the coordination chemistry of terminal alkynes on a metal center.

A second acetylene molecule could be inserted into the metal–carbon double bond yielding an exo-methylene metallacyclobutene complex (c [14]), as e.g. realized in

$$[\overline{Cp^*_2Ti\text{-}CH{=}CH\text{-}C}{=}CH_2]$$
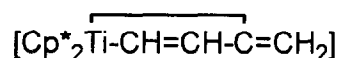
[15]. Such an insertion is in agreement with a mechanism, proposed by Alt et al. [2].

Our following suggestions of the ring opening differ from Alt's mechanism (path ii) and can proceed also along path i (Scheme 1). The rearrangement of the metallacycle c (path ii) has been assumed in previous works [2,16], in which the so formed allenylidene–carbene complex e allows the insertion of an additional acetylene

Table 1
Polymerization of acetylene by metallocene catalysts

Catalyst	Solvent	Volume [ml]	T [°C]	Yield PA [mg PA/mmol 'Cp$_2$Ti']	Configuration
[Cp$_2$Ti(Me$_3$SiC $\equiv$ CSiMe$_3$)]	THF	20	RT	< 50	cis + trans
	n-hexane	20	RT	< 50	cis + trans
	toluene	20	RT	770	cis + trans
	pyridine	20	RT	250	trans
	pyridine	50	60	3300	trans
[Cp$_2$Ti(C(SiMe$_3$)=C(SiMe$_3$)-COOTiCp$_2$]	THF	50	0	< 50	cis + trans
	THF	50	RT	4340	cis + trans
	THF	20	RT	1230	cis + trans
	toluene	50	60	1140	cis + trans
	pyridine	20	60	2590	trans
[Cp$_2$Ti(PMe$_3$)$_2$]	toluene	50	RT	≈ 2000	trans [a]

[a] See H.G. Alt et al. [2]
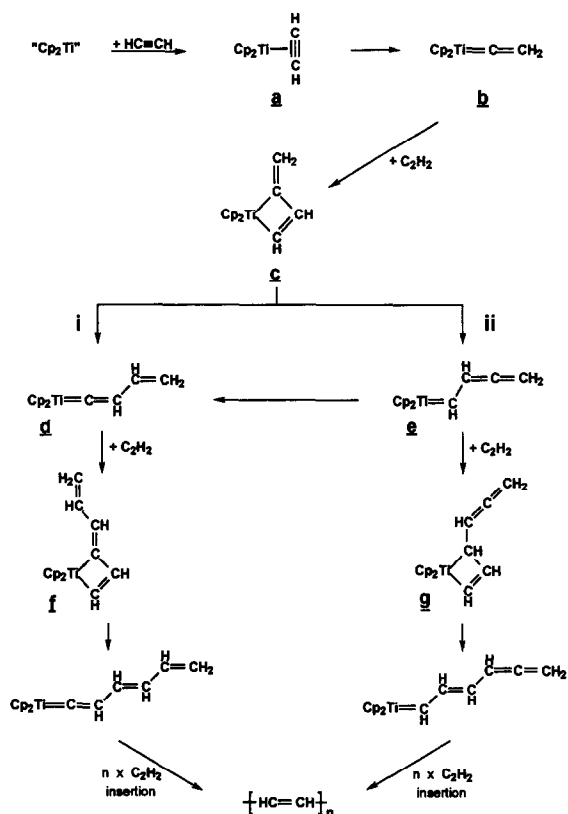
Scheme 1. Suggested reaction mechanism for the formation of *trans*-PA: Conversion of an η^2-alkyne complex a through a 1,2-H-shift leading to a vinylidene intermediate b as the catalytically active metallocene species.

molecule into a M=C bond yielding a metalla-cyclobutene **g**. Repeated insertions of C_2H_2 yield polyacetylene.

On the other hand the ring opening of the metallacycle **c** may also be understood as an 1,3-H-shift (path **i** directly) or more likely through **e** and a η^3-vinylcarbene complex [17] with a formation of a vinylidene complex **d** which by insertion of C_2H_2 produces an exo-al-lylidene metallacycle **f**, comparable to **c**, but probably stabilized by an additional conjugation of double bonds. Recurrent ring openings and acetylene insertions produce polyacetylene. The proposed (as yet experimentally unverified) mechanism could also explain the favoured yield of *trans*-PA in the experiments. In the case of strongly donating ligands such as PMe_3 [2] and

pyridine exclusively *trans*-polyacetylene is formed.

The investigated catalytic reactions of ti-tanocene alkyne complexes once again reveal the capacity and variability of metallocene systems. In the catalyses the alkyne complexes of $Me_3SiC\equiv CSiMe_3$ possess surprising activities, which even in non-optimized experiments lead to results comparable to those described in the literature for analogous reactions using other systems.

3. Experimental

All operations were carried out in an inert atmosphere (argon) with standard Schlenk techniques. Solvents used for polymerizations were treated with sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker ARX 300, IR, Nicolet Magna 500 (Nujol mulls using KBr plates), GC, Hewlett Packard 5890 with FID detector.

3.1. Polymerization reaction

A typical reaction was performed as follows. A Schlenk tube (250 ml) was charged with the titanocene complex (~ 0.5 mmol) and the given volume of the solvent (Table 1) under argon. The tube was cooled to $-78°C$, stirred for 10 min and then evacuated. Following the addition of C_2H_2 the solution was allowed to warm up to room temperature. The reaction vessel was kept open to the acetylene supply (continuous supply) and the mixture was stirred during the reaction. An insoluble black residue resulted from a violent reaction which is terminated 10 min after the last acetylene provision (reaction time of about 2–3 h). After closing of the gas supply the acetylene was removed by evacuating and replaced by argon. The polyacetylene was isolated by filtration, washed with THF and dried in vacuo. The polymer was always han-

dled under an inert atmosphere and characterized by IR spectroscopy (characteristic absorptions: cis-PA: 445, 740, 1329 cm^{-1}; trans-PA: 1015 cm^{-1}) and elemental analysis. Product distribution and yields are presented in Table 1.

Acknowledgements

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