

# The influence of cocatalysts on phenylacetylene oligo- and polymerization

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## Abstract

Titanium bisphenolate complexes [Ti(edbp)Cl<sub>2</sub>] (**1**), [Ti<sub>2</sub>(μ-OEt)<sub>2</sub>(edbp)<sub>2</sub>(OEt)<sub>2</sub>] (**2**) and [Ti<sub>2</sub>(μ-OMe)<sub>2</sub>(edbp)<sub>2</sub>(Me)<sub>2</sub>] (**3**) (edbpH<sub>2</sub> = 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol) combined with trialkyl aluminium AlR<sub>3</sub> (R = Me, Et, <sup>i</sup>Bu) activators induce phenylacetylene (PA) oligo- and/or polymerization. It was found that the catalytic activity and products formation depend strongly on the used cocatalyst. The **1**/AlEt<sub>3</sub> catalyst has the highest activity and selectivity (96% conversion; 98% *trans*-PPA). The PPA has low *M<sub>n</sub>* values (2200) and PDI exceeding 1.04. Instead, **1**/Al<sup>*t*</sup>Bu<sub>3</sub> produces only cyclotrimers. Polymer formed by **2**/AlEt<sub>3</sub> possesses lower polydispersion index (PDI values 2.5) but high molecular weight (*M<sub>n</sub>* ca. 13 × 10<sup>3</sup>) and was the mixture of *cis* and *trans* stereoisomers of PPA. The compound **3** containing terminal methyl groups was unable to promote PA polymerization in absence of activators, only cyclotrimerization products (10% conversion) were formed.

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**Keywords:** Polymerization; Cyclotrimerization; Acetylenes; Titanium; Bisphenolate complexes

## 1. Introduction

Transition metal mediated polymerization of acetylenes generated polyenes with π-conjugated backbones. The products might lead to new synthetic materials with unique physical properties such as photoconductivity, optical nonlinear susceptibility, ferromagnetism and oxygen permeability [1–4]. Titanium(IV) complexes exhibit various kind of reaction towards acetylenes including dimerization, cyclization and oligomerization depending on the structure of acetylenes and the reaction conditions [5–8]. Efficient polymerization of acetylenes is achieved by using titanocene alkyne complexes [9] or Ziegler–Natta (Z–N) catalysts based on titanium(IV) alkoxides and AlEt<sub>3</sub> as a cocatalyst [10]. Monosubstituted alkynes polymerize in the presence of Z–N catalysts only in the case of uncrowded monomers bearing primary or secondary aliphatic groups. Moreover, there is little information

concerning the role of cocatalyst (AlR<sub>3</sub>) in active metal site formation during polymerization process.

We have recently been interested in revealing the catalytic properties of bisphenoxo titanium complexes having 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol) (edbpH<sub>2</sub>) as an ancillary ligand in olefin polymerization [11]. The class of these catalytic systems has been proved to give excellent results both in terms of catalytic activity and narrow polydispersion index. Only few reports are found on relevant complexes in reactions with alkynes and only cyclotrimerization products were detected [12–14]. The well-controlled polymerization of phenylacetylene has been only demonstrated using an ill-defined Ti(IV)alkoxides/AlEt<sub>3</sub> catalytic system [10]. Therefore it was interesting to investigate the influence of the cocatalyst on the catalytic properties of **1** and **2** in the polymerization and/or cyclotrimerization of PA and compare it with complex **3** having methyl group bonded to titanium without cocatalyst.

Here, we report the properties of bisphenoxo titanium precursors: [Ti(edbp)Cl<sub>2</sub>] (**1**), [Ti<sub>2</sub>(μ-OEt)<sub>2</sub>(edbp)<sub>2</sub>(OEt)<sub>2</sub>] (**2**)

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and  $[\text{Ti}_2(\mu\text{-OMe})_2(\text{edbp})_2(\text{Me})_2]$  (**3**) in the polymerization of phenylacetylene and evolution of catalytic system using  $\text{AlR}_3$  (R = Me, Et,  $^i\text{Bu}$ ) compounds as a cocatalysts.

## 2. Experimental

### 2.1. Materials

All the reactions and operations were performed under an inert atmosphere using standard Schlenk techniques. Reagents were purified by standard methods: thf, distilled from CuCl, predried over NaOH, and then distilled from Na/benzophenone; *n*-hexane, distilled from Na. Phenylacetylene (PA) (Aldrich) was dried over  $\text{CaH}_2$  and distilled under dinitrogen prior to use;  $\text{AlR}_3$  (R = Me, Et,  $^i\text{Bu}$ ) (1 M solution in *n*-hexane, Aldrich) and all deuterated solvents (Cambridge Isotope Laboratories) were used as received.  $[\text{Ti}(\text{edbp})\text{Cl}_2]$  (**1**) [11],  $[\text{Ti}_2(\mu\text{-OEt})_2(\text{edbp})_2(\text{OEt})_2]$  (**2**) [15] and  $[\text{Ti}_2(\mu\text{-OMe})_2(\text{edbp})_2(\text{Me})_2]$  (**3**) [11] were prepared according to the published procedures.

### 2.2. Characterization techniques

IR spectra were measured on Perkin-Elmer 180 instrument in Nujol mulls or KBr pallets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were detected at room temperature using a Bruker ESP 300E spectrometer. Chemical shift data are reported in parts per million and referenced to the residual protons in deuterated solvents. Monomer conversion and yields of cyclotrimers were determined by gas chromatography (GC–MS; HP-5890 II + 5971A). The yields of polymers were determined gravimetrically. The weights and number-average molecular weights were determined by gel permeation chromatography (GPC; HPLC-HP 1090 II with DAD–UV–vis and RI detector HP 1047A) using polystyrene calibration.

### 2.3. Catalytic reactions in Schlenk tube

A typical procedure was as follow. To a stirred solution of **1** or **2** in 5.0 ml of *n*-hexane or thf the cocatalyst solution  $\text{AlR}_3$  ( $[\text{Ti}]/[\text{Al}]$  = from 1:1 to 1:10) at room temperature was added. After 10 min the PA ( $[\text{Ti}]/[\text{PA}] = 1/50$ ) with GLC internal standard was syringed. Samples were withdrawn from the reaction mixture at time intervals and disappearance of the monomer was followed by GLC. The reactions were then treated with a small amount of methanol (1 ml). The resulting polymeric product was filtered off, washed with methanol and dried under vacuum. Polyphenylacetylenes were purified by crystallization from  $\text{CH}_2\text{Cl}_2$  and methanol.

### 2.4. Determination of polyene stereochemistry

The stereochemistry of the polyphenylacetylene (PPA) obtained in all experiments was determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. For *cis*-transoidal-PPA  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.95–6.93

(m, 3H, *m*- and *p*- $\text{H}(\text{C}_6\text{H}_5)$ ), 6.64–6.62 (m, 2H, *o*- $\text{H}(\text{C}_6\text{H}_5)$ ), 5.84 (s, 1H,  $\text{C}=\underline{\text{CH}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 142.9 and 139.3 (quaternary carbons), 131.8 ( $\text{C}=\underline{\text{CH}}$ ), 127.8 and 127.5 (*o*- and *m*-Ar), 126.7 (*p*-Ar). For *trans*-cisoidal-PPA:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.2 (very broad);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 128.0 (very broad). The microstructure details of the polymers were calculated from the  $^1\text{H}$  NMR integrals according to the generally accepted equation [16].

### 2.5. Determination of cyclotrimers stereochemistry

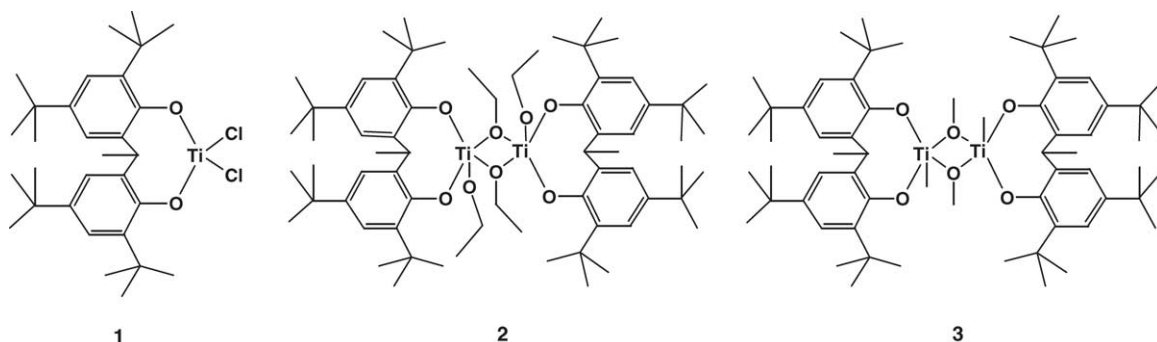
After isolation of the polymer (in all experiments), the filtrate was evaporated to dryness and the residue was dissolved in  $\text{CDCl}_3$ . The solution was analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. For 1,3,5-triphenylbenzene:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.77, 7.68, 7.46, 7.37;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 142.3 and 141.1 (quaternary carbons, 129–125 (CH)). For 1,2,4-triphenylbenzene:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.84, 7.77, 7.46, 7.37;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 141.4, 141.0, 140.9, 140.5, 140.3, 139.5 (quaternary carbons), 129–125 (CH).

## 3. Results and discussion

The reaction of 2,2'-ethylidenebis(4,6-di-*tert*-butylphenol) ( $\text{edbpH}_2$ ) containing two acidic protons with  $\text{TiCl}_4$  in a 1:1 molar ratio in *n*-hexane proceeded with spontaneous evolution of HCl resulting in red crystals of  $[\text{Ti}(\text{edbp})_2\text{Cl}_2]$  (**1**) [11]. By selecting the  $\text{edbpH}_2$  ligand, which contains phenols with *tert*-butyl "tails", we expected to obtain titanium compounds with markedly improved solubility in hydrocarbons, and an increased likelihood of compound stability in the presence of the alkyl aluminium cocatalyst. The precursor **2** was obtained by direct reaction of  $\text{Ti}(\text{OEt})_4$  with 1 equiv. of  $\text{edbpH}_2$  in *n*-hexane at room temperature or by substitution of two chlorine atoms in **1** by OEt groups [15]. Compound **3** was obtained by straightforward terminal OMe group replacement in  $[\text{Ti}_2(\mu\text{-OMe})_2(\text{edbp})_2(\text{OMe})_2]$  by the methyl group of  $\text{AlMe}_3$  in toluene [11].

### 3.1. Polymerization or/and cyclotrimerization of phenylacetylene

The titanium complexes  $[\text{Ti}(\text{edbp})\text{Cl}_2]$  (**1**) and  $[\text{Ti}_2(\mu\text{-OEt})_2(\text{edbp})_2(\text{OEt})_2]$  (**2**) (Scheme 1) were initially used as catalyst precursors for the polymerization of PA. Compound **1** presents no catalytic activity in reaction with phenylacetylene but monomer conversion was observed after addition of  $\text{AlR}_3$ . The reaction course depends on the alkyl group in  $\text{AlR}_3$ . The results are collected in Table 1. The monomer conversion is the highest for the  $1/\text{Al}(^i\text{Bu})_3$  catalyst but only cyclotrimerization products were detected (entry 3). When the catalytic reaction was performed using  $1/\text{AlEt}_3$  (entry 2) formation of *trans*-PPA as main product was observed. The polymeric material thus formed had low  $M_n$  values (2200) and polydispersion index (PDI) 1.04. The  $1/\text{AlMe}_3$  catalytic system (entry



Scheme 1. The schematic structures of the titanium complexes **1–3** used as a precursor for phenylacetylene polymerization.

Table 1  
Oligo- and polymerization of PA catalyzed by **1**/AlR<sub>3</sub><sup>a</sup> (R = Me, Et, <sup>i</sup>Bu)

Entry	Cocatalyst	Conversion (%)	Selectivity (%)		<i>M<sub>n</sub></i>	PDI
			Cyclotrimers <sup>b</sup>	Polymer		
1	AlMe <sub>3</sub>	42	18	82	4000	1.20
2	AlEt <sub>3</sub>	96	2	98	2200	1.04
3	Al <sup>i</sup> Bu <sub>3</sub>	100 <sup>c</sup>	100	–	–	–

<sup>a</sup> Reaction conditions: [Ti]/[Al] = 1/3, [Ti]/[PA] = 1/50, *n*-hexane, room temperature, reaction time = 20 min.

<sup>b</sup> 1,3,5- and 1,2,4-triphenylbenzene.

<sup>c</sup> Reaction was completed in 5 min.

**1**) under similar conditions is less active (42% monomer conversion). The PPA polymer has mainly *trans* geometry, as revealed by the NMR analysis and contains 18% of the cyclotrimerization products. Polymers formed by **2**/AlEt<sub>3</sub>, which was employed to compare the difference in activity of dimeric **2** with monomeric **1**, possesses higher polydispersion index (PDI values 2.5) but high molecular weight (*M<sub>n</sub>* ca.  $13 \times 10^3$ ). Stereoselectivity of the catalyst based on **2** was lower than for **1** because the polymer was a mixture of *cis* and *trans* stereoisomers of polyphenylacetylenes. Unfortunately,

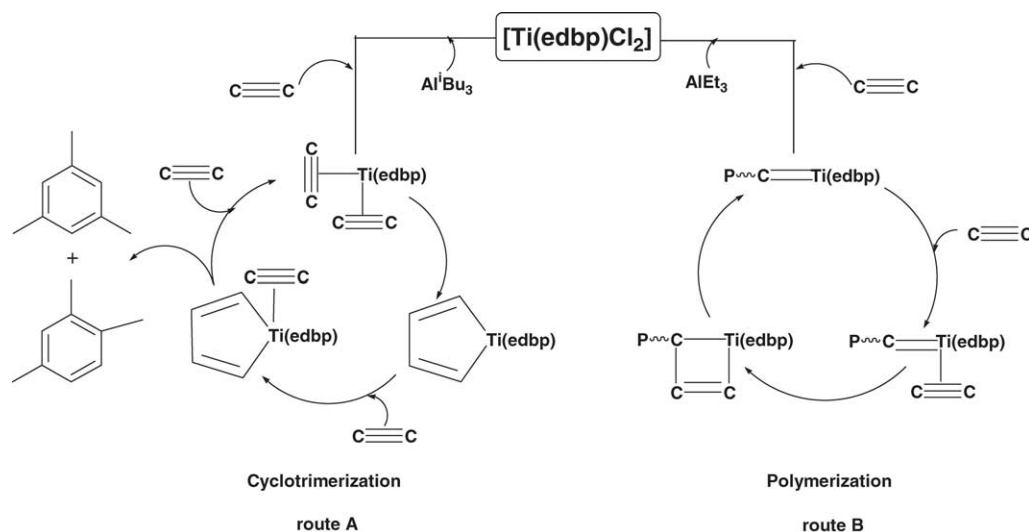
the <sup>1</sup>H NMR signals are too broad to determine the correct ratio of both isomers.

The catalytic behavior of the titanium dimer **3** containing terminal methyl groups (Scheme 1) in the absence of cocatalyst was then investigated. This compound was unable to promote polymerization of phenylacetylene, only cyclotrimerization products (10% conversion) were formed.

### 3.2. The influence of cocatalysts on product formation

The catalytic reactions were examined using different AlR<sub>3</sub> (R = Me, Et, <sup>i</sup>Bu) species as cocatalysts. When **1**/AlEt<sub>3</sub> was employed as a catalyst the high activity and selective formation of *trans*-PPA was observed (Table 1, entry 2). Activation of **1** by Al<sup>i</sup>Bu<sub>3</sub> improved catalytic activity (monomer consumption was faster, 100% conversion of PA) but only cyclotrimerization products were obtained. Instead, reaction of **1**/AlMe<sub>3</sub> with PA gives the mixture of *trans*-PPA polymer and cyclotrimers product (Table 1, entry 1).

From the data presented in Table 1 and from NMR studies the polymerization and cyclotrimerization processes are likely to follow the course described in Scheme 2. The



Scheme 2. The mechanism proposed for cyclotrimerization and polymerization of phenylacetylene by **1**/AlR<sub>3</sub> system.

Table 2  
The effect of cocatalysts molar ratio on PA conversion for **1**/AlEt<sub>3</sub><sup>a</sup>

Entry	Cocatalyst	Cocatalyst molar ratio [Ti]/[Al]	Conversion (%)
1	AlEt <sub>3</sub>	1/2	90
2	AlEt <sub>3</sub>	1/3	96
3	AlEt <sub>3</sub>	1/4	81
4	AlEt <sub>3</sub>	1/10	52

<sup>a</sup> Reaction conditions: [Ti]/[PA] = 1/50, *n*-hexane, room temperature, reaction time = 20 min.

Table 3  
The effect of solvent and temperature on PA conversion catalyzed by **1**/AlR<sub>3</sub><sup>a</sup> (R = Me, Et, <sup>i</sup>Bu)

Entry	Cocatalyst	Solvent	Temperature (°C)	Conversion (%)
1	AlMe <sub>3</sub>	<i>n</i> -Hexane	25	42
	AlMe <sub>3</sub>	<i>n</i> -Hexane	0	25
	AlMe <sub>3</sub>	thf	25	20
	AlMe <sub>3</sub>	thf	0	–
2	AlEt <sub>3</sub>	<i>n</i> -Hexane	25	96
	AlEt <sub>3</sub>	<i>n</i> -Hexane	0	80
	AlEt <sub>3</sub>	thf	25	62
	AlEt <sub>3</sub>	thf	0	–
3	Al <sup>i</sup> Bu <sub>3</sub>	<i>n</i> -Hexane	25	100
	Al <sup>i</sup> Bu <sub>3</sub>	<i>n</i> -Hexane	0	95
	Al <sup>i</sup> Bu <sub>3</sub>	thf	25	73
	Al <sup>i</sup> Bu <sub>3</sub>	thf	0	–

<sup>a</sup> Reaction conditions: [Ti]/[PA] = 1/50, reaction time = 20 min.

*trans*-PPA polymer is formed in catalytic reaction of **1**/AlEt<sub>3</sub> or **2**/AlEt<sub>3</sub> with PA. The most probable is that these reaction courses proceeds via β-hydrogen elimination of ethyl group to give the hydride or carbene derivatives, which has been reported earlier [17]. In contrast to **1**/AlEt<sub>3</sub>, when AlMe<sub>3</sub> or Al<sup>i</sup>Bu<sub>3</sub> are added to catalytic system the transfer of alkyl groups from aluminium to titanium with formation of alkyl metalorganic intermediates seems to be the most likely reaction route. Similar, the titanium compound [Ti{1,1'-(2,2',3,3'-OC<sub>10</sub>H<sub>5</sub>SiPh<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>} obtained by Schaverien and co-workers [12] with two dibenzyl groups without cocatalyst forms only the cyclotrimerization products.

It is worth to notice that the PA conversion is depending on molar ratio of used trialkylaluminium species to titanium initiators as well as on temperature and solvent used. The best results were obtained when 3 equiv. of AlEt<sub>3</sub> were used in *n*-hexane for 1 equiv. of **1** in 25 °C (Tables 2 and 3).

#### 4. Conclusions

We have synthesized a series of titanium bis(phenolate) precursors which after activation by AlR<sub>3</sub> (R = Me, Et, <sup>i</sup>Bu) form efficient PA polymerization catalytic system. The selectivity of the polymerization products strongly depends on used titanium species and aluminium activators. Polymeriza-

tion of PA based on the **1**/AlEt<sub>3</sub> catalyst proceeds according to the route B with selective *trans*-PPA formation [9,18], while cyclotrimerization of PA with Al<sup>i</sup>Bu<sub>3</sub> follows the route A [19] (Scheme 2). Stereoselectivity of the catalyst based on **2** was lower because the polymer was a mixture of *cis* and *trans* stereoisomers. The compound **3** containing terminal methyl groups was unable to promote PA polymerization in absence of activators.

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#### References

- [1] D. Damato, T. Sone, M. Tabata, Y. Sadahivo, M.V. Russo, A. Furlani, *Macromolecules* 31 (1989) 8660.
- [2] Yu.P. Yampolskii, A.P. Korikov, V.P. Shantarovich, K. Nagai, D.B. Freeman, T. Masuda, M. Teraguchi, G. Kwak, *Macromolecules* 34 (2001) 1788.
- [3] J.L. Bredas, C. Adant, P. Tackx, A. Persoons, *Chem. Rev.* 94 (1994) 243.
- [4] B.R. Weinberger, E. Ehrenfreund, A. Pron, A.J. Heeger, A.G. Heeger, A.G. MacDiarmid, *J. Chem. Phys.* 72 (1980) 4749.
- [5] P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, V.V. Burlakov, V.B. Shur, *Angew. Chem. Int. Ed.* 42 (2003) 1414.
- [6] U. Rosenthal, P.M. Pellny, F.G. Kirchbauer, V.V. Burlakov, *Acc. Chem. Res.* 33 (2000) 119.
- [7] K. Mach, R. Gyepes, M. Horáček, L. Petrusová, J. Kubišta, *Collect. Czech. Chem.* 68 (2003) 1877.
- [8] P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, V.V. Burlakov, V.B. Shur, *Angew. Chem. Int. Ed.* 42 (2003) 1414.
- [9] A. Ohff, V.V. Burlakov, M. Rosenthal, *J. Mol. Catal. A* 108 (1969) 119.
- [10] G. Natta, G. Mazzanti, P. Corradini, *Atti. Acad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend.* 45 (1976) 348.
- [11] M. Kobyłka, L.B. Jerzykiewicz, J.T. Patton, S. Przybylak, P. Sobota, Józef Utko, in preparation.
- [12] A. Van der Linden, C.J. Schaverien, N. Meijboom, C. Ganterond, A.G. Orpen, *J. Am. Chem. Soc.* 117 (1995) 3008.
- [13] R.A. Himes, P.E. Fanwick, J.P. Rothwell, *Chem. Commun.* 18 (2003).
- [14] E.S. Johnson, G.J. Balaich, P.E. Fanwick, J.P. Rothwell, *J. Am. Chem. Soc.* 119 (1997) 11086.
- [15] M. Kobyłka, L.B. Jerzykiewicz, P. Sobota, E. Zych, *Inorg. Chem.*, in preparation.
- [16] M. Tabata, T. Sone, Y. Sadahivo, *Macromol. Chem. Phys.* 200 (1999) 265.
- [17] F. Basuli, B.C. Bailey, J. Tomaszewski, J.C. Huffman, D.J. Mindiola, *J. Am. Chem. Soc.* 125 (2003) 6052.
- [18] T.C. Clarke, C.S. Yannoni, T.J. Katz, *J. Am. Chem. Soc.* 105 (1983) 7787.
- [19] E. Solari, C. Floriani, K. Schenk, A. Chiesi-Villa, C. Rizzoli, M. Rosi, A. Sgamellotti, *Inorg. Chem.* 33 (1994) 2018.