

# Cyclotrimerization of phenylacetylene and living polymerization of *tert*-butylacetylene by $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ –Lewis acid systems

Renata Matusiak, Antoni Keller\*

Faculty of Chemistry, Institute of Chemistry, University of Wrocław, Joliot-Curie 14, PL-50-383 Wrocław, Poland

Received 28 June 2002; received in revised form 13 September 2002; accepted 17 September 2002

## Abstract

$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ -LA catalysts (LA =  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{EtAlCl}_2$ ) induce monosubstituted acetylene (phenylacetylene and *tert*-butylacetylene) to cyclotrimerize and/or to polymerize. The catalytic ability of these catalyst as well as the structure of polymers formed strongly depends on the Lewis acid and solvent. The systems with  $\text{TiCl}_4$  and  $\text{GeCl}_4$  trimerize phenylacetylene with high selectivity. The system with  $\text{TiCl}_4$  also cyclotrimerizes *tert*-butylacetylene, but  $\text{SnCl}_4$  and  $\text{GeCl}_4$  systems polymerize *tert*-butylacetylene with 100% conversion. In the latter system the polymerization of *tert*-butylacetylene follows a living mechanism.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Acetate; Acetylenes; Cyclotrimerization; Dimolybdenum; Polymerization

## 1. Introduction

Metathesis polymerization of substituted acetylenes attracts much interest as a method for the preparation of polymers offering useful applications, for example as conducting [1–3] or non-linear optical materials [3–5]. Most of transition metals which are metathesis catalysts (mainly Mo and W but also Rh, Ta and Nb) induce polymerization of a variety of substituted acetylenes, yielding polymers with alternating double bonds in the main chain [6–8]. Recently, we investigated polymerization of monosubstituted acetylenes by  $M(\text{NO})_2(\text{O}_2\text{CR})_2$ –Lewis acid ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) catalysts [9,10]. These catalysts induced these acetylenes to polymerize and the kind of the used Lewis acid used, as well as of the sol-

vent, depends on the conversion ratios, selectivity and structure of the polymers. Reaction of the catalyst precursor with Lewis acid caused that free coordination sites were reached for formation of the carbene catalyst. The catalytic ability of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ –Lewis acid systems in polymerization of acetylenes may appear to be interesting. The dimolybdenum complexes with a quadruple Mo–Mo bond are known as effective catalyst or precatalyst for many catalytic reactions.  $\text{Mo}_2(\text{O}_2\text{CR})_4$  on silica and alumina were used as catalysts for propene metathesis [11,12]. In the presence of aluminum, titanium and zirconium alkoxides they are good catalyst for alkyne metathesis [13].  $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4\text{-Al}_2\text{O}_3$  and/or  $\text{SiO}_2$  metathesizes hex-1-ene and also polymerizes ethylene [14,15]. In the presence of  $\text{EtAlCl}_2$ , the ROMP reaction is catalyzed by the complexes  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  and  $\text{K}_4[\text{Mo}_2\text{Cl}_8]$  [16],  $(\text{Et}_4\text{N})_2[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Br}_4]$  and  $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{MeCN})_n](\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$  [17],  $[\text{Mo}_2(\mu\text{-(-)-ment})_2(\text{MeCN})_n](\text{BF}_4)_2$  [18],  $[\text{Mo}_2(\text{MeCN})_8](\text{BF}_4)_2$ ,

\* Corresponding author. Tel.: +48-71-229281;

fax: +48-71-3282348.

E-mail address: akeller@wchuwr.chem.uni.wroc.pl (A. Keller).

$[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{MeCN})_6](\text{BF}_4)_2$  and  $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{MeCN})_6](\text{BF}_4)_2\text{-SiO}_2$  [19] and  $[\text{Mo}_2\{\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2\}(\text{men})_x](\text{BF}_4)_2$  ( $n = 2\text{--}8$ ) [20].  $\text{Mo}_2(\text{O}_2\text{-CCF}_3)_4$  was found to polymerize 1-methylnorbornene in the absence of cocatalyst [16]. The dimolybdenum(II,II) complexes  $[\text{Mo}_2(\text{MeCN})_8](\text{BF}_4)_2$  and  $[\text{Mo}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{MeCN})_n](\text{BF}_4)_2$  were also found to be efficient catalyst for the cationic polymerization of cyclopentadiene and dicyclopentadiene [21]. Our goal was to obtain information about the catalytic activity of  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-LA}$  systems (LA =  $\text{EtAlCl}_2$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{GeCl}_4$ ) in reaction with monosubstituted acetylenes.

## 2. Experimental

### 2.1. General data

All the experiments were carried out either under argon atmosphere using Schlenk techniques or in vacuum-line systems. Reagents were purified by standard methods. Solvents were distilled under argon using appropriate drying agents.  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  was prepared according to the published method [22]. The IR spectra were recorded using a Nicolet Impact 400 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured at room temperature using a Bruker 300 spectrometer.

### 2.2. Cyclotrimerization and/or polymerization reactions

A standard cyclotrimerization and/or polymerization procedure was as follow: (a) for binary cata-

lysts ( $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-MCl}_4$ ;  $M = \text{Ti, Sn, Ge}$ ): to the solution of complex (25 mM) with the monomer (phenylacetylene or *tert*-butylacetylene) and internal standard the appropriate solution of  $\text{MCl}_4$  was added, (b) for ternary catalysts ( $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-PA-MCl}_4$ ): to the solution of complex (25 mM) with phenylacetylene and internal standard the solution of  $\text{MCl}_4$  and next norbornene were added. These reactions were quenched when adding a small amount of methanol. The formed polymers were isolated by precipitation in methanol; other reaction products (cyclotrimers and dimers) were isolated from the remaining solution. Monomer conversion and yields of cyclotrimers and dimers 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 ( $\bar{M}_w$  and  $\bar{M}_n$ , respectively) were determined by gel permeation chromatography (GPC; HPLC-HP 1090 II with DAD-Uv/Vis and IR detector HP 1047A) using polystyrene calibration.

## 3. Results and discussion

### 3.1. Cyclotrimerization or/and polymerization of phenylacetylene by $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-Lewis acid}$

#### 3.1.1. The effect of Lewis acid

The complex  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$  presents no catalytic activity in reaction with phenyl- and other acetylenes, but after addition of Lewis acid to the solution of this complex and the terminal acetylene, conversion of the monomer was observed. Table 1 shows the effect of Lewis acid (LA) on cyclotrimerization or/and

Table 1

The effect of Lewis acid on cyclotrimerization or/and polymerization of phenylacetylene (PA) by  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4\text{-Lewis acid}$  (LA) catalysts<sup>a</sup>

LA	Conversion (%)	Selectivity (%)		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Structure of polymer <sup>c</sup>
		Cyclotrimers	Polymer <sup>b</sup>			
$\text{TiCl}_4$	98.7	95.7	3.6	0.91	2.34	<i>trans</i> -Cisoidal
$\text{SnCl}_4$	86.5	48.8	51.2	5.10	2.16	<i>trans</i> -Cisoidal
$\text{GeCl}_4$	82.0	93.4	5.9	13.21	1.72	<i>cis</i> -Transoidal
$\text{EtAlCl}_2^d$	100	94.2	5.0	2.02	1.20	<i>trans</i> -Cisoidal

<sup>a</sup> Reaction conditions:  $[\text{Mo}_2]/[\text{LA}] = 1/2$ ,  $[\text{Mo}_2]/[\text{FA}] = 1/100$ ,  $\text{CH}_2\text{Cl}_2$ , room temperature,  $t_r = 24$  h.

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

<sup>c</sup> Characterized by IR and  $^1\text{H}$  NMR spectra [23,24].

<sup>d</sup>  $[\text{Mo}_2]/[\text{Al}] = 1/6$ ,  $\text{PhCl}$ ,  $t_r = 15$  min.

polymerization of phenylacetylene (PA) examined in  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ –Lewis acid systems in  $\text{CH}_2\text{Cl}_2$ . The monomer conversion is highest for the system with  $\text{EtAlCl}_2$  and its activity is also the highest (100% conversion at 15 min). This system is a highly stereoselective catalyst for cyclotrimerization (94.2%). The systems with  $\text{TiCl}_4$  and  $\text{GeCl}_4$  as Lewis acids are also highly stereoselective in the cyclotrimerization reaction (95.7% and 93.4%, respectively). On the other hand, stereoselectivity of  $\text{SnCl}_4$  system is low; for cyclotrimerization—48.8% and for polymerization—51.2% (conversion 86.5%). In this system only cyclotrimers and polymer insoluble in methanol ( $\bar{M}_n = 5.1 \cdot 10^3$ ,  $\bar{M}_w/\bar{M}_n = 2.16$ ) were formed, while in the others formation of dimer (under 0.8%) was observed.

### 3.1.2. The effect of solvent

Activities of the systems tested strongly depend on the applied solvent. The effect of solvent on conversion of phenylacetylene, selectivity, molecular weight and structure of formed polymer was examined in  $\text{CH}_2\text{Cl}_2$ ,  $\text{PhCl}$ , toluene and  $\text{CCl}_4$  and the results are shown in Table 2. The cyclotrimerization reaction of phenylacetylene was never selective in 100% in the systems tested. It was always accompanied (less or more) by polymerization reaction. The most effective catalyst of cyclotrimerization is the system with

$\text{TiCl}_4$  in  $\text{CH}_2\text{Cl}_2$  (98.7% conversion and selectivity 95.7%); this system is also highly selective in other solvents used (93.1–89.2%). Similar selectivity, independent on the solvent, was found for the system with  $\text{GeCl}_4$  (93.4–91.1%). In all the examined systems, the conversion of phenylacetylene increased as the solvent polarity increased. In the case of  $\text{TiCl}_4$  and  $\text{GeCl}_4$  systems, selectivity of cyclotrimerization reaction increased, too. For the polymerization reaction, in general, the polymerization rate was reduced as the solvent polarity increased [8,25]. In the both latter systems such trends were observed, too. In the system with  $\text{SnCl}_4$  the highest monomer conversion was in  $\text{CH}_2\text{Cl}_2$  solution (86.5%; 55.2% after 3.5 h). In other solvents ( $\text{PhCl}$ , toluene and  $\text{CCl}_4$ ), conversion was about 60%, however such conversion in toluene was reached even after 3.5 h. The system in toluene exhibits the highest selectivity, but in polymerization reaction (71.8%). The kind of useful solvents depends on the structure of formed (even in small amounts) polymers (Table 2). In the  $\text{TiCl}_4$  system, only in  $\text{CCl}_4$  solution the *cis*-transoidal polymer is formed (in other *trans*-cisoidal), while in the  $\text{SnCl}_4$  system only the *trans*-cisoidal polymer was detected in  $\text{CH}_2\text{Cl}_2$  solution. In the system with  $\text{GeCl}_4$  the *cis*-transoidal polymers were obtained independent on the applied solvents.

Table 2

The effect of solvent on cyclotrimerization or/and polymerization of phenylacetylene (PA) examined with  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$ - $\text{MCl}_4$  catalyst<sup>a</sup>

M	Solvent	Conversion (%)	Selectivity (%)		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Structure of polymer <sup>c</sup>
			Cyclotrimers	Polymer <sup>b</sup>			
Ti	$\text{CH}_2\text{Cl}_2$	98.7	95.7	3.6	0.91	2.34	<i>trans</i> -Cisoidal
	$\text{PhCl}$	89.2	93.1	6.1	0.68	1.79	<i>trans</i> -Cisoidal
	Toluene	70.0	91.0	8.2	0.61	1.44	<i>trans</i> -Cisoidal
	$\text{CCl}_4$	19.43	89.2	10.1	0.94	2.14	<i>cis</i> -Transoidal
Sn	$\text{CH}_2\text{Cl}_2$	86.5 (55.2) <sup>d</sup>	48.8	51.2	5.10	2.16	<i>trans</i> -Cisoidal
	$\text{PhCl}$	66.0	63.1	36.2	1.91	4.36	<i>cis</i> -Transoidal
	Toluene	61.3 (60.0) <sup>d</sup>	28.2	71.8	10.10	1.91	<i>cis</i> -Transoidal
	$\text{CCl}_4$	60.4	55.7	34.4	3.23	4.09	<i>cis</i> -Transoidal
Ge	$\text{CH}_2\text{Cl}_2$	82.0	93.4	5.9	13.20	1.72	<i>cis</i> -Transoidal
	$\text{PhCl}$	70.4	93.1	6.1	11.54	1.91	<i>cis</i> -Transoidal
	Toluene	66.0	91.1	8.1	11.11	1.90	<i>cis</i> -Transoidal

<sup>a</sup> Reaction conditions:  $[\text{Mo}_2]/[\text{LA}] = 1/2$ ,  $[\text{Mo}_2]/[\text{FA}] = 1/100$ , room temperature,  $t_r = 24$  h.

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

<sup>c</sup> Characterized by IR and  $^1\text{H}$  NMR spectra [23,24].

<sup>d</sup> After  $t_r = 3.5$  h.

Table 3

The effect of the  $[\text{Mo}_2]/[\text{LA}]$  ratio on cyclotrimerization or/and polymerization of phenylacetylene (PA) by  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4\text{-MCl}_4$  catalyst<sup>d</sup>

LA	$[\text{Mo}_2]/[\text{LA}]$	Conversion (%)	Selectivity (%)		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Structure of polymer <sup>c</sup>
			Cyclotrimers	Polymer <sup>b</sup>			
SnCl <sub>4</sub> <sup>d</sup>	1/1	65.0	61.5	38.5	2.3	3.35	Trans
	1/2	86.5	48.8	51.2	5.1	2.16	Trans
	1/3	60.5	46.1	53.9	5.9	2.01	Trans
TiCl <sub>4</sub> <sup>e</sup>	1/1	70.7	92.6	6.9	0.75	1.50	Trans
	1/2	89.2	91.0	8.2	0.68	1.79	Trans
	1/3	52.9	90.1	8.	0.60	1.80	Trans

<sup>a</sup> Reaction conditions:  $[\text{Mo}_2]/[\text{FA}] = 1/100$ , room temperature,  $t_r = 24$  h.<sup>b</sup> 1,3,5- and 1,2,4-isomers.<sup>c</sup> Characterized by IR and <sup>1</sup>H NMR spectra [23,24].<sup>d</sup> In CH<sub>2</sub>Cl<sub>2</sub>.<sup>e</sup> In PhCl.

### 3.1.3. The effect of the complex/Lewis acid molar ratio

The effect of the complex/Lewis acid molar ratio ( $[\text{Mo}_2]/[\text{LA}]$ ) on the activity in cyclotrimerization or/and polymerization of phenylacetylene was examined for SnCl<sub>4</sub> (in CH<sub>2</sub>Cl<sub>2</sub>) and TiCl<sub>4</sub> (in PhCl) as Lewis acids, for 1/1, 1/2 and 1/3 molar ratios (Table 3). Both these systems achieved the highest activity for  $[\text{Mo}_2]/[\text{LA}] = 1/2$ . The  $[\text{Mo}_2]/[\text{LA}]$  ratio also had an effect on the reaction selectivity—the cyclotrimerization ratio was reduced (polymerization ratio increased) as the concentration of Lewis acid increased.

### 3.2. Living polymerization of *tert*-butylacetylene

The system  $\text{Mo}(\text{O}_2\text{CCH}_3)_4\text{-MCl}_4$  in reaction with *tert*-butylacetylene is more active than with phenylacetylene (Table 4). The complete monomer conver-

sion was obtained after 30 min for GeCl<sub>4</sub> and after 90 min for SnCl<sub>4</sub> and TiCl<sub>4</sub> systems. After these times, the yields of polymer was 100% for the system with GeCl<sub>4</sub> and SnCl<sub>4</sub> ( $\bar{M}_n = 6.83 \cdot 10^5$ ,  $\bar{M}_w/\bar{M}_n = 1.50$  and  $\bar{M}_n = 4.19 \cdot 10^5$ ,  $\bar{M}_w/\bar{M}_n = 1.74$ , respectively) but for the TiCl<sub>4</sub> system it was only 24% ( $\bar{M}_n = 6.12 \cdot 10^5$ ,  $\bar{M}_w/\bar{M}_n = 1.45$ ) and the major product was 1,3,5-tri-*tert*-butylbenzene (74%).

Living polymerization of substituted acetylenes was achieved by using ternary catalysts based on MoOCl<sub>4</sub> [27–30], Schrock carbenes [31–34] and rhodium complexes [35]. Recently, it was found that dinitrosylmolybdenum complexes also result in living polymerization of *tert*-butylacetylene [36]. The investigation of polymerization of *tert*-butylacetylene by  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4\text{-GeCl}_4$  catalyst indicates that this reaction proceeds through a living mechanism. The reaction was carried out in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Fig. 1 shows the number average molecular

Table 4

The effect of Lewis acid on polymerization or/and cyclotrimerization of *tert*-butylacetylene (t-BA) by  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4\text{-MCl}_4$  catalyst in CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

LA	$t_r$	Conversion	Selectivity (%)		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	% <i>cis</i> <sup>b</sup>
			Cyclotrimer	Polymer			
GeCl <sub>4</sub>	30	100		100	6.83	1.48	50
SnCl <sub>4</sub>	90	100		100	4.19	1.74	43
TiCl <sub>4</sub>	90	100	74 <sup>c</sup>	24	6.12	1.45	37

<sup>a</sup> Reaction conditions:  $[\text{Mo}_2]/\text{LA} = 1/2$ ,  $[\text{Mo}_2]/[t\text{-BA}] = 1/50$ , room temperature.<sup>b</sup> Determined by <sup>13</sup>C NMR [26].<sup>c</sup> Only 1,3,5-isomer.

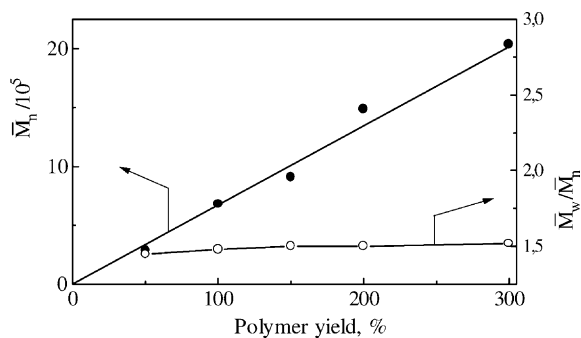


Fig. 1. The dependence of number average molecular weight ( $\bar{M}_n$ ) vs. polymer yield for polymerization of *tert*-butylacetylene by  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-GeCl}_4$  (1:2) (polymerized in  $\text{CH}_2\text{Cl}_2$  at room temperature;  $[\text{Mo}_2] = 25 \text{ mM}$ ;  $[\text{t-BA}]_0 = 1.25 \text{ M}$ ).

weight ( $\bar{M}_w$ ) and the polydispersity ratio ( $\bar{M}_w/\bar{M}_n$ ) versus the yield of poly-*tert*-butylacetylene. Monomer feeds were supplied thrice repeatedly. The  $\bar{M}_n$  of the polymer increased in the direct proportion to the polymer yield. Meanwhile, the polydispersity ratios varied from 1.45 to 1.52. The initiation rate lower than the rate of propagation leads to polymers with broad polydispersity [37]. Fig. 2 presents the number average molecular weight versus  $[\text{monomer}]/[\text{initiator}]$  ratio ( $[\text{M}]/[\text{I}]$ ) for the same polymer, again giving a linear relationship. These results clearly indicate that the polymerization reaction of *tert*-butylacetylene using  $\text{Mo}(\text{O}_2\text{CCH}_3)_4\text{-GeCl}_4$  system is a living polymerization.

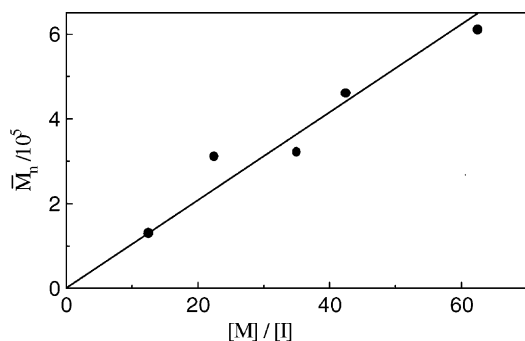
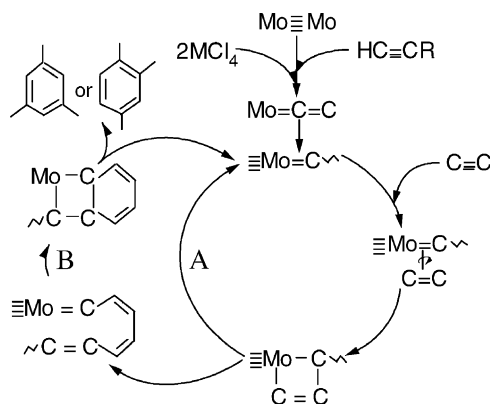


Fig. 2. The effect of the monomer/initiator ratio ( $[\text{M}]/[\text{I}]$ ) on number average molecular weight ( $\bar{M}_n$ ) for the polymerization of *tert*-butylacetylene by  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-GeCl}_4$  (1:2) catalyst ( $\text{CH}_2\text{Cl}_2$ , room temperature, 100% conversion).

### 3.3. Mechanism of the cyclotrimerization or/and polymerization of phenylacetylene and *tert*-butylacetylene

Many transition metal based catalyst catalyze polymerization of acetylenes. These catalysts are considered to promote polymerization by a metathesis mechanism [23,38]. Depending on the system, the product may be linear polymer only, cyclic trimer only, or a mixture of linear polymer and cyclic trimer [6–8]. Masuda [8] proposed a mechanism of polymerization (by metal carbene) and cyclotrimerization (by metallacyclopentadiene) of acetylenes for systems with metal chloride-based catalyst. When the catalysts are metal carbenes, cyclic trimers are formed only through the cis-cisoidal-induced backbiting reaction and so long as monomer adds in the same direction to the propagating metal carbene complex, there is good chance of forming linear polymer, so that one might have expected backbiting reactions to yield only the 1,3,5-substituted cyclic trimer, but if a molecule of monomer adds in reverse fashion, there is a strong probability of backbiting to form 1,2,4-isomers [7,37]. As is follows in Tables 1–4, in the systems under investigation phenylacetylene and *tert*-butylacetylene undergo cyclotrimerization and/or polymerization, which reaction prevails depends on the Lewis acid and the solvent. We proposed the carbene mechanism for the both reactions (Scheme 1). The reactions of precursor catalysts with Lewis acid causes that free coordination sites are reached.



Scheme 1. The mechanism proposed for cyclotrimerization and polymerization of phenylacetylene and *tert*-butylacetylene by  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4\text{-Lewis acid}$  systems.

Table 5  
ROMP<sup>a</sup> of norbornene (NB) by ternary Mo<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>-LA-PA catalyst<sup>b</sup>

LA	Conversion (%)	Selectivity (%)		$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
		Linear oligomer	Polymer		
SnCl <sub>4</sub>	36	91.7	8.3	4.36	4.83
GeCl <sub>4</sub>	39	86.7	13.3	1.25	1.78
TiCl <sub>4</sub>	86	89.5	10.5	1.02	1.51

<sup>a</sup> Characterized by IR [42,43] and <sup>13</sup>C NMR [43–45] spectra.

<sup>b</sup> Reaction conditions: [Mo<sub>2</sub>]/LA/PA = 1/2/2, [Mo<sub>2</sub>]/[NB] = 1/100, toluene, room temperature,  $t_r$  = 24 h.

- (i) When the Lewis acid was EtAlCl<sub>2</sub>, the carbene catalyst was formed by  $\alpha$ -hydrogen elimination mechanism [39]. The carbene complex formed in such system is also active in ROMP of 1-methylnorbornene [16] and in metathesis of pent-1-ene; after 30 min. 20% of pen-1-ene was converted into ethylene and oct-4-ene (reaction conditions: [Mo<sub>2</sub>] = 25 mM, [Mo<sub>2</sub>]/[Al] = 1/6, [Mo<sub>2</sub>]/[pent-1-ene] = 1/100, room temperature).
- (ii) When the Lewis acid was MCl<sub>4</sub> (added in the presence of terminal acetylene) it coordinated to the metal forming vinylidene [40,41] and next carbene complex. The vinylidene complex is also active in the ROMP of norbornene (Table 5).

The polymerization proceeds on the route A, while cyclotrimerization on the route B (Scheme 1), i.e. by backbiting of propagating carbenes in cis-cisoidal grown chain to form 1,3,5- or 1,2,4- three substituted benzene derivatives, depending on the manner in which monomer adds (in the same direction or in reverse fashion) to the propagating carbene complex. When the free coordination sites are blocked by, for instance, chlorines of Lewis acids, inactive adducts can be formed and reaction is terminated (Table 2, e.g.  $M = \text{Sn}$ ). This step is also dependent on the kind of solvent (differences in solubilities of catalysts and their coordinational abilities), as well as on the presence of bulky groups on the monomer or, for instance, solvent coordinated to the Lewis acid metal. The presence of bulky group on the monomer also causes that the tendency towards backbiting is markedly reduced (the system with TiCl<sub>4</sub> cyclotrimerizes *tert*-butylacetylene, but only 1,3,5-isomer was formed, Table 4) or totally eliminated (systems with SnCl<sub>4</sub> and GeCl<sub>4</sub> give high polymer; MW ~ 10<sup>6</sup>, in the latter system the reaction is a living polymerization, Table 4).

Reaction of the precursor complex with Lewis acids does not result in breaking the multiple Mo–Mo bond in the precursor complex. The IR spectra of Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>-MCl<sub>4</sub> (1:2) adducts contain prominent carboxylate vibrations (e.g. for  $M = \text{Sn}$ ;  $\nu_{\text{as}}(\text{OCO})$  at 1545, 1515 and 1495 cm<sup>-1</sup> and  $\nu_{\text{s}}(\text{OCO})$  at 1443, 1415 and 1404 cm<sup>-1</sup>) with the value  $\Delta\nu(\text{OCO})$  ( $\nu_{\text{as}} - \nu_{\text{s}} = 76 \text{ cm}^{-1}$ , calculated without frequencies at 1545 and 1404 cm<sup>-1</sup>) in keeping with that recorded for complexes in which the acetate ligand bridges short  $M$ – $M$  bonds [46] (e.g.  $\Delta\nu(\text{OCO}) = 79 \text{ cm}^{-1}$  for Mo<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>;  $\nu_{\text{as}}(\text{OCO}) = 1515, 1495 \text{ cm}^{-1}$  and  $\nu_{\text{s}}(\text{OCO}) = 1440, 1412 \text{ cm}^{-1}$  [47]). The frequencies at 1545 and 1404 cm<sup>-1</sup> we assigned as the vibrations of acetate ligands bridged Mo and Lewis acid metal ( $\Delta\nu(\text{OCO}) = 141 \text{ cm}^{-1}$ ).

## Acknowledgements

Financial support from the Polish State Committee for Scientific Research (grant no. PBZ–KBN 15/09/T09/99/01d) is gratefully acknowledged.

## References

- [1] I.V. Krivoschel, M. Skoroboatov, Polyacetylene and Polyarylenes: Synthesis and Conducting Properties, Gordon and Breach Science, New York, 1991.
- [2] H.G. Kiess (Ed.), Conjugated Conducting Polymers, Springer, Berlin, 1992.
- [3] T. Kobayashi, T. Hattori, A. Terasaki, K. Kurokawa, in: P.N. Prasad, D.R. Ulrich (Eds.), Nonlinear Optical and Electroactive Polymers, Plenum Press, New York, 1987, p. 137.
- [4] J. Zyss, D.S. Chemla, in: D.S. Chemla, J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, vol. 1, Academic Press, Orlando, FL, 1987, p. 23.

- [5] P.N. Prasad, D.J. Williams, in: *Introduction in Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991, p. 132.
- [6] K.J. Ivin, in: *Olefin Metathesis*, Academic Press, London, 1983.
- [7] K.J. Ivin, J.C. Mol, in: *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, London, Boston, New York, Sydney, Tokyo, Toronto, 1997.
- [8] T. Masuda, T. Higashimura, in: J.P. Kennedy (Eds.), *Synthesis, Mechanism, Polymer Drugs, Polyacetylenes with Substituents: Their Synthesis and Properties*, Springer, Berlin, Heidelberg, *Adv. Polym. Sci.* 81 (1987) 121.
- [9] A. Keller, R. Matusiak, *J. Mol. Catal.* 142 (1999) 317.
- [10] A. Keller, R. Matusiak, *J. Mol. Catal.* 142 (1999) 127.
- [11] J. Smith, W. Mowat, D.A. Whan, E.A.V. Ebsworth, *J. Chem. Soc. Dalton Trans.* 16 (1974) 1742.
- [12] Q. Zhuang, A. Fukuoka, T. Fujimoto, K. Tanaka, M. Ichikawa, *J. Chem. Soc. Chem. Commun.* 11 (1991) 745.
- [13] S.P. Diefenbach, US Patent 4,704,577 (1987).
- [14] J.R. Candlin, Germany Patent 221 3947 (1973).
- [15] J.P. Candlin, H. Thomas, *Adv. Chem. Ser.* 132 (1974) 212.
- [16] J.G. Hamilton, K.J. Ivin, M. McCann, J.J. Rooney, *Macromol. Chem.* 186 (1985) 1477.
- [17] M. McCann, P. Guinan, *Polyhedron* 10 (1991) 2283.
- [18] P. Guinan, M. McCann, *Polyhedron* 11 (1992) 205.
- [19] M. McCann, E. Mac Giolla Coda, K. Maddock, *J. Chem. Soc. Dalton Trans.* (9) (1994) 1489.
- [20] E. Whelan, M. Devereux, M. McCann, V. McKee, *Chem. Commun.* 5 (1997) 427.
- [21] M. McCann, E. MacGiolla Coda, *J. Mol. Catal.* 109 (1996) 99.
- [22] T.A. Stephenson, E. Bannister, G. Milkinson, *J. Chem. Soc.* 7 (1964) 2538.
- [23] C. Simionescu, V. Percec, S. Dumitresku, *J. Polym. Sci., Polym. Chem. Ed.* 15 (1977) 2497.
- [24] C. Simionescu, V. Percec, *J. Polym. Sci., Polym. Chem. Ed.* 18 (1980) 147.
- [25] T. Masuda, N. Sasaki, T. Higashimura, *Macromolecules* 8 (1975) 717.
- [26] T. Masuda, H. Izumikawa, Y. Misumi, T. Higashimura, *Macromolecules* 29 (1996) 1167.
- [27] T. Yoshimura, T. Masuda, T. Higashimura, *Macromolecules* 21 (1988) 1899.
- [28] T. Mizumoto, T. Masuda, T. Higashimura, *Macromol. Chem. Phys.* 196 (1995) 1769.
- [29] T. Masuda, H. Izumikawa, Y. Misumi, T. Higashimura, *Macromolecules* 29 (1996) 1167.
- [30] S. Hyano, T. Itoh, T. Masuda, *Polymer* 40 (1999) 4071.
- [31] H.H. Fox, R.R. Schrock, *Organometallics* 11 (1992) 2163.
- [32] H.H. Fox, M.O. Wolf, R. O'Dell, B.L. Lin, R.R. Schrock, M.S. Wrighton, *J. Am. Chem. Soc.* 116 (1994) 2827.
- [33] R.R. Schrock, S. Luo, N. Zanetti, H.H. Fox, *Organometallics* 13 (1994) 3396.
- [34] R.R. Schrock, S. Luo, J.C. Lee, N. Zanetti, M.W. Davis, *J. Am. Chem. Soc.* 118 (1996) 3883.
- [35] Y. Kishimoto, T. Miyatake, T. Ikariya, R. Noyori, *Macromolecules* 29 (1996) 5054.
- [36] A. Keller, R. Matusiak, *J. Mol. Catal.* 188 (2002) 17.
- [37] J.F. Kunzler, V. Percec, *Polym. Bull.* 18 (1987) .
- [38] T.J. Katz, T.H. Ho, N.-Y. Shih, Y.-c. Ying, I.W. Van Stuard, *J. Am. Chem. Soc.* 106 (1984) 2659.
- [39] R.H. Grubbs, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 8, Pergamon Press, New York, 1982, p. 499.
- [40] J.S. Filippo Jr., A.F. Aowinski, L.J. Romano, *J. Am. Chem. Soc.* 97 (1975) 1599.
- [41] S.I. Landon, P.M. Schulman, G.L. Geoffroy, *J. Am. Chem. Soc.* 107 (1985) 6739.
- [42] H. Balcar, M. Pacovská, *J. Mol. Catal.* 115 (1997) 101.
- [43] T.J. Katz, S.J. Lee, N. Acton, *Tetrahedron Lett.* 47 (1976) 4247.
- [44] C. Larroche, J.P. Laval, A. Lattes, M. Lconte, F. Quignard, J.M. Basset, *J. Org. Chem.* 47 (1982) 2019.
- [45] T. Steinhäusler, W.J. Koros, *J. Polym. Sci. Part B: Polym. Phys.* 24 (1997) .
- [46] G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227.
- [47] L. Dubicki, R.L. Martin, *Aust. J. Chem.* 22 (1969) 1571.