Metathesis polymerization of substituted acetylenes by Mo(NO)$_2$(O$_2$CR)$_2$–Lewis acid catalysts

A. Keller [*], R. Matusiak

Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland

Abstract

Mo(NO)$_2$(O$_2$CR)$_2$–Lewis acid catalysts (Lewis acid = TiCl$_4$, SnCl$_4$, EtAlCl$_2$; R = phenyl, methylvaleric, ethylhex-anoic) induce monosubstituted acetylenes (phenylacetylene, *tert*-butylacetylene) to polymerize. The catalytic ability of these catalyst strongly depends on the Lewis acid and solvent. The system with SnCl$_4$ in benzene is almost selective in polymerization of phenylacetylene (conversion: 60%, yield of polymer 56%) while in toluene cyclotrimers are the main products (conversion: 70%, yield of cyclotrimers: 69%). However, the TiCl$_4$ system trimerized phenylacetylene in PhCl solution (conversion: 76%, yield of cyclotrimers: 66.5%). The structure of obtained polymers and mechanisms of polymerization and cyclotrimerization reactions were determined. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metathesis polymerization of acetylenes offers useful applications as a method for the preparation of polymers. For example, poly-acetylene is the best-known conducting polymer, whose doped form exhibits metallic conductivity [1–3]. Other polyacetylenes with suitable substituents possess often better processibility and novel interesting properties. Various polyacetylenes with aromatic and related pendant groups have been prepared and studied [4–14]. The substituted acetylene that has been most often employed to study is probably phenylacetylene [15–27]. This monomer under-goes polymerization by thermal [28,29], radical [28–32], cationic [33,34], Ziegler-Natta [35–38] mechanism, and also by transition metal based catalysts [11,17,18,23,27,39–41]. The latter are considered to promote polymerization by a metathesis mechanism, similar to the metathesis catalysts (carbene complexes) [18,23,41–45]. The mechanism of polymerization of phenyl-acetylene and microstructure of its polymers strongly depends on the catalyst, thermal history of the polymerization reaction and often on the solvent [19,20,27,45]. No literature data on polymerization of acetylenes by nitrosyl molyb-denum complexes are available.

Here, we report the Mo(NO)$_2$(O$_2$CR)$_2$–Lewis acid systems which serve as effective catalysts in the polymerization or cyclotrimerization of monosubstituted acetylenes. The polymerization

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[*] Corresponding author. Tel.: +48-229281; E-mail: akeller@wchuwr.chem.uni.wroc.pl

and cyclotrimerization mechanism and structure of the polymerization products have also been investigated.

2. Experimental

All experiments were carried out under argon atmosphere using Schlenk techniques either in vacuum-line systems. Reagents were purified by standard methods. Solvents were distilled using appropriate drying agents under argon.

The IR spectra were recorded on a Nicolet Impact 400 spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured at room temperature on a Bruker 300 spectrometer. Tetramethylsilane was used as an internal standard. $Mo(NO)_2(acac)_2$ (acac = acetylacetone) [46], {$Mo(NO)_2(O$-i-$Pr)_2$}$_2$ [47] and $Mo(NO)_2(O_2CPh)_2$ [48] were prepared according to published procedures.

2.1. Synthesis of $Mo(NO)_2(O_2CR)_2$ where $R = CH_3(CH_2)_3(C_2H_5)CH$ (EH) and $(CH_3)_2CHCH_2$-CH_2 (MV)

New complexes of the type $Mo(NO)_2$-$(O_2CR)_2$ ($R = CH_3(CH_2)_3(C_2H_5)CH$ (EH); $(CH_3)_2CHCH_2CH_2$ (MV)) were synthesized in the same manner as described for this type complex where $R = Ph$ [48]. The complexes were characterized by IR and ^{1}H NMR spectroscopy and their purities were checked by elemental analyses:

2.1.1. $Mo(NO)_2(O_2CEH)_2$

IR (nujol mulls): ν_{NO} 1806 vs, 1688 vs cm^{-1}. ^{1}H NMR (in CD$_2$Cl$_2$): δ 2.44 (s, br, 2H; CO$_2$CH(CH$_2$CH$_3$)–); δ 1.66 (s, br, 4H; CO$_2$CH (CH_2CH$_3$)–); δ 1.33 (s, br, 12H; –(CH_2)$_3$CH$_3$); δ 0.95 (d, 12H; –CH(CH$_2$CH_3)(CH$_2$)$_3$CH_3) ppm. Anal.: Calc. for C$_{16}$H$_{30}$N$_2$MoO$_6$: C 43.44, H 6.84, N 6.33%. Found: C 43.15, H 6.98, N 6.12%.

2.1.2. $Mo(NO)_2(O_2CMV)_2$

IR (nujol mulls): ν_{NO} 1809 vs, 1680 vs cm^{-1}. ^{1}H NMR (in CD$_2$Cl$_2$): δ 2.20 (t, 4H;

CO$_2$CH_2CH$_2$–); δ 1.22–1.33 (m, 6H; –CH_2CH (CH$_3$)$_2$); δ 0.66 (d, 12H; –CH(CH_3)$_2$) ppm. Anal.: Calc. for C$_{12}$H$_{22}$N$_2$MoO$_6$: C 37.32, H 5.74, N 7.25%. Found: C 37.11, H5.90, N 7.04%.

2.2. Synthesis of $Mo(NO)_2(O$-i-$Pr)_2(MCl_4)_2$ and $Mo(NO)_2(O_2CR)_2(MCl_4)_2$ ($M = Ti$, Sn; $R = Ph$, EH, MV)

The CH$_2$Cl$_2$ solution of MCl$_4$ was added to CH$_2$Cl$_2$ solution of appropriate complex in molar ratio of 1:2. The yellow-brown precipitate was filtered off, washed with CH$_2$Cl$_2$ and hexane and dried in vacuo.

2.2.1. $Mo(NO)_2(O$-i-$Pr)_2(MCl_4)_2$

M = Ti. IR (nujol mulls): ν_{NO} 1809 vs, 1798 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 4.18 (br, 2H; –CH(CH$_3$)$_2$), δ 1.17 (br, 12H; –CH(CH_3)$_2$) ppm. Anal.: Calc. for C$_6$H$_{14}$N$_2$Cl$_8$MoO$_4$Ti$_2$: C 11.03, H 2.16, N 4.29, Cl 43.40%. Found: C 10.94, H 2.39, N 4.00, Cl 43.29%.

M = Sn. IR (nujol mulls): ν_{NO} 1802 vs, 1700 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 4.22 (br, 2H; –CH(CH$_3$)$_2$), δ 1.19 (br, 12H; –CH(CH_3)$_2$) ppm. Anal.: Calc. for C$_6$H$_{14}$N$_2$Cl$_8$MoO$_4$Sn$_2$: C 9.06, H 1.77, N 3.52, Cl 35.67%. Found: C 8.90, H 1.90, N 3.38, Cl 35.50%.

2.2.2. $Mo(NO)_2(O_2CR)_2$

R = Ph; M = Ti. IR (nujol mulls): ν_{NO} 1816 vs, 1699 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 8.09–7.50 (m, 4H, *ortho*-); δ 7.50–7.64 (m, 6H, *meta*-, *para*-) ppm. Anal.: Calc. for C$_{14}$H$_{10}$N$_2$Cl$_8$MoO$_6$Ti$_2$: C 21.63, H 1.38, N 3.60, Cl 36.48%. Found: C 21.41, H 1.42, N 3.39, Cl 36.39%.

R = Ph; M = Sn. IR (nujol mulls): ν_{NO} 1818 vs, 1701 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 7.95–8.45 (m, 4H, *ortho*-); δ 7.22–7.85 (m, 6H, *meta*-, *para*-) ppm. Anal.: Calc. for C$_{14}$H$_{10}$N$_2$Cl$_8$MoO$_6$Sn$_2$: C 18.29, H 1.10, N 3.05, Cl 30.85%. Found: C 18.10, H 1.17, N 2.89, Cl 30.75%.

R = EH; M = Ti. IR (nujol mulls): ν_{NO} 1834 vs, 1715 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 2.20–2.34 (m, 2H; CO$_2$*CH*(CH$_2$CH$_3$)–); δ 1.27–1.52 (m, 16H; CO$_2$CH(*CH$_2$*CH$_3$)-(*CH$_2$*)$_3$CH$_3$); δ 0.84–1.05 (m, 12H; CO$_2$CH-(CH$_2$*CH$_3$*)(CH$_2$)$_3$*CH$_3$*) ppm. Anal.: Calc. for C$_{16}$H$_{30}$N$_2$Cl$_8$MoO$_6$Ti$_2$: C 23.39, H 3.68, N 3.41, Cl 34.51%. Found: C 23.19, H 3.77, N 3.11, Cl 34.63%.

R = EH; M = Sn. IR (nujol mulls): ν_{NO} 1815 vs, 1707 vs cm^{-1}. ^{1}H NMR (in CD$_2$Cl$_2$): δ 2.35–2.75 (m, 2H; CO$_2$*CH*(CH$_2$CH$_3$)–); δ 1.63 (s, br, 8H; CO$_2$CH (*CH$_2$*CH$_3$)*CH$_2$*(CH$_2$)$_2$CH$_3$); δ 1.31 (s, br, 8H CO$_2$CH(CH$_2$CH$_3$)CH$_2$(*CH$_2$*)$_2$-CH$_3$); δ 0.75–1.05 (m, 12H; CO$_2$CH(CH$_2$-*CH$_3$*)(CH$_2$)$_3$*CH$_3$*) ppm. Anal.: Calc. for C$_{16}$-H$_{30}$N$_2$Cl$_8$MoO$_6$Sn$_2$: C 19.95, H 3.14, N 2.91, Cl 29.44%. Found: C 19.79, H 3.23, N 2.70, Cl 29.57%.

R = MV; M = Ti. IR (nujol mulls): ν_{NO} 1818 vs, 1715 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 2.25–2.44 (m, 4H; CO$_2$*CH$_2$*CH$_2$–); δ 1.42–1.54 (m, 6H; –*CH$_2$CH* (CH$_3$)$_2$); δ 0.75–1.05 (m, 12H; –CH(*CH$_3$*)$_2$) ppm. Anal.: Calc. for C$_{12}$H$_{22}$N$_2$Cl$_8$MoO$_6$Ti$_2$: C 18.83, H 2.90, N 3.66, Cl 37.04%. Found: C 18.69, H 2.97, N 3.39, Cl 37.14%.

R = MV; M = Sn. IR (nujol mulls): ν_{NO} 1828 vs, 1708 vs cm^{-1}. ^{1}H NMR (in CD$_3$CN): δ 2.26–2.36 (m, 4H; CO$_2$*CH$_2$*CH$_2$–); δ 1.45–1.58 (m, 6H; –C*H$_2$*CH (CH$_3$)$_2$); δ 0.80–0.90 (m, 2H; –CH(*CH$_3$*)$_2$) ppm. Anal.: Calc. for C$_{12}$H$_{22}$N$_2$Cl$_8$MoO$_6$Sn$_2$: C 15.89, H 2.44, N 3.09, Cl 31.26%. Found: C 15.69, H 2.54, N 2.89, Cl 31.31%.

2.3. Polymerization reaction

A standard polymerization procedure was as follows: (a) for binary catalysts (complex–MCl$_4$; M = Ti, Sn)—to the solution of complex (0.25 mmol in 5 ml) and the monomer with internal standard ([Mo]/[monomer] = 1/50), the appropriate solution of MCl$_4$ ([Mo]/[MCl$_4$] = 1/2) was added, (b) for ternary catalysts (complex–PA–MCl$_4$)—to the solution of com-

plex (0.25 mmol in 5 ml), phenylacetylene (PA) and MCl$_4$ ([Mo]/[PA]/[MCl$_4$] = 1/1/2), the solution of monomer (diphenylacetylene (DPA) or norbornene (NB); [Mo]/[monomer] = 1/50) was added, (c) for the complex–EtAlCl$_2$ catalysts—to a stirred solution of complex (0.25 mmol in 5 ml), EtAlCl$_2$ in hexane was added at −20°C ([Mo]/[Al] = 1/4). After 10 min, phenylacetylene with internal standard was added at room temperature.

The polymerization reactions were quenched by adding a small amount of methanol to the polymerizing systems. The formed polymers were isolated by precipitation in methanol; other reaction products (dimers, trimers and oligomers) were isolated from the remaining solution. Monomer conversions were determined by gas chromatography (GC-MS; HP-5890 II + 5971A). The yield of polymerization was determined gravimetrically. The weight- and number-average molecular weights ($\overline{M}_w$ and $\overline{M}_n$, respectively) were determined by the 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. Interaction of dinitrosylmolybdenum complexes with Lewis acid

Dinitrosylmolybdenum complexes of the type {Mo(NO)$_2$(OR)$_2$}$_n$ and Mo(NO)$_2$(O$_2$CR)$_2$ with EtAlCl$_2$ are very active catalysts of olefin metathesis [47–51]. Reactions between the components of these systems yield the appropriate ethylidenedinitrosyl complexes, which were characterized spectrally [49,52–54]. They are examples of low-valent carbene complexes with nucleophilic alkylidene ligands. These ethylidene complexes are the products of transformation of the precursor complexes—EtAlCl$_2$ (1:2) adducts [49,53]. The complexes under consideration form similar 1:2 adducts with other Lewis

acids as $TiCl_4$ and $SnCl_4$. The adducts $Mo(NO)_2(OR)_2(MCl_4)_2$ (R = *i*-Pr; M = Ti, Sn) and $Mo(NO)_2(O_2CR)_2(MCl_4)_2$ (R = Ph, EH, MV; M = Ti, Sn) were synthesized and characterized by IR and ^1H NMR spectroscopy (see Section 2). All these adducts are yellow-brown precipitates sensitive on air. They are insoluble in alkanes, benzene, PhCl and CH_2Cl_2, except the adduct with R = EH, which is soluble in PhCl and CH_2Cl_2. Their IR spectra contain two $\nu(NO)$ bands typical of *cis*-$\{Mo(NO)_2\}^6$ cores [55,56] and the ^1H NMR spectra—all the signals of the protons of coordinated ligands.

3.2. Polymerization of acetylenes—the effect of catalyst system

None of the adducts exhibits catalytic activity in the polymerization reaction of phenyl- and other acetylenes, but after addition of a Lewis acid (LA; $TiCl_4$ or $SnCl_4$) to $Mo(NO)_2(O_2CR)_2$ and an excess of phenylacetylene (PA) conversion was observed. The results of polymerization experiments in CH_2Cl_2, where the molar ratio PA/complex was 50 and LA/complex was 2, are given in Table 1. No polymerization occurred without Lewis acid and in the systems based on dialkoxydinitrosyl complexes, for example $\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_n$–$MCl_4$. The steric

Table 1
Polymerization of phenylacetylene by dinitrosylmolybdenum complexes–Lewis acid catalysts in CH_2Cl_2[a]

Complex	Lewis acid	Conversion [%]	Yield[b] [%]
$Mo(NO)_2(O_2CPh)_2$	$TiCl_4$	12	4
	$SnCl_4$	27	7
$Mo(NO)_2(O_2CMV)_2$	$TiCl_4$	6	3
	$SnCl_4$	43	11
$Mo(NO)_2(O_2CEH)_2$	$TiCl_4$	4	1
	$SnCl_4$	32	9
$Mo(NO)_2(acac)_2$	$TiCl_4$	5	0
	$SnCl_4$	24	9
$\{Mo(NO)_2(O\text{-}i\text{-}Pr)_2\}_n$	$TiCl_4$	0	
	$SnCl_4$	0	

[a] Reaction conditions: concentration of complex [Mo] = 0.25 mmol; [LA]/[Mo] = 2; [PA]/[Mo] = 50; 24 h; room temperature.
[b] Methanol insoluble part.

effect, easier formation of a stable adduct caused a lack of catalytic activity in this system.

The monomer conversion (43%) and the yield of a methanol-insoluble product (11%) are highest with $Mo(NO)_2(O_2CMV)_2$ and $SnCl_4$ as Lewis acid. $SnCl_4$ was the most effective catalyst component with other dicarboxylic complexes, too. In the system based on dinitrosylmolybdenum complex with another chelating ligand coordinating by oxygen atoms (e.g., acetylacetone) the same effect of Lewis acid was observed.

The weight-average molecular weights ($\overline{M}_w$) of the obtained polymers were very low, a little above 1×10^3. Low molecular weight of polyphenylacetylene can by caused by kinetic effects as well as by possible degradation induced by the polymerization reaction catalysts. This result corresponds with the literature data on the polymerization of phenylacetylene which show that phenylacetylene with no substituent at *ortho* position does not form high molecular weight polymers in the presence of Mo-based catalysts [57].

3.3. The effect of Lewis acid

Table 2 shows the effect of Lewis acid on polymerization of phenylacetylene examined in $Mo(NO)_2(O_2CPh)_2$ based systems. Activity of these systems in polymerization reaction of other substituted acetylenes (*tert*-butylacetylene, diphenylacetylene) was investigated, too.

Monomer conversion was the highest (100% after 4 h) with $EtAlCl_2$ as Lewis acid. The yield of the polymer was also relatively high (80%), although its molecular weight was very low (ca. 10^3). $\overline{M}_w/\overline{M}_n = 1.15$. Similarly, only oligomers were obtained with other dinitrosylmolybdenum-based catalysts (i.e., $\{Mo(NO)_2(OEt)_2\text{-}EtOH\}_n$–$EtAlCl_2$ or $Mo(NO)_2(CHMe)(O\text{-}i\text{-}Pr)_2(AlCl_2)_2(EtAlCl_2)$) [50]. The highest value of $\overline{M}_w$ (3×10^4) was that of polymer formed with $TiCl_4$, but the yield was less than 5% with high (76%) monomer

Table 2
Effect of Lewis acid on polymerization of phenylacetylene by $Mo(NO)_2(O_2Ph)_2$–Lewis acid catalysts in PhCl[a]

Lewis acid	Monomer	Conversion [%]	Polymer[b]			Other products
			Yield [%]	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	
$EtAlCl_2$	PA	100[c]	80	1.0	1.15	cyclotrimers + linear oligomer
$TiCl_4$	PA	76	6	11	7.01	cyclotrimers and 1-phenylnapthalene (< 2%)
$SnCl_4$	PA	45	20	2	4.72	
$TiCl_4$–THF[d]	PA	36	4	1.6		
$EtSnCl_2$	PA	0				
$TiCl_4$	DPA	0				
$SnCl_4$	DPA	0				
$SnCl_4$	TBA		10[e]			

[a] Reaction conditions: concentration of complex [Mo] = 0.25 mmol; [LA]/[Mo] = 2; [PA]/[Mo] = 50; 24 h; room temperature.
[b] Methanol insoluble part.
[c] After reaction time 4 h.
[d] The system was prepared as follows: to the solution of complex and phenylacetylene, $TiCl_4$ and next THF were added ([Ti]/[THF] = 1/1).
[e] Insoluble in organic solvents.

conversion. Polydispersity of this polymer was high, $\overline{M}_w/\overline{M}_n = 7.01$. Decreasing acid properties of the Ti and Sn compounds causes a decrease ($TiCl_4$–THF) and even disappearance (Et_2SnCl_2) of the catalytic activity of the systems.

The differences found between monomer conversion and the polymer yield (Table 2) are mainly due to the formation of the triphenylbenzene derivatives and partially (< 2%) 1-phenylnaphthalene, except the $EtAlCl_2$ system, where 1-phenylnaphthalene was not found and, together with small amounts of cyclotrimers, the linear oligomers were formed.

In the system with $SnCl_4$ also *tert*-butylacetylene polymerizes (Table 2), however, the yield of polymer insoluble in any organic solvent was only 10%.

3.4. The effect of solvent

Activities of the systems tested strongly depend on the solvent. The effect of solvent on conversion of phenylacetylene, yield of polymer and its molecular weight was examined with $Mo(NO)_2(O_2CPh)_2$–MCl_4 (M = Ti, Sn) catalysts and the results are shown in Table 3. Polymerization hardly proceeds in CH_2Cl_2 with either $TiCl_4$ or $SnCl_4$ Lewis acid. The reason is most probably the relatively high polarity of this solvent [18,45]. The most effective catalyst polymerization is the system with $SnCl_4$ in benzene, where monomer conversion is 60% and yield of polymer is 56%. Thus, this system is almost selective in polymerization of phenylacetylene. Conversion of the monomer in toluene is even higher (70%), but the yield of polymer is very low (3%) and the main products (66%) are triphenylbenzene derivatives. In toluene this system is almost selective catalyst of the reaction of trimerization of phenylacetylene. In the system with $SnCl_4$ one observes an increase of the degree of conversion of monomer depending on the solvent as follows: PhCl (48%) < benzene (60%) < toluene (70%), while the activity of system with $TiCl_4$ in this order is decreased: conversion in PhCl is 76%, in benzene 24%, and in toluene this system is inactive. This decrease of activity is undoubtedly caused by increasing interactions $TiCl_4$–solvent, which equally weaken its acidity, like in $TiCl_4$–THF (Table 2). The systems with $TiCl_4$ mainly cyclotrimerize phenylacetylene independent on the solvent (Table 3) and/or on the carboxylic ligand in the complex (Table 1). However, for low yields of polymers their molecular weights ($\overline{M}_w$) are in general the highest (above 10^4).

Table 3
Effect of the solvent on polymerization of phenylacetylene by $Mo(NO)_2(O_2CPh)_2$–MCl_4 catalysts (M = Ti, Sn)[a]

Solvent	MCl_4	Conversion [%]	Polymer[b]			Yield of cyclotrimers
			Yield [%]	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	
CH_2Cl_2	Ti	12	4	1.6	3.00	7.8
	Sn	27	7	1.0	1.25	19.6
PhCl	Ti	76	6	11	7.01	66.5
	Sn	48	20	2	4.72	27
Benzene	Ti	24	5	16	7.03	18
		20[c]	5	1.8	3.02	14.5
	Sn	60	56	4	3.75	4
Toluene	Ti	0				
	Sn	70	3	1.0	1.31	66

[a] Reaction conditions: concentration of complex [Mo] = 0.25 mmol; [LA]/[Mo] = 2; [PA]/[Mo] = 50; 24 h; room temperature.
[b] Methanol insoluble part.
[c] After reaction time 3 h.

3.5. Reaction mechanism and structure of polymers

As it follows from Tables 1–3, in the systems under investigation phenylacetylene undergoes cyclotrimerization, oligomerization or polymerization; which reaction prevails depends on the complex, Lewis acid and solvent. Masuda and Higashimura [45] 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, the cyclic trimers are formed only through the *cis*-cisoidal-induced backbiting and/or intramolecular reactions [27]. Undoubtely, cyclomerization in the systems $Mo(NO)_2(O_2CR)_2$–$EtAlCl_2$ (Table 2) proceeds with this mechanism. In these systems carbene complexes of the type $Mo(NO)_2(CHMe)$-$(O_2CR)_2(AlCl_2)_2(EtAlCl_2)_2$ are formed [54] and polymerization reaction has a mechanism similar to that of polymerization of cycloolefins, i.e., propagation proceeds through metal carbenes [18,23,41–45].

For the $Mo(NO)_2(O_2CR)_2$–MCl_4 systems we propose the following mechanism of polymerization and cyclotrimerization of phenylacetylene. Reaction of catalyst precursor complexes with Lewis acids causes that free coordination sites are reached in *trans* positions towards NO ligands [48]. If phenylacetylene is present in the reaction system, it coordinates to the metal forming vinylidene complex [58,59] and further polymerization proceeds by metal carbene mechanism. The trimerization mechanism is backbiting of propagating carbenes in a *cis*-cisoidal grown chain to form triphenylbenzene derivatives. When the free coordination sites are blocked by, for instance, chlorines of the Lewis acids, inactive adducts are formed and reaction is terminated. The route of reaction (polymerization or/and cyclotrimerization) depends mainly on the Lewis acid and on the solvent.

^{1}H NMR investigations of the $Mo(NO)_2$-$(O_2CR)_2$–$SnCl_4$–PA ([Mo]/[Sn]/[PA] = 1/2/1) system in CD_2Cl_2 (R = MV) and C_6D_6

Table 4
Polymerization of diphenylacetylene (DPA) and ROMP[a] of norbornene (NB) by $Mo(NO)_2(O_2CPh)_2$ /PA/LA in PhCl[b]

LA	Monomer	Yield of polymer[c] [%]	% *cis*
$SnCl_4$	DPA	10[d]	–
$SnCl_4$	NB	30[d]	77.3[e]

[a] Characterized by IR spectra [60].
[b] Reaction conditions: concentration of complex [Mo] = 0.25 mmol; [LA]/[Mo] = 2; [PA]/[Mo] = 2; [DPA]/[Mo] and [NB]/[Mo] = 50; t = 24 h; room temperature.
[c] Methanol insoluble part.
[d] Polymer insoluble in organic solvents.
[e] Calculated using IR spectra [61,62].

(R = Ph) did not allow to identify the vinylidene complexes, because of their fast reaction with the molecules of phenylacetylene (even at the concentration ratio of reagents [Mo]/[Sn]/[PA] = 1/2/1). Therefore, these spectra contain the proton resonances of polyphenylacetylene, (δ = 7.20–7.30 ppm) and signals in 12.00–13.50 ppm (12.00 and 12.50 ppm for R = MV, 13.20 and 13.30 ppm for R = Ph), most probably due to H_α of the carbene ligands formed. Catalytic activity of the system $Mo(NO)_2(O_2CPh)_2 - SnCl_4 - PA$ ([Mo]/[Sn]/[PA] = 1/2/1) in the polymerization reaction of diphenylacetylene (conversion: 10%) and ROMP of norbornene (conversion: 30%) (Table 4) prove that carbene complexes are formed in this system.

Values of the chemical shift of polyphenylacetylene proton resonances (7.20–7.30 ppm) in spectra of these systems indicate the *trans*-cisoidal structure [19,20] of the polymers formed. These spectra show also weak signals at about 5.9, 6.7 and 6.8 ppm due to proton resonances of a small amount of polymer with *cis*-transoidal structure [19,20] and weak signals at δ = 7.60–7.80 ppm, due to the protons of triphenylbenzene [20,27]. Structure of all the obtained polyphenylacetylenes were determined by ^{1}H NMR and IR spectroscopy [18–20,23,27]. We identified these polyphenylacetylenes as *trans*-cisoidal ones. The ^{1}H NMR spectra of the polymers show also weak signals of proton resonances of polymer with *cis*-transoidal structure, and in addition weak and broad singlets at δ = 3.5–4.0 ppm. These singlets correspond to the methynic proton signal arising from the 1,3- and or 1,4-cyclohexadiene structures [20,27].

When the mechanism of polymerization could be described by propagation through metal carbenes and cyclometallabutene intermediates, the polymer structure is determined by two mechanisms: (i) isomerization prior to double bond formation—resulting in *cis*-transoidal isomer or *trans*-cisoidal isomer depending on the mode of cyclometallabutene opening [21,22,24,27,63], (ii) thermal isomerization after double bond formation—resulting in the *cis* to *trans* isomerization and cyclohexadiene sequences. The cyclohexadiene structure can undergo further rearrangement leading to chain scission and aromatization products (benzene, 1,3,5-triphenylbenzene, 1-phenylnaphthalene) [21,22,24,27,63].

The reaction polymerization products, ^{1}H NMR investigation of the same systems and ^{1}H NMR spectra of the polymers suggest that the latter mechanism decides on the microstructure of polyphenylacetylene obtained in $Mo(NO)_2(O_2CR)_2$–Lewis acid systems.

Acknowledgements

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