

FIRST EXAMPLES OF HOMOGENEOUS CATALYTIC CYCLOTRIMERIZATION AND POLYMERIZATION OF PHENYLACETYLENE AND COPOLYMERIZATION OF PHENYLACETYLENE AND NORBONENE WITH DINUCLEAR COMPLEXES CONTAINING UNBRIDGED METAL–METAL QUADRUPLE BOND

Konstantinos MERTIS^{a1,*}, Stavros ARBILIAS^a, Demos ARGYRIS^a, Nikos PSAROUDAKIS^{a2}, Jiří VOHLÍDAL^b, Olivier LAVASTRE^{c1} and Pierre H. DIXNEUF^{c2}

^a University of Athens, Inorganic Chemistry Laboratory, Panepistimiopolis, 15701 Athens, Greece; e-mail: ¹ cmertis@cc.uoa.gr, ² psaroudakis@chem.uoa.gr

^b Charles University, Department of Physical and Macromolecular Chemistry, Laboratory of Specialty Polymers, Albertov 2030, CZ-12840 Prague 2, Czech Republic; e-mail: vohlidal@natur.cuni.cz

^c Université de Rennes 1, Laboratoire de Chimie de Coordination et Catalyse, 35042 Rennes, France; e-mail: ¹ lavastre@univ-rennes.fr, ² dixneuf@univ.rennes-1.fr

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Dedicated to Professor F. A. Cotton for his discovery of the metal–metal quadruple bond.

First examples of application of dinuclear complexes containing unbridged metal–metal quadruple bond as catalysts in cyclotrimerization, oligomerization and polymerization of substituted acetylene are reported. The d⁴–d⁴ dinuclear complexes (Bu₄N)₂[Re₂X₈] (**1**) (**1a**, X = Cl; **1b**, X = Br and **1c**, X = I) show low activity and the complex [Mo₂Cl₄(MeOH)₂(PPh₃)₂] (**2**) medium activity in cyclotrimerization and oligomerization of phenylacetylene (PA). In contrast, the tungsten-based d⁴–d⁴, complex Na₄[W₂Cl₈] (**3**) exhibits high polymerization activity (polymer yield above 90%) and *ca* 75% *cis*-selectivity in tetrahydrofuran. The activity and *cis*-stereoselectivity of these single-component catalysts decrease in the order **3** >> **2** >> **1**, which is proportional to the metal–metal quadruple bond propensity towards ligand addition reactions. Complex **3** induces metathesis polymerization of norbornene (NBE) to poly(cyclopentene-1,3-diylvinylene) with 82% *cis*-selectivity and copolymerization of PA and NBE to almost all-*cis* high-molecular-weight copolymer containing cyclopentene-1,3-diylvinylene units, which is free of longer sequences of both PA and NBE units. This suggests that also homopolymerization of PA with **3** proceeds by the metathesis mechanism and that the PA/NBE copolymer structure is close to the alternating one.

Keywords: Cyclotrimerizations; Dinuclear complexes; Metal–metal quadruple bond; Alkenes; Alkynes; ROMP; Metathesis polymerizations; Single-component catalysts; Rhenium; Tungsten; Molybdenum.

Dinuclear complexes containing metal–metal multiple bonds possess several attractive properties, which make them potential catalysts for various organic transformations. Most importantly, the $[M-M]^{n+}$ core can act as a template for coordination and activation of organic substrates and as an electron reservoir for facile multi-electron redox processes accompanied by interconversions between the $[M-M]^{n+}$ species of different bond orders^{1,2}.

Metal–metal quadruple bonds were discovered 36 years ago³ and since that time molybdenum and tungsten complexes carrying carboxylate, allyl, halide and nitrile ligands have been used as uni- or bicomponent homogeneous or heterogeneous catalysts in hydrogenation of alkenes and alkynes⁴, metathesis of acyclic olefins⁵⁻⁷, ring opening metathesis polymerization (ROMP) of cyclic olefins⁸⁻¹⁰ and polymerization of cyclopentadiene and dicyclopentadiene^{11,12}.

Although certain complexes containing formally double and triple bonds, e.g. $[M_2Cl_6(tht)_3]$ (where M is Nb¹³, Ta¹³ or Mo¹⁴ and *tht* is tetrahydrothiophene) and $[M_2(OR)_6]$ (where¹⁵ M is Mo and R is isopropyl, *tert*-butyl or neopentyl or where¹⁶ M is W and R is (*t*-Bu)Me₂SiO-), are capable of cyclotrimerizing and polymerizing alkynes, there is very little information on analogous reactions induced with complexes containing the metal–metal quadruple bond¹⁷. The only known examples are the heterometallic complexes $[Mo_2(\mu-OCOR)_2\{Al(\mu-OR')_4\}_2]$ (where R is Me, *t*-Bu, CF₃ and R' is phenyl or substituted phenyl) or analogous species generated *in situ* from the reaction of homonuclear $[M\equiv M]^{4+}$ or heterodinuclear $[M\equiv M']^{4+}$ (M is Mo and M' is W) complexes with various alkoxides or phenoxides of aluminium and titanium, which are capable of inducing the metathesis of specific internal alkynes¹⁸. Also, the $[Mo\equiv Mo]^{4+}$ bridged complexes such as *cis*- $[Mo_2(OAc)_2(\mu-en)_2(en)_2]\cdot(AcO^-)_2\cdot en$ (*en* is ethylenediamine) and $[Mo_2(Me_2NCH_2CH_2NMe_2 \text{ or } Me_2PCH_2CH_2PMe_2)(\mu-OAc)_4]_n$ catalyze coupling, oligomerization and metathesis of internal alkynes $RC\equiv CR'$, where R and R' is alkyl C₁–C₁₀ or aryl¹⁹.

In view of the isolation and structural characterization of the $[M\equiv M]^{4+}$ complex $[Mo_2(en)_4(\mu-4-MeC_6H_4C\equiv CH)(\mu-OAc)]\cdot(AcO^-)_2\cdot(en)_2$ ²⁰ and also the facile additions of alkynes to the Ta=Ta doubly and W≡W triply bonded halide complexes $[Ta_2Cl_4(\mu-Cl)_2(\mu-tht)(tht)_2]$ ^{21,22} and $Na[W_2Cl_7(thf)_5]$ ²³ yielding the metallotetrahedrane derivatives $[M_2Cl_4(\mu-Cl)_2(\mu-RC\equiv CR')(thf)_2]$ (M is Ta or W and $RC\equiv CR'$ is MeC≡CMe, EtC≡CEt, HC≡CH or PhC≡CH), we have examined the reactivity of the d⁴–d⁴ complexes (Bu₄N)₂[Re₂X₈] (**1**) (**1a**, X = Cl^{24a}; **1b**, X = Br^{24b} or **1c**, X = I^{24c}), $[Mo_2Cl_4(MeOH)_2(PPh_3)_2]$ ²⁵ (**2**) and $Na_4[W_2Cl_8]$ ²⁶ (**3**) which have unbridged metal–metal quadruple bonds and the $\sigma^2\pi^4\delta^2$ electronic configuration (see Chart 1) towards phenylacetylene

as a representative of substituted acetylene. The results of these experiments are reported in this paper (see Scheme 1 and Table I).

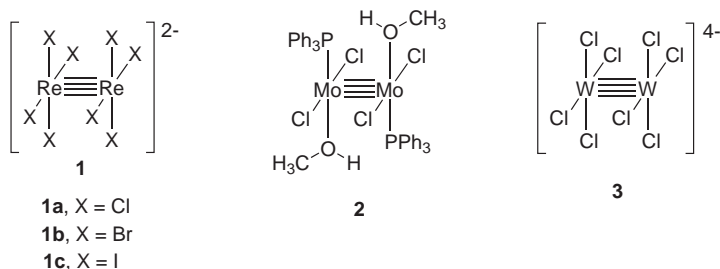
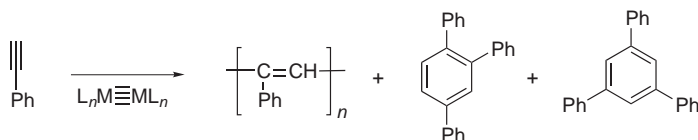


CHART 1



SCHEME 1

TABLE I

Results of reactions of PA with quadruply bonded dinuclear complexes of Re, Mo and W. Initial concentrations: $[1]_0 = 7.35$ mmol/l, $[PA]_0 = 1.470$ mol/l; $[2]_0 = 2.14$ mmol/l, $[PA]_0 = 0.107$ mol/l; $[3]_0 = 2.88$ mmol/l, $[PA]_0 = 0.576$ mol/l

Catalyst	Solvent	T, °C	Reaction time, h	Yield, %		$M_n \times 10^{-3}$
				cyclo-trimers	polymer (oligomers)	
1a	1,2-dichlorobenzene	130	6	2.5	15	1.1
1a + EtAlCl ₂ (1 : 1)	THF	25	6	2.3	11	1.1
1b	toluene	90	6	3.9	14	1.1
1c	toluene	70	6	3.0	7	1.1
2	CH ₃ OH	25	4	18	40	4.0
2	THF	25	4	–	–	–
3	THF	25	3	7	91	140

EXPERIMENTAL

Materials

All operations were performed under pure argon using the Schlenk technique and all solvents and reagents (from Aldrich) were deoxygenated before use by freeze-vacuum-thaw cycles except for methanol which was degassed by purging with argon for 30 min. Tetrahydrofuran (THF) and diethyl ether were distilled from Na/Ph₂CO, hexane and toluene were distilled from Na, CH₂Cl₂ and 1,2-dichlorobenzene were distilled from CaH₂, and methanol was distilled from the corresponding magnesium alkoxide. Phenylacetylene (PA) and norbornene (NBE) were dried by stirring with CaH₂ under argon, distilled under vacuum and stored in a dark place under argon. The metal–metal quadruple-bonded complexes were prepared and checked for purity as referenced earlier: **1a**^{24a}, **1b**^{24b} and **1c**^{24c}, **2**²⁵, and **3**²⁶.

Methods

NMR spectra (δ , ppm) were recorded on a Varian Unity Plus 300 instrument operating at frequency 299.948 MHz for ¹H and 75.429 MHz for ¹³C NMR using samples dissolved in CDCl₃ and hexamethyldisilane (1%, v/v) for referencing ¹H (δ +0.04 ppm) spectra. ¹³C NMR spectra were referenced to the solvent (δ +76.99 ppm). The relaxation delay was set to 5 s. Signals of protonated and nonprotonated carbons were distinguished by the APT (attached proton test) method with the *J*-modulation period minimized by ¹³C and ¹H refocusing pulses. IR spectra were recorded on a Perkin–Elmer 883 IR spectrometer. UV–VIS spectra were recorded on a Hitachi U-2000 spectrometer. Size exclusion chromatography (SEC) analyses were made on a TSP (Thermo Separation Products, Florida, U.S.A.) chromatograph equipped with a UV detector operating at 254 nm and a series of two PL-gel columns (Mixed-B and Mixed-C (Polymer Laboratories Bristol, U.K.), THF eluent, flow rate 0.7 ml/min) or, alternatively, on a modular instrument consisting of a Waters Model 510 pump, a Waters Model U6K sample injector, a Waters Model 401 differential refractometer and a set of four μ -Styragel columns with a porosity from 10³ to 10⁶ Å housed in a thermostated box (THF, flow rate 1 ml/min). Molecular weight averages relative to polystyrene standards are reported. A Varian Star 3400CX GC/MS/MS gas chromatograph equipped with a high-resolution capillary column DB-5MS (30 m) and with a mass spectrometric detector Saturn 2000 was used for monitoring the reactions.

Procedures

All reactions were carried out in Schlenk tubes under dry argon. Experiments with **1b** and **1c** were performed in the absence of light. In a typical experiment, a measured volume of PA was added to the catalyst suspension (**1**) or solution (**2**, **3**) in an appropriate solvent and the mixture was allowed to react under stirring at a required temperature for a given time (see Table I). The reaction progress was monitored by GC–MS and/or ¹H NMR methods. After a chosen reaction time, all volatiles were removed in vacuum, collected in a cold trap (liquid N₂) and further analyzed as above. The non-volatile residue was extracted several times with CH₂Cl₂ or THF, the obtained extract was concentrated to a minimum volume and separated by chromatography on neutral alumina under strictly anaerobic conditions because of poly(PA) (PPA) sensitivity to molecular oxygen^{27–29}. The following mobile phases were used in the chromatography: hexane/diethyl ether for elution of PA cyclotrimers, diethyl

ether for elution of PA oligomers and THF for elution of PPA. Control experiments performed in the absence of catalyst precursors have shown negligible oligomerization but neither cyclotrimerization nor polymerization of PA. The reactions of **3** with NBE and a mixture of PA/NBE were carried out similarly. The polymer in the former reaction was isolated by precipitation in ethanol acidified by a few drops of concentrated HCl, whereas in the latter by precipitation in acidified methanol. All polymers were dried *in vacuo* at 30 °C.

RESULTS AND DISCUSSION

Rhenium complex **1a** does not react with PA at room temperature or by refluxing in CH₂Cl₂, CHCl₃, CH₃CN, C₆H₆, C₆H₅CH₃ or THF. However in 1,2-Cl₂C₆H₄ at 130 °C produces a yellow-brown reaction mixture, from which colorless PA cyclotrimers, 1,2,4-triphenylbenzene (**4a**), 1,3,5-triphenylbenzene (**4b**) and yellow PA oligomers (**5**) (number-average molecular weight $M_n \approx 1000$) of *trans*-structure, can be isolated in low yield (**4a** and **4b** 2.5–3.9%, **5** 7–15%). This oligomerization of PA is the first partly successful application of the [Re₂Cl₈]²⁻ ion as a polymerization catalyst. A weak broad signal at 3.8 ppm in the ¹H NMR spectrum of oligomer **6** suggests the presence of cyclohexadiene sequences^{30–32} in the oligomer. Oligomer **6** shows the following characteristics: ¹H NMR (CDCl₃, 25 °C): 7.20 (broad, ≈6–7.7, 6 H, aromatic and olefinic *trans*-units); 3.8 (broad weak signal, cyclohexadiene sequences). ¹³C-{¹H} NMR: 125–133 (aromatic, olefinic); 142 (weak, quaternary carbon atoms). IR (KBr): bands at 692, 756, 912, 964, 1258, 1441 and 1482 cm⁻¹; absence of absorption bands characteristic of *cis*-units at 740, 895 and 1380 cm⁻¹.

Complexes **1b** and **1c** are slightly more reactive requiring temperatures of 90 and 70 °C, respectively. The reactivity of **1a** can be greatly enhanced by introducing a co-catalyst. Thus, addition of a two-molar excess of AlEtCl₂ to the green-blue solution of **1a** in CH₂Cl₂ causes immediate precipitation of an air sensitive solid, sparingly soluble in CH₂Cl₂ or THF. This after filtration reacts with PA in the above media at room temperature yielding the same products as **1a**.

The alkali salts of the [Mo₂Cl₈]⁴⁻ anion are insoluble in most common organic solvents and salts with bulky organic cations such as Ph₄P⁺ or Bu₄N⁺ are unstable to be isolated. Therefore, complex **2** has been employed in our tests as a representative of the Mo-based dinuclear complexes. This is stable in MeOH but unstable in weakly coordinating solvents (CH₂Cl₂, C₆H₆, THF), in which it polymerizes to an insoluble and unreactive compound having the formula [Mo₂Cl₄(PPh₃)_n]²⁵ containing Mo₄ rectangular units as tetrametal cyclobutadiynes. The reaction of **2** with PA in MeOH proceeded at room temperature resulting in a brown solution from which cyclotrimers

4a and **4b** (18% total) and a yellow, low-molecular-weight polymer (40%) were isolated. The polymer denoted as PPA (**2**) is of irregular *cis*–*trans* structure according to both NMR (broad signals) and IR spectra. ^1H NMR (CDCl_3 , 25 °C): 7.15 (strong, aromatic and olefinic *trans*-units); 6.70 (shoulder, 2 H *ortho* aromatic in *cis*-units); 5.80 (weak, 1 H, olefinic *cis*-units). ^{13}C - $\{^1\text{H}\}$ NMR: 126, 128 (broad, strong, aromatic, olefinic); 142 (weak, quaternary carbon atoms). IR (KBr): absorptions at 740, 895, 1380 cm^{-1} are not discernible. The content of *cis*-units calculated from the relative intensity of the signal at 5.80 ppm is approximately 50%, similar to that observed for substituted acetylene polymers prepared with MoCl_5 ³³ or MoOCl_4 ³⁴ based catalysts.

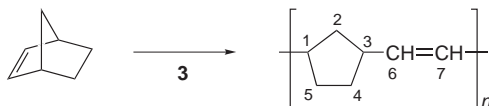
Complex **3** is unstable above -10 °C, therefore PA was added to a THF solution of **3** at -15 °C. Upon warming to the room temperature, the original brilliant blue solution becomes red-brown affording nearly quantitatively (91%), auburn to orange, prevalingly *cis* ($\approx 75\%$ *cis* according to both IR and ^1H NMR data), high-molecular-weight ($M_n = 140\,000$) polymer (denoted as PPA (**3**)) and a small amount of cyclotrimers (7%). Spectroscopic data for PPA (**3**): ^1H NMR (CDCl_3 , 25 °C): 6.95 (strong, 3 H, aromatic); 6.80 (shoulder, 2 H, *ortho* aromatic in *cis*-units); 5.84 (weak, 1 H, olefinic in *cis*-units). ^{13}C - $\{^1\text{H}\}$ NMR: 127, 128, 132 (strong, aromatic and olefinic in *trans*-units); 140, 143 (quaternary carbon atoms). IR (KBr): characteristic absorptions at 692, 738, 754, 801, 884, 910, 1024, 1068, 1329, 1387, 1438 and 1484 cm^{-1} . The product selectivity of **3** for *cis*-configuration of main-chain double bonds strongly contrasts with that of WCl_6 -based catalysts, which typically provide high-*trans*-PPA³⁵.

This new-class initiators (**2** and **3**) differ from the relevant unicomponent halide catalysts such as NbCl_5 and TaCl_5 ^{36,37}, $[\text{MoCl}_3(\text{thf})_3]^{14}$, $[\text{M}_2\text{Cl}_6(\text{tht})_3]$ (where M is Nb¹³, Ta¹³, Mo¹⁴), which exclusively cyclotrimerize PA to a mixture of the 1,3,5- and 1,2,4-isomers. They also differ from the archetypal high-valent chlorides MoCl_5 , WCl_6 which require activation by a co-catalyst in order to produce PPA in comparable yields, but resemble to the binary MoCl_5 or $\text{WCl}_6/\text{Ph}_4\text{Sn}$ systems³⁵ as for polymer yield and molecular weight. It should be noted here that the observed enhancement of the *cis*-stereoselectivity of **3** could be induced by THF which was used as solvent for this catalyst, since 1,4-dioxane induces a similar effect in polymerization of various substituted acetylenes with WOCl_4 and WCl_6 based catalysts^{33–36}.

The observed catalyst activity can be well correlated with the metal–metal quadruple bond reactivity, which decreases in the order $\text{W}_2^{4+} > \text{Mo}_2^{4+} > \text{Re}_2^{6+}$. The most active catalyst is derived from complex **3**, which contains the

tungsten–tungsten quadruple bond that is known to be extremely reactive in oxidation and ligand addition reactions¹. This enhanced reactivity delayed the isolation of **3** and the development of W_2^{4+} chemistry in general for nearly two decades, but in contrast, when suitably exploited, it can provide robust catalysis involving δ -bonds³⁸.

The complexity of the system and multiplicity of pathways available makes difficult in obtaining mechanistic information, especially on the primary step(s). Our efforts to isolate and characterize catalytically active, yield-related intermediates have not yet been successful. Therefore, we decided to obtain at least information about propagation mechanism, *i.e.*, to solve the question whether the polymerization of PA induced by **3** proceeds *via* metathesis or insertion mechanism. This information can be obtained indirectly by examining the catalytic activity of **3** in the ring opening metathesis polymerization of NBE and in the copolymerization of NBE and PA.



SCHEME 2

Polymerization of NBE with **3** proceeds rather slowly and provides only 12% of poly(norbornene), PNBE, after 19 h of reaction. PNBE prepared had $M_n = 86\ 000$ and well resolved NMR spectra. Spectroscopic characteristics of PNBE: ¹H NMR (CCl₄, 25 °C): 5.25 (weak unresolved m, H6 and H7 in *trans*-units); 5.11 (strong m, H6 and H7 in *cis*-units); 2.70 (strong s, H1 and H3 in *cis*-units); 2.40 (weak s, H1 and H3 in *trans*-units); 0.85–1.90 (m, main signals at 1.75, 1.3 and 0.95, H4, H5 and H2). ¹³C-¹H NMR: 133.99 (very strong, olefinic carbons C6 and C7 in *ccc* triads); 133.21 w, 130.06 w and shoulders at 134.08, 133.8, 133.28 (C6 and C7 in other triads); multiplet of carbons C1 and C3 (position, diad): 43.67 *tc* weak, 43.43 *tt* weak, 38.88 *cc* strong, 38.67 *ct* weak (all); multiplet of carbon C2 (position, diad): 42.88 *cc* strong, 42.24 *ct* weak, 41.52 *tt* w; multiplet of carbons C4 and C5 (position, diad): 33.39 *cc* strong, 33.18 *ct* weak, 32.61 *tc* weak, 32.42 *tt* weak. Signal observed at 31.89 (weak) was not assigned. The signals assignment was done according to literature data³⁹. Content of *cis*-units in the polymer was determined to be 82% when calculated from the intensity ratio of signals at 5.12 (*cis* CH=CH) and 5.25 (*trans* CH=CH) as well as the intensity ratio of signals of C1 and C3 carbons at 2.73 (*cis*-units) and 2.38 ppm (*trans*-units). ¹³C NMR spectrum shows high blockiness of the pre-

pared PNBE, which is used to be characterized by the product $r_c r_t$, where r_c and r_t are intensity ratios of signals of given carbons in diads composed of *cis* (*c*) and *trans* (*t*) units: $r_c = (cc)/(ct)$ and $r_t = (tt)/(tc)$. If the double bond distribution is random (Bernoullian), $r_c r_t = 1$. Values of $r_c r_t > 1$ prove existence of blocks of *cis*-units and *trans*-units in a given polymer: the higher is the value of the product $r_c r_t$ the higher is the blockiness of given polymer³⁹. We found the following values for PNBE prepared with **3**: multiplet of carbons and C3: $r_c = 7.4$, $r_t = 1.3$ and $r_c r_t = 9.6$; multiplet of carbon C2 $r_c = 7.5$, $r_t = 1.3$ and $r_c r_t = 9.75$. The average value $r_c r_t \cong 9.7$ found for our polymer ranges to the highest values of PNBE blockiness ever observed³⁹.

The above results clearly indicate that complex **3** induces metathesis polymerization of NBE, which suggests that also polymerization of PA with complex **3** proceeds *via* metathesis mechanism. To obtain further evidence supporting this conclusion, we copolymerized PA and NBE with complex **3**. Reacting an equimolar mixture of PA and NBE with **3**, we achieved total conversion of both monomers within 1 h of polymerization and obtained a yellowish rubbery copolymer poly(NBE-*co*-PA) (isolated yield 86%, $M_n = 19\,000$) and, in addition, a low-molecular-weight fraction isolated from the supernatant after the copolymer isolation. NMR characteristics of poly(NBE-*co*-PA): ¹H NMR (CCCl₃, 25 °C): 7.5–6.5 broad unresolved multiplet (aromatic protons); 5.35 m (very weak, H6 and H7 in *trans*-units); 5.21 m (strong, H6 and H7 in *cis*-units); 3.75 br s and 3.42 br s (both related to PA units); 2.82 m (strong, H1 and H3 in *cis*-units); 2.45 m (very weak, H1 and H3 in *trans*-units); 0.85–2.00 m (main signals at 1.75, 1.40 and 1.02, H4, H5 and H2). ¹³C-¹H NMR: 141 and 139.5 (quaternary carbons); 134.72, 134.09, 133.54 and 132.99 (well resolved signals of olefinic carbons in PA units and C6 and C7 of NBE units); 130–125 (broad, unresolved, aromatic carbons in PA units); 42.65 (multiplet with maxima at 43.19, 42.96, 42.65, 42.42 and 42.10, C1, C2 and C3); 38.24 (quadruplet with maxima at 39.43, 38.93, 38.24 and 37.75, C1 and C3); 33.19 (poorly resolved multiplet with maxima at 33.44, 33.19 and 33.03, C4 and C5). It should be emphasized here that resolved signals characteristic of olefinic hydrogen (5.84 ppm) and *o*-hydrogens of phenyl ring (6.85 ppm) in PPA (**3**) are practically missing in ¹H NMR spectrum of poly(NBE-*co*-PA), which proves absence of longer sequences of PA units in the copolymer. Also the fine structure of ¹³C NMR spectrum of poly(PA-*co*-NBE) is different from that of PNBE. These observations clearly indicate that the polymer formed is a real copolymer and that its structure is close to the alternating one. High intensities of ¹H NMR signals characteristic of *cis*-NBE units together with very low intensity of all signals characteristic of *trans*-NBE units prove to an almost all-*cis* structure

of poly(PA-*co*-NBE) prepared with **3**. More detailed structure characterization of this copolymer requires further investigation, which is beyond the scope of this article. Nevertheless, it is clear that the polymer formed in common polymerization of PA and NBE is a copolymer and not a mixture of two homopolymers.

The yellow low-molecular-weight fraction (14%) contains traces of cyclotrimers **4** and a copolymer involving longer sequences of *cis*-PA units and, most probably, isolated NBE units. The presence of longer sequences of *cis*-PA units is evidenced in ^1H NMR: 6.6–6.8 (*o*-hydrogens of benzene ring); 5.85 (olefin protons in *cis*-units). ^{13}C NMR: 142.9, 139.4 (quaternary carbons); 131.4 (olefinic protons) and broad signal of aromatic protons with local maxima at 128.6, 127.6 and 127.2. The fine structure of ^{13}C NMR signals found for this low-molecular-weight fraction is practically identical with that found for poly(NBE-*co*-PA), whereas the fine structure found for PNBE is missing. This proves the absence of longer sequences of NBE units.

Summarizing the above, it can be concluded that the polymerization of PA and NBE as well as copolymerization of these monomers induced with tungsten complex **3** proceed *via* metathesis mechanism. Further reactivity studies and attempts to understand the mechanism of these reactions and structure of the above polymers are in progress.

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