Polymerization of alkynes on nickelocene based catalysts: considerations on polymerization mechanism

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Dedicated to Professor Józef J. Ziółkowski on the occasion of his 70th birthday in recognition of his outstanding contributions to coordination chemistry.

Abstract

Novel nickelocene based catalysts were used for polymerization of 2-butyne, 1-phenyl-1-propyne, bis(trimethylsilyl)acetylene and trimethylsilylacetylene. The catalyst prepared in the reaction of nickelocene with organolithium compounds in the presence of alkyne was previously isolated and fully characterized. It enabled us to explain the mechanism of the polymerization. Polymerization of alkynes proceeds according to coordination-insertion mechanism. Coordinated acetylene molecule inserts into Ni–C bond. An active catalytic species of polymerization appeared to be {CpNiR} stabilized by alkyne molecule. Cyclization is catalyzed by {CpNiH} species.
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1. Introduction

Metallocene catalysts have not been used for polymerization of acetylenes up to now, although they are widely applied for olefin polymerization (Kaminsky, Brinzinger). For acetylene and its derivatives Ziegler–Natta polymerization catalysts are mainly applied [1,2]. Acetylenic monomers also appeared to undergo polymerization with conventional olefin metathesis catalysts [3]. Some efforts have been made to use nickelocene as a catalyst for polymerization of monosubstituted acetylenes [4]. It was found that nickelocene itself was not active, while the system $NiCp_2/AlBr_3$ (mole ratio 1:2) led to cyclotrimerization of at about 10% yield. Douglas found that nickelocene and other cyclopentadienylnickel compounds $(NiCp)_2 \cdot CHCPh$; $[CpNi(CO)]_2$; CpNiNO; $CpNi(GeBr_3)$; $CpNi(PR_3)Cl$ catalyzed the reaction of phenylacetylene under solvent-free conditions, yielding at 115 °C a mixture of cyclotrimers, linear oligomers and poly(phenylacetylene) [5,6]. No reaction of di-substituted acetylenes ($Me_3SiC\equiv CSiMe_3$, $PhC\equiv CSiMe_3$, $PhC\equiv CPh$) occurred under solvent-free conditions.

The aim of this paper was to study polymerization of 2-butyne, 1-phenyl-1-propyne, bis(trimethylsilyl)acetylene and trimethylsilylacetylene using nickelocene based catalysts and to explain the mechanism of these reactions.

2. Experimental

All reactions were carried out under atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. 2-Butyne, 1-phenyl-1-propyne, bis(trimethylsilyl)acetylene and trimethylsilylacetylene (Aldrich) were used as purchased. Phenyl-, methyllithium and lithium phenylacetylide were prepared by standard procedures.

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Mercury (400 MHz) spectrometer with chemical shifts given in ppm from the internal TMS. IR spectra were

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Table 1
Polymerization of 1-phenyl-1-propyne on {CpNiR} catalysts (R = CH$_3$, Ph, C≡CPh)

Catalyst	Solvent	Polymers			Oligomers	
		Yield (%)	M_w[a]	M_w/M_n[a]	Yield (%)	Cyclic/linear ratio (%)
{CpNiCH$_3$·CH$_3$C≡CPh}	THF	41	1092	1.10	25	75/25
{CpNiCH$_3$·CH$_3$C≡CPh}	Toluene	32	1177	1.75	41	84/16
{CpNiPh·CH$_3$C≡CPh}	THF	36	1204	1.49	31	62/38
{CpNiPh·CH$_3$C≡CPh}	Toluene	24	1053	1.34	29	82/18
{CpNiC≡CPh·CH$_3$C≡CPh}	THF	46	1145	1.65	32	70/30
{CpNiC≡CPh·CH$_3$C≡CPh}	Toluene	27	1105	1.35	34	52/38

[a] Determined by GPC on the basis of polystyrene calibration.

recorded in KBr pellets on a "Biorad FT-IR" spectrometer. The molecular weights of the polymers were measured by gel-permeation chromatography (GPC) at 25 °C in THF solution (Shimadzu C-R4 Chromatopac apparatus, the column calibration was made using standard samples of monodispersed polystyrene). MALDI TOF mass spectra were recorded on "Kratos Kompact MALDI 4 V 5.2.1" spectrometer with nitrogen laser 337 nm. Samples were dissolved in THF or CH$_2$Cl$_2$ (5 mg cm^{-3}) and mixed with matrix solution (2,5-dihydroxobenzoic acid with CF$_3$COOAg; 0.2 M in THF). GC/MS analyses were performed on a Hewlett Packard 5971 Series Mass Selective Detector with a HP 35 Column (30 m × 0.25 mm).

Yield of products was defined as the ratio of the amount of the product to the amount of the monomer used.

2.1. Polymerization of 1-phenyl-1-propyne {CpNiR} catalyst (R = CH$_3$, Ph, C≡CPh)

A solution of organolithium compound (methyllithium, phenyllithium or lithium phenylacetylide) was added to a cooled to −78 °C and vigorously stirred solution of nickelocene and 1-phenyl-1-propyne in THF or toluene (15 cm^3). The reaction mixture was allowed to warm up to room temperature and stirred for further 24 h. The 80 cm^3 of hexane and 60 cm^3 of 12% aqueous HCl was then added and the mixture was stirred for 3 h at 75–80 °C. Two layers were separated and 350 cm^3 of methanol was added to the organic one. The white polymer precipitated. It was filtered off, washed with methanol and dried. Poly(1-phenyl-1-propyne) was characterized by means of FT-IR, ^{1}H and ^{13}C NMR and MALDI TOF mass spectroscopy.

FT-IR (KBr, cm^{-1}): 2954 (br, s), 2922 (br, s), 2854 (br, s), 2066 (w), 1942 (w), 1869 (w), 1773 (w), 1717 (w), 1699 (w), 1653 (m), 1559 (m), 1490 (m), 1464 (s), 1377 (s), 1261 (s), 1095 (br, s), 1023 (br, s), 803 (s), 774 (m), 702 (m), 698 (s) and 668 (m).
^{1}H NMR (CDCl$_3$), δ (ppm): 1.58 (broad signal of aliphatic protons (methyl protons), [–CH$_3$C≡CPh–]$_n$), 7.10–7.31 (signals of aromatic protons, [–CH$_3$C≡CPh–]$_n$).
^{13}C NMR (CDCl$_3$), δ (ppm): 126.7–141.4 (aromatic and olefinic carbons), 25.3 and 30.9 (methyl carbons).

Methanol soluble products consisted of low molecular weight, cyclic and linear oligomers of 1-phenyl-1-propyne. They were identified by means of GC/MS analysis (Table 1).

All reactions were carried out using 0.4–0.5 g (0.21–0.26 mmol) of NiCp$_2$; mole ratio of reactants: NiCp$_2$:CH$_3$C≡CPh:LiR = 1:40:1.1.

2.2. Polymerization of 2-butyne on {CpNiR} catalyst (R = CH$_3$, Ph, C≡CPh)

All reactions were carried out using 0.4–0.5 g (0.21–0.26 mmol) of NiCp$_2$; mole ratio of reactants: NiCp$_2$:CH$_3$C≡CCH$_3$:LiR = 1:25:1.1. Poly(2-butyne) was characterized by means of FT-IR, ^{1}H and ^{13}C NMR and MALDI TOF mass spectroscopy.
FT-IR (KBr, cm^{-1}): 2963 (s), 2905 (s), 2882 (w), 1664 (w), 1558 (m), 1446 (m), 1412 (s), 1380 (m), 1261 (s), 1093 (br, s), 1020 (br, s), 846 (s), 800 (br, s), 702 (s) and 661 (s).
^{1}H NMR (CDCl$_3$), δ (ppm): 1.61 (broad signal of aliphatic protons, [–CH$_3$C≡CCH$_3$–]$_n$ and chain end-group), 7.16–7.31 (signals of aromatic protons).

Table 2
Polymerization of 2-butyne on {CpNiR} catalysts (R = CH$_3$, Ph, C≡CPh)

Catalyst	Solvent	Polymers			Oligomers	
		Yield (%)	M_w[a]	M_w/M_n[a]	Yield (%)	Cyclic/linear ratio (%)
{CpNiCH$_3$·CH$_3$C≡CCH$_3$}	THF	51	1015	1.54	24	64/36
{CpNiCH$_3$·CH$_3$C≡CCH$_3$}	Toluene	46	1104	1.48	32	72/28
{CpNiPh·CH$_3$C≡CCH$_3$}	THF	38	936	1.26	33	72/28
{CpNiPh·CH$_3$C≡CCH$_3$}	Toluene	31	1072	1.30	36	77/23
{CpNiC≡CPh·CH$_3$C≡CCH$_3$}	THF	49	795	1.17	28	69/31
{CpNiC≡CPh·CH$_3$C≡CCH$_3$}	Toluene	44	828	1.04	33	73/27

[a] Determined by GPC on the basis of polystyrene calibration.

Table 3
Polymerization of trimethylsilylacetylene on {CpNiR} catalysts (R = CH$_3$, Ph, C≡CPh)

	Solvent	Polymers			Oligomers	
		Yield (%)	M_w[a]	M_w/M_n[a]	Yield (%)	Cyclic/linear ratio (%)
{CpNiCH$_3$·HC≡CSi(CH$_3$)$_3$}	THF	51	1011	1.35	42	18/82
{CpNiCH$_3$·HC≡CSi(CH$_3$)$_3$}	Toluene	16	1148	1.26	35	30/70
{CpNiPh·HC≡CSi(CH$_3$)$_3$}	THF	49	1079	1.28	39	20/80
{CpNiPh·HC≡CSi(CH$_3$)$_3$}	Toluene	14	923	1.09	29	19/81
{CpNiC≡CPh·HC≡CSi(CH$_3$)$_3$}	THF	49	870	1.39	44	23/77
{CpNiC≡CPh·HC≡CSi(CH$_3$)$_3$}	Toluene	22	792	1.30	36	25/75

[a] Determined by GPC on the basis of polystyrene calibration.

^{13}C NMR (CDCl$_3$), δ (ppm): 29.6 ([–CH_3C=CCH$_3$–]$_n$), 137.5 ([–CH$_3$$C$=CCH$_3$–]$_n$) 31.1 (CH$_3$ end-groups) and 123.3–132.0 (aromatic carbons of end-groups).

Methanol soluble products consisted of low molecular weight, cyclic and linear oligomers of 2-butyne identified by means of GC/MS analysis (Table 2).

2.3. Polymerization of trimethylsilylacetylene {CpNiR} catalyst (R = CH$_3$, Ph, C≡CPh)

All reactions were carried out using 0.4–0.5 g (0.21–0.26 mmol) of NiCp$_2$; mole ratio of reactants: NiCp$_2$:HC≡CSi(CH$_3$)$_3$:LiR = 1:20:1.1. Poly(trimethylsilyl-acetylene) was characterized by means of FT-IR, ^{1}H and ^{13}C NMR and MALDI TOF mass spectroscopy.

FT-IR (KBr, cm^{-1}): 2963 (s), 2905 (s), 1653 (w), 1558 (w), 1446 (m), 1412 (s), 1248 (s), 1093 (br, s), 1026 (br, s), 928 (s), 841 (s), 798 (s) and 702 (s).

^{1}H NMR (CDCl$_3$), δ (ppm): 0.07 (signal of methyl protons, [–HC=CSi(CH_3)$_3$–]$_n$), 5.72 ([–HC=CSi(CH$_3$)$_3$–]$_n$ and end-groups), 1.25 (CH$_3$), 7.26–7.44 (signals of aromatic protons).

^{13}C NMR (CDCl$_3$), δ (ppm): 1.05 ([–HC=CSi(CH_3)$_3$–]$_n$), 141.2 ([–HC=CSi(CH$_3$)$_3$–]$_n$), 137.6 ([–HC=CSi(CH$_3$)$_3$–]$_n$), 29.6 (CH$_3$) and 126.4–128.7 (aromatic carbons).

Methanol soluble products consisted of low molecular weight, cyclic and linear oligomers of trimethylsilylacety-lene. They were identified by means of GC/MS analysis (Table 3).

Table 4
Polymerization of bis(trimethylsilyl)acetylene on {CpNiR} catalysts (R = CH$_3$, Ph, C≡CPh)

Catalyst	Solvent	Oligomers	
		Yield (%)	Cyclic/linear ratio (%)
{CpNiCH$_3$·(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$}	THF	38	67/33
{CpNiCH$_3$·(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$}	Toluene	44	55/45
{CpNiPh·(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$}	THF	32	62/38
{CpNiPh·(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$}	Toluene	39	64/36
{CpNiC≡CPh·(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$}	THF	36	70/30
{CpNiC≡CPh·(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$}	Toluene	41	52/38

2.4. Polymerization of bis(trimethylsilyl)acetylene {CpNiR} catalyst (R = CH$_3$, Ph, C≡CPh)

All reactions were carried out using 0.4–0.5 g (0.21–0.26 mmol) of NiCp$_2$; mole ratio of reactants: NiCp$_2$:(CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$:LiR = 1:30:1.1. The polymer has not precipitated. Methanol soluble products consisted of low molecular weight unidentified oligomers (Table 4).

3. Results and discussion

A metallocene catalysts prepared in the reaction of nickelocene with organolithium compound LiR (R = CH$_3$, Ph, C≡CPh) were applied for polymerization of 2-butyne, 1-phenyl-1-propyne, bis(trimethylsilyl)acetylene and trimethylsilylacetylene. The catalyst was prepared as follows: a solution of organolithium compound in diethyl ether or THF was added drop by drop at −78 °C to a stirred solution of nickelocene and alkyne in THF or toluene. Molar ratio of NiCp$_2$:LiR = 1:1.1. Polymerization was carried out for 24 h, gradually increasing temperature to 25 °C. A 12% solution of HCl was then added and the mixture was heated to 75–80 °C in order to decompose organonickel compounds formed. The organic layer was then separated and methanol was added to precipitate polymeric products.

1-Phenyl-1-propyne was polymerized in the presence of the nickelocene catalyst to form a white polymer. The white precipitate was separated, washed with methanol and dried. The filtrate contained some amount of cyclic and linear 1-phenyl-1-propyne oligomers soluble in the solvent/methanol mixture. The oligomers were analysed by GC–MS analysis (Table 1). Distinguishing linear oligomers from the corresponding cyclic ones was possible as the molecular weight of cyclic oligomers was equal to the multiplied molecular weight of the monomer, while the molecular weight of linear oligomers was increase the weight of the end-groups.

The polymer was characterized by means of FT-IR, ^{1}H, ^{13}C NMR and MALDI-TOF-MS. ^{1}H NMR spectrum consisted of wide signal at 1.58 ppm corresponding to methyl group protons and also wide signals at 7.10–7.31 ppm of aromatic protons. ^{13}C NMR showed signals of methyl carbons at 25.3 and 30.9 ppm, signals of aromatic and sp^2 carbons at
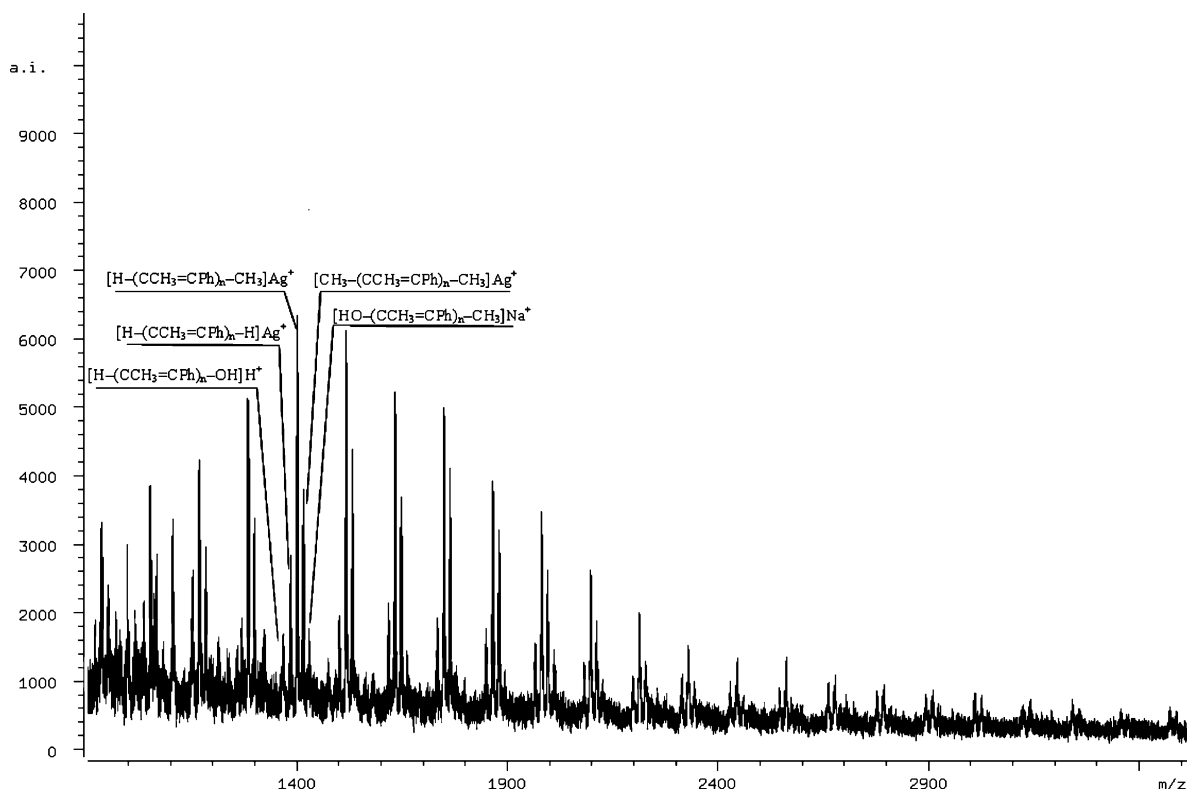
Fig. 1. MALDI TOF spectrum of poly(1-phenyl-1-propyne) (nickelocene and methyllithium catalyst).

126.7–141.4 ppm. These NMR data were in good agreement with literature ones [7,8].

In the FT-IR spectrum bands at 1653 and 1559 cm^{-1} are characteristic for alternating C=C bonds in a polymer chain. Bands at 2000–1700, 774 and 698 cm^{-1} due to phenyl groups and bands at 2954, 2854, 1464 and 1377 cm^{-1} due to methyl groups confirmed linear structure of the polymer [7,8].

Poly(1-phenyl-1-propyne) does not posses protons in the main chain, therefore its geometrical structure cannot be determined by means of the IR spectra [7]. Initially, the polymer has mostly *cis* structure due to the *cis*-insertion during chain propagation reaction. It should be however presumed, that during hydrolysis of the reaction mixture carried out at 75–80 °C, isomerization to *trans* polymer occurs [9]. This isomerization can be facile due to a large steric hindrance between the bulky groups in the *cis* structure [7].

MALDI-TOF-MS spectrum of poly(1-phenyl-1-propyne) formed in the presence of {CpNiCH$_3$} catalyst is presented in Fig. 1. Five sets of signals corresponding to 1-phenyl-1-propyne polymers were present in the spectrum. The mass difference in each set 116 corresponded to MW of the monomer. The most intensive set of signals corresponded to polymers with hydrogen and methyl as end-groups (adduct with Ag$^+$). The second set of signal exhibited two methyl groups as end-groups (adduct with Ag$^+$), the third one had two hydrogen as end-groups (adduct with Ag$^+$), the fourth set of signal exhibited methyl and hydroxy groups as end-group (adduct with Na$^+$) and the last set exhibited hydrogen and hydroxy group as

end-groups (adduct with H$^+$). The MW range corresponded to 7–27 (1-phenyl-1-propyne) molecules in chains.

MALDI-TOF-MS spectra of poly(1-phenyl-1-propyne) obtained with the other studied catalysts {CpNiPh} and {CpNiC≡CPh} revealed the presence of the following end-groups—for {CpNiPh}: H and Ph, Ph and Ph, H and H, HO and H; for {CpNiC≡CPh}: H and H, PhC≡C and C≡CPh, H and C≡CPh, HO and H. The origin of the end-groups was as follows: R, derived from the catalyst used; H, from {CpNiH} formed in the reaction course and OH, introduced during hydrolysis of the reaction mixture.

2-Butyne was polymerized in the presence of the same catalyst to form a white substance. The white precipitate was separated, washed with methanol and dried. The filtrate contained some amount of cyclic and linear 2-butyne oligomers soluble in the solvent/methanol mixture. The oligomers were analysed by GC–MS (Table 2).

The polymer was characterized by means of FT-IR, ^{1}H, ^{13}C NMR. In the IR spectrum bands at 1664 and 1558 cm^{-1} are characteristic for conjugated double bonds in a polymer chain [8,10]. Also bands at 2963, 2882, 1446 and 1380 cm^{-1} due to methyl groups confirmed linear structure of the polymer [11]. Similar to poly(1-phenyl-1-propyne), poly(dimethylacetylene) does not posses protons in the main chain, therefore its geometrical structure cannot be determined by means of the IR spectra.

^{1}H NMR spectrum consists of wide signal at $\delta = 1.61$ ppm due to methyl protons, [–C*H$_3$*C=CC*H$_3$*–]$_n$. Additional sig-

nals of aromatic protons at 7.16–7.31 ppm were present in ^{1}H NMR spectra of polymers obtained in reactions catalyzed by {CpNiC≡CPh} and {CpNiPh}, what indicates the presence of the phenyl as the end-group of the polymer.

^{13}C NMR reveals signals at δ = 29.6 ppm of methyl carbons, [–CH_3C=CCH_3–]$_n$, 137.5 of sp^2 carbons, [–$CH_3$$C$=$C$CH₃–]$_n$, and depending on the catalyst used, signals of corresponding end-groups: at δ = 31.1 ppm (CH_3) or wide signals at 123.3–132.0 ppm of aromatic carbons. The above results confirmed linear structure of the obtained polymer.

MALDI-TOF-MS spectrum of poly(2-butyne) formed in the presence of {CpNiCH$_3$} exhibited four sets of signals corresponding to 2-butyne polymers. The mass difference in each set was 54 what corresponded to MW of the monomer. The most intensive set of signals corresponded to polymers with two methyl groups as end-groups (adduct with Ag$^+$). The second set of signal exhibited two hydrogen as end-groups (adduct with Na$^+$), the third one had methyl and hydroxy groups as end-groups (adduct with Ag$^+$) and the fourth set exhibited hydrogen and methyl group as end-group (adduct with K$^+$). The MW range corresponded to 12–25 monomer molecules in chains.

MALDI-TOF-MS spectra of poly(2-butyne) obtained with other catalysts: {CpNiPh} and {CpNiC≡CPh} showed the presence of the following end-groups—for {CpNiPh}: Ph and Ph, H and H, Ph and H, HO and Ph; for {CpNiC≡CPh}: PhC≡C and C≡CPh, H and H, HO and C≡CPh, H$_3$C and H (methyl group was introduced with residual amounts of methyllithium used for synthesis of lithium phenylacetylide).

Polymerization of trimethylsilylacetylene was carried out as described above. The product was light yellow polymer insoluble in methanol and cyclic and linear oligomers soluble in methanol (Table 3).

The polymer was characterized by means of FT-IR, ^{1}H, ^{13}C NMR and MALDI-TOF-MS.

The following signals were present in ^{1}H NMR spectra: δ = 0.07 ppm (signal of methyl protons, [–HC=CSi(CH_3)$_3$–]$_n$), 5.72 (signal of olefinic protons, [–HC=CSi(CH$_3$)$_3$–]$_n$), 1.25 (CH$_3$ end-group protons (in polymer obtained with {CpNiCH$_3$} catalyst) and wide signals), 7.26–7.44 (phenyl end-group protons (in polymers obtained with {CpNiPh} and {CpNiC≡CPh} catalysts)).

^{13}C NMR spectra contained the following signals: δ = 1.05 ppm (methyl carbons, [–HC=CSi(CH_3)$_3$–]$_n$), 141.2 (olefinic carbon, [–HC=CSi(CH$_3$)$_3$–]$_n$) and 137.64 (sp^2 carbon of the polymer chain, [–HC=CSi(CH$_3$)$_3$–]$_n$). For polymer obtained with {CpNiCH$_3$} catalyst the signal of CH$_3$ end-group at δ = 29.6 ppm was observed, and for polymers obtained with {CpNiPh} and {CpNiC≡CPh} catalysts signals of carbons of phenyl end-groups at 126.4–128.7 ppm were present.

In FT-IR spectra bands at 1653 or 1558 cm^{-1} confirmed the presence of a conjugated C=C double bonds system in a polymer chain. Bands characteristic for SiC–H vibrations at 1248 cm^{-1} and for C–Si at 841 cm^{-1} were also present in

the spectra [12,13]. Bands at 928 and 1026 cm^{-1} indicated *trans* structure of the polymer forced by a steric hindrance of bulky trimethylsilyl group. Isomerization proceeds during heating the reaction mixture to ~80 °C.

MALDI-TOF-MS spectrum of poly(trimethylsilylacetylene) formed in the presence of {CpNiCH$_3$} as catalyst exhibited three sets of signals. The mass difference in each set was 98, what is MW of the monomer. The first set of signals corresponded to polymers with two hydrogen atoms as end-groups (adduct with Ag$^+$). The second set of signal exhibited hydrogen and methyl group as end-groups (adduct with Ag$^+$), the third one had hydrogen and hydroxy group as end-groups (adduct with K$^+$). The MW range corresponded to 6–17 (trimethylsilyl)acetylene molecules in chains.
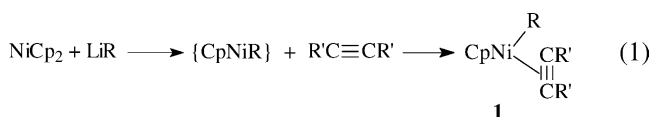
MALDI-TOF-MS spectra of poly(trimethylsilylacetylene) obtained with other catalysts: {CpNiPh} and {CpNiC≡CPh} exhibited the presence of the following end-groups—for {CpNiPh}: H and Ph, H and H, HO and H; for {CpNiC≡CPh}: H and C≡CPh, H and H, HO and H.

Bis(trimethylsilyl)acetylene did not polymerize on studied catalysts. Only some unidentified linear oligomers soluble in the solvent/methanol mixture were formed in the reactions carried out at analogous as above conditions (Table 4).

The lack of polymerization was caused by steric hindrance of bulky trimethylsilyl groups what made an insertion of alkyne molecule into Ni–R bond impossible. For R = CH$_3$ a hydrogen elimination, followed by the trimethylsilyl group migration, proceeded with the final formation of π-allyl complex [14].
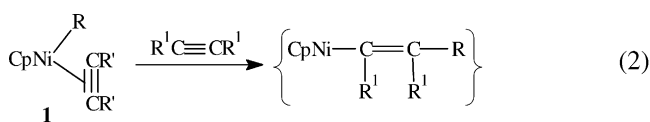
Previous [14] and present studies on the molecular structure of the catalysts, isolation of products of single and multiple insertion of alkyne into Ni–R bond of the catalyst [15,16], and determination of end-groups of oligomers and polymers, allowed us to describe mechanism of polymerization and cyclization of studied alkynes.

Nickelocene reacts with organolithium compound forming unstable {CpNiR} species. This catalytically active species reacts with alkyne to form an isolated and characterized π-complex **1** (Eq. (1)):

$$NiCp_2 + LiR \longrightarrow \{CpNiR\} + R'C\equiv CR' \longrightarrow \underset{\mathbf{1}}{CpNi\overset{R}{\underset{CR'}{\overset{|}{\diagdown}}}\overset{CR'}{\underset{CR'}{\overset{|||}{}}}} \qquad (1)$$

Complex **1**, depending on R group and on the kind of alkyne, can form several isolated and fully characterized nickel complexes and clusters [17–19].

If reaction (1) is carried out in the excess of alkyne then *cis*-insertion reaction proceeds (Eq. (2)):

$$\underset{\mathbf{1}}{CpNi\overset{R}{\underset{CR'}{\overset{|}{\diagdown}}}\overset{CR'}{\underset{CR'}{\overset{|||}{}}}} \xrightarrow{R^1C\equiv CR^1} \left\{ CpNi\!-\!\underset{R^1}{\overset{|}{C}}\!=\!\underset{R^1}{\overset{|}{C}}\!-\!R \right\} \qquad (2)$$

In case of phenylacetylene [15] and trimethylsilylacetylene, an insertion product were isolated and characterized (Eqs. (3) and (4)):

$$\text{(3)}$$

$$\text{(4)}$$
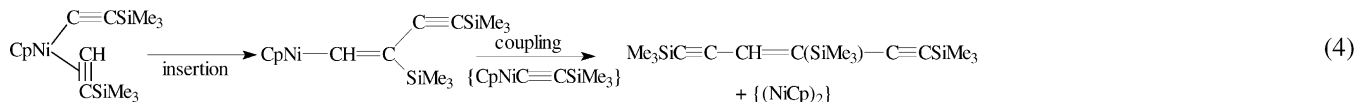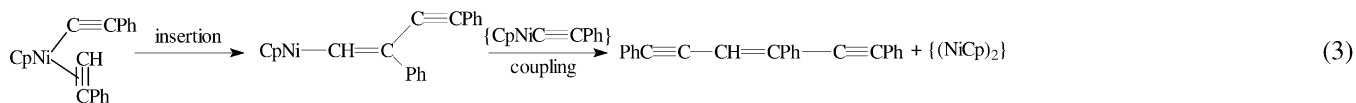
In case of 2-butyne a cyclic product of trimerization of the alkyne was isolated and characterized [16].

An insertion (Eq. (2)) created a free coordination site what enable the further complexation of alkyne molecule (Eq. (5)):

$$\text{(5)}$$

Repeated insertion and complexation reactions lead to the polymer chain growth. The polymer formed initially has *cis*-transoidal conformation, which at elevated temperature transforms to *trans*-cisoidal one (Eq. (6)):

$$\text{(6)}$$
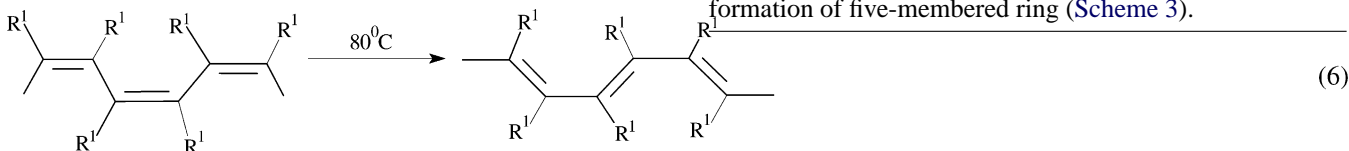
Cyclization reaction proceeds differently. The mechanism of cyclization with the formation of benzene derivatives is presented in Scheme 1.

The above cyclization proceeds only for terminal alkynes (e.q. trimethylsilylacetylene). The possibility of the forma-

tion of cyclic trimer is determined by a mode of the first insertion step. If the first trimethylsilylacetylene molecule inserts that hydrogen and R group are bonded to the terminal carbon atom and conformation of a growing chain is *cis*-cisoidal, then hydrogen transfer to the nickel occurs, with the ring closure and the formation of {CpNiH} species. {CpNiH} can act further as a catalyst for trimerization, regardless of a mode of the first insertion step. If insertion step proceeds in the reverse mode than a linear polymer with conformation *cis*-transoidal is formed (Scheme 2).

For internal alkynes (2-butyne, 1-phenyl-1-propyne) the formation of unstable {CpNiH} is determined by the possibility of H-elimination from methyl group what leads to the formation of five-membered ring (Scheme 3).

{CpNiH} catalyses further cyclization, analogously as in cyclization of trimethylsilylacetylene (Scheme 1).

Polymerization of bis(trimethylsilyl)acetylene does not occur because bulky trimethylsilyl groups prevent insertion of monomer into Ni–C bond.

Based on MALDI-TOF-MS analysis we have found that linear polymers of alkynes contained R as end-groups, de-

Scheme 1.
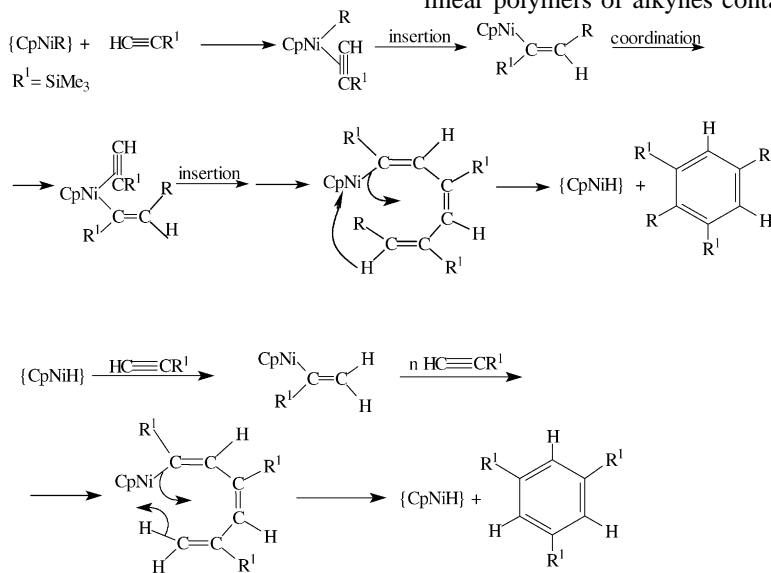
Scheme 2.

Scheme 3.

Scheme 4.
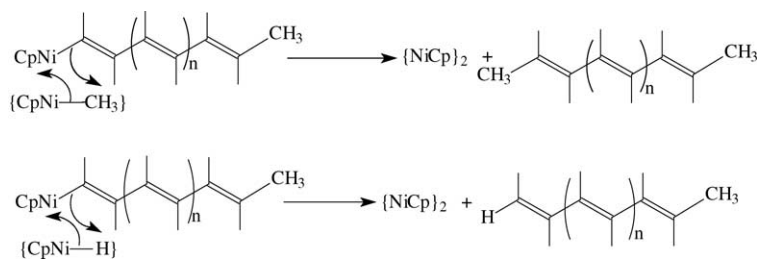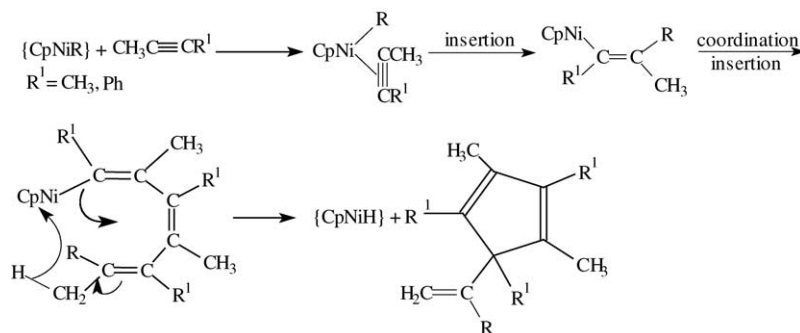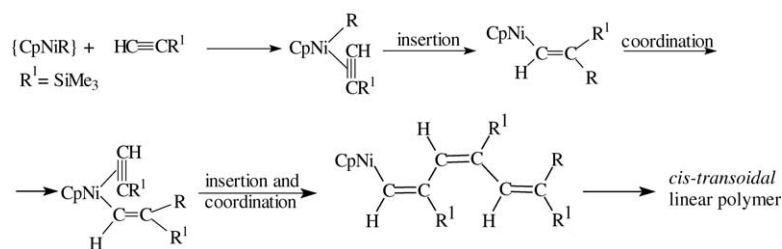
pending on {CpNiR} catalyst used (R = CH$_3$, Ph, C≡CPh). The other end-groups were OH and H. For example, in polymerization of 2-butyne on {CpNiCH$_3$} the end-groups were hydrogen and methyl. This could be explained by coupling of the growing chain with CH$_3$ or H from catalysts {CpNiCH$_3$} or {CpNiH} (Scheme 4).

The above coupling reactions led to the formation of (NiCp)$_n$ species and to the deactivation of the catalyst.

The presence of OH as an end-group could be explained by the course of hydrolysis during work-up of the reaction mixture.

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