APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 583–588

Nickelocene catalysts for polymerization of alkynes: mechanistic aspects

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Received 17 December 2003; Accepted 31 January 2004

Novel nickelocene-based catalysts were used for polymerization of diphenylacetylene and phenylacetylene. The catalyst obtained in the reaction of nickelocene with organolithium compounds in the presence of alkyne was previously isolated and fully characterized. This enabled us to explain the mechanism of the polymerization. Polymerization of alkynes proceeds according to a coordination–insertion mechanism. Coordinated acetylene molecule inserts into an Ni–C bond. An active catalytic species of polymerization appeared to be {CpNiR} stabilized by alkyne molecule. Cyclization is catalyzed by {CpNiH} species. The mechanism of polymerization and cyclization reaction was determined based on the composition of the reaction products formed, gel-permeation chromatography and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry measurements. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: alkynes; polymerization; nickel; catalysts

INTRODUCTION

We have previously found that nickelocene-based catalyst polymerized diphenylacetylene to form a high molecular weight (MW) polymer.[1] It was the first active metalocene catalyst applied in polymerization of acetylenes. Metalocene catalysts have not been used for polymerization of acetylenes up to now, although they are widely applied for olefin polymerization (Kaminsky, Brinziger). For acetylene and its derivatives, polymerization Ziegler–Natta catalysts are mainly applied.[2,3] Acetylenic monomers also appeared to undergo polymerization with conventional olefin metathesis catalysts.[4] Some efforts have been made to use nickelocene as a catalyst for polymerization of monosubstituted acetylenes.[5] It was found that nickelocene itself was not active, whereas the system $NiCp_2/AlBr_3$ (mole ratio 1:2) led to cyclotrimerization at about 10% yield. Douglas[6,7] found that nickelocene and other cyclopentadienylnickel compounds ($(CpNi_2) \cdot CHCPh$; $[CpNi(CO)]_2$; CpNiNO; $CpNi(GeBr_3)$; $CpNi(PR_3)Cl$) catalysed the reaction of phenylacetylene under solvent-free conditions, giving a mixture of cyclotrimers, linear oligomers and poly(phenylacetylene) at 115 °C. 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 diphenylacetylene and phenylacetylene using nickelocene-based catalysts and to explain the mechanism of these reactions.

EXPERIMENTAL

All reactions were carried out under atmosphere of dry argon using Schlenk tube techniques. Solvents were dried by conventional methods. Phenylacetylene and diphenylacetylene (Aldrich) were used as purchased. Phenyllithium, 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 parts per million from the internal tetramethylsilane. IR spectra were recorded in KBr pellets on a Biorad FT-IR spectrometer. The MWs of the polymers were measured by gel-permeation chromatography (GPC) at 25 °C in tetrahydrofuran (THF) solution (Shimadzu C-R4 Chromatopac apparatus; the column calibration was made using standard samples of monodispersed polystyrene). Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectra were recorded on Kratos Kompact MALDI

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Contract/grant sponsor: Ministry of Scientific Research and Information Technology; Contract/grant number: 4 T09A 012 25.

4 V 5.2.1 spectrometer with nitrogen laser at 337 nm. Samples were dissolved in THF or CH_2Cl_2 (5 mg cm^{-3}) and mixed with matrix solution (2,5-dihydroxobenzoic acid; 0.2 M in THF). Gas chromatography—mass spectrometry (GC–MS) analyses were performed on a Hewlett Packard 5971 Series mass selective detector with an 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.

Polymerization of diphenylacetylene on {CpNiR·PhC≡CPh} catalyst (R=CH_3, Ph, C≡CPh)

A solution of organolithium compound (methyllithium, phenyllithium or lithium phenylacetylide) was added to a vigorously stirred solution of nickelocene and diphenylacetylene in 15 cm^3 THF cooled to −78 °C. The reaction mixture was warmed slowly to room temperature. A change of colour from green to brown was observed, and after 1 h a yellow polymer began to precipitate. The mixture was stirred for a further 24 h. The product was filtered off, washed with methanol and dried under reduced pressure. The polymer was insoluble in all commonly used solvents. It was characterized by FT-IR spectrometry (KBr; cm^{-1}): 3081(s), 3050(s), 3017(m), 2954(br, s), 2924(br, s), 1599(s), 1492(s), 1464(s), 1441(s), 1377(s), 1261(m), 1076(m), 1029(s), 900(s), 804(br, m), 768(m), 756(s), 686(s), 553(m). The reactions were carried out using 0.4–0.5 g (0.21–0.26 mmol) of $NiCp_2$; molar ratio of reactants: $NiCp_2$: PhC≡CPh : LiR = 1 : 50 : 1.1. The yield of polydiphenylacetylene depended on the catalyst used and was as follows: 74%; for {$CpNiCH_3$ · PhC≡CPh}; 59% for {CpNiPh · PhC≡CPh}; 65% for {CpNiC≡CPh · PhC≡CPh}.

Polymerization of phenylacetylene on {CpNiR·HC≡CPh} catalyst (R=CH_3, Ph, C≡CPh)

A solution of organolithium compound (methyllithium, phenyllithium or lithium phenylacetylide) was added to a vigorously stirred solution of nickelocene and phenylacetylene in 15 cm^3 THF cooled to −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for a further 24 h. 80 cm^3 of hexane and 60 cm^3 of 15% aqueous HCl were then added and the mixture was stirred for 3 h at 75–80 °C. Two layers were separated, and 300 cm^3 of methanol was added to the organic layer. An orange polymer precipitated. This was filtered off, washed with methanol and dried. Polyphenylacetylene was characterized by means of FT-IR, ^1H and ^{13}C NMR and MALDI-TOF-MS. FT-IR (KBr; cm^{-1}): 3053(m), 3020(m), 2955(br, s), 2926(br, s), 2854 (s), 1653(s), 1599(s), 1490(s), 1457(s), 1377(s), 1261(s), 1095(br, s), 1026(br, s), 916(m), 881(m), 802(s), 755(m), 696(s).

^1H NMR ($CDCl_3$); δ ppm: 7.25–8.00 broad signal of aromatic protons; 5.87 C=CH; 1.56 CH_3. ^{13}C NMR ($CDCl_3$); δ ppm: 141.4–126.5 aromatic carbon atoms; 131.5 C=$\underline{C}$H; 26.4 CH_3.

The filtrate contained low MW cyclic and linear oligomers of phenylacetylene. The oligomers 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: $NiCp_2$: PhC≡CH : LiR = 1 : 20 : 1.1.

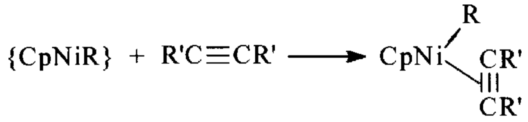
RESULTS AND DISCUSSION

Unstable 16-VE {CpNiR} species is formed in the reaction of nickelocene with organolithium compounds:[1]

$$NiCp_2 + LiR \longrightarrow \{CpNiR\} + LiCp$$

where R = Ph, CH_3,C≡CPh

If the above reaction is carried out in the presence of alkyne, then π-complex {CpNiR · R′C≡CR′} **1** is formed:



$$\{CpNiR\} + R'C\equiv CR' \longrightarrow \overset{R}{CpNi}\begin{matrix}CR'\\ |||\\ CR'\end{matrix}$$

1

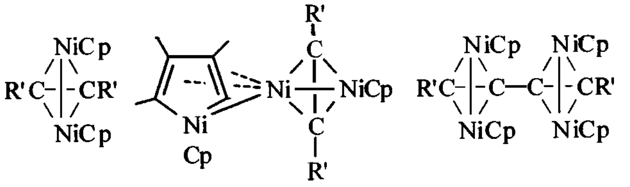
Complex **1** was previously prepared and characterized in the reaction of nickelocene with alkyllithium in the presence of 2-butyne and bis(trimethylsilyl)acetylene at −78 °C.[8]

Table 1. Polymerization of phenylacetylene on {CpNiR · PhC≡CH} catalyst (R=CH_3, Ph, C≡CPh)

		Polymers			Oligomers	
Catalyst	Solvent	Yield (%)	M_w[a]	M_w/M_n[a]	Yield (%)	Cyclic/linear ratio (%)
{$CpNiCH_3$ · HC≡CPh}	THF	58	1105	1.35	17	56/44
{$CpNiCH_3$ · HC≡CPh}	Toluene	53	1124	1.28	24	59/41
{CpNiPh · HC≡CPh}	THF	54	1015	1.54	15	70/30
{CpNiPh · HC≡CPh}	Toluene	48	1078	1.33	21	80/20
{CpNiC≡CPh · HC≡CPh}	THF	47	672	1.30	22	64/36
{CpNiC≡CPh · HC≡CPh}	Toluene	43	853	1.47	27	44/56

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

For a molar ratio of {CpNiR}/R′C≡CR′ ≈ 1/1 complex **1** undergoes transformations upon heating to room temperature to form several cyclopentadienylnickel complexes and clusters depending on the R groups of the alkyne.[9–12] If alkyne is used in the excess, then polymerization, oligomerization and cyclization reactions proceed in good yield at room temperature.



Diphenylacetylene polymerized in the presence of catalyst **1** to form a yellow polymer. The product was separated by filtration, washed with methanol, dried and characterized by means of FT-IR spectrometry. The MW of the polydiphenylacetylene was not determined, owing to the insolubility of the polymer in all commonly used solvents. The reaction could be continued by addition of new portions of the monomer, which is evidence for the living character of the polymerization. The structure of polydiphenylacetylene was established as cis-transoidal based on FT-IR analysis. The bands at 1599, 1377, 1261 and 553 cm^{-1} characteristic for the cis conformation suggested a cis-transoidal configuration of the product.[13]

Polymerization of phenylacetylene, with the same catalysts as above, was carried out for 12 h at room temperature and then a 20% solution of HCl was added to decompose the catalyst and other nickel compounds formed. The reactions mixture was then heated to 75–80 °C for 3 h. The organic layer was separated and an excess of methanol was added. The orange–yellow precipitate was separated, washed with methanol and dried. The filtrate contained a small amount of cyclic and linear phenylacetylene oligomers soluble in the solvent–methanol mixture. The oligomers were identified by GC–MS analysis.

The polymer was characterized by means of FT-IR, ^{1}H, and ^{13}C NMR spectrometry and MALDI-TOF-MS. The spectral analysis showed that the polymer had a mainly trans-cisoidal configuration. This configuration was probably the result of isomerization of initially formed cis-transoidal polymer, during heating of the reaction mixture to 75–80 °C.[14]

Bands at 696, 755, 802, 916 and 1261 cm^{-1} present in the FT-IR spectra are characteristic for *trans*-polyphenylacetylene, and the bands at 881 and 1377 cm^{-1} corresponding to *cis*-conformation suggested the presence of the mixture of trans-cisoidal and cis-transoidal isomers.[15–18]

The presence of cis-transoidal isomers was also confirmed by the appearance of the signals at δ 5.87 ppm in the ^{1}H NMR spectra and at δ 131.5 ppm in the ^{13}C NMR spectra, assigned previously to C=CH and ^{13}C C=$\underline{C}$H respectively.[14,16] The MW and end groups of the polyphenylacetylene were determined by means of MALDI-TOF-MS.

The MALDI-TOF-MS spectrum of polyphenylacetylene formed in the presence of {CpNiC≡CPh · CH≡CPh} catalyst is presented on Fig. 1. Three sets of signals corresponding to phenylacetylene polymers were present in the spectrum. The mass difference in each set was 102, which corresponded to the MW of the monomer. The most intense set of signals corresponded to polymers with two –C≡CPh or two hydrogen atoms as end groups; the average MW was 817. The second set of signal (average MW 831) exhibited

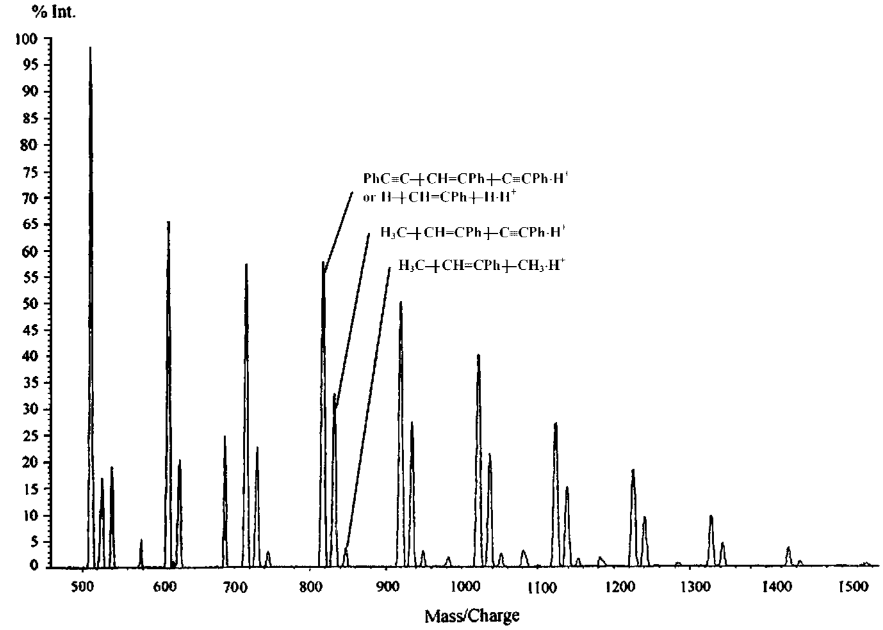


Figure 1. MALDI-TOF spectrum of polyphenylacetylene (nickelocene and lithium phenylacetylide catalyst).

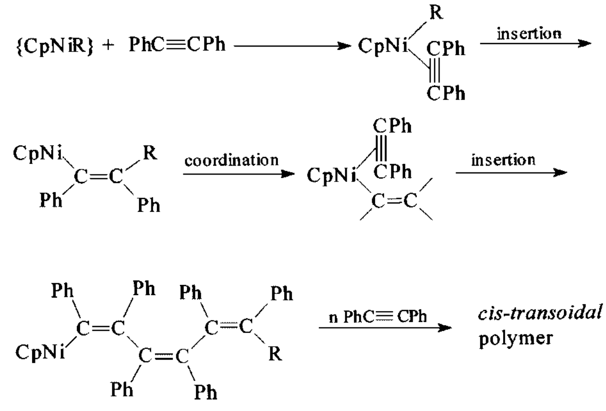
–C≡CPh and CH_3 as end groups, and the third set (average MW 847) had two methyl groups as end groups. All three sets of signals appeared as adducts with H^+. The MW range corresponded to 5–15 phenylacetylene molecules in chains.

The MALDI-TOF-MS spectrum of polyphenylacetylene ({$CpNiCH_3 \cdot CH{\equiv}CPh$} as catalyst) exhibits three sets of signals corresponding to phenylacetylene polymers with various end groups. The most intense set corresponded to polymers with two hydrogen atoms as end groups (adduct with H^+, average MW 716). The second set, with average MW 731, corresponded to polymers with a methyl group and hydrogen as end groups (adduct with H^+), and the third set (average MW 774) corresponded to polymers with a hydroxy group and hydrogen as end groups (adduct with K^+). All fractions contained from 4 to 12 phenylacetylene molecules in chains.

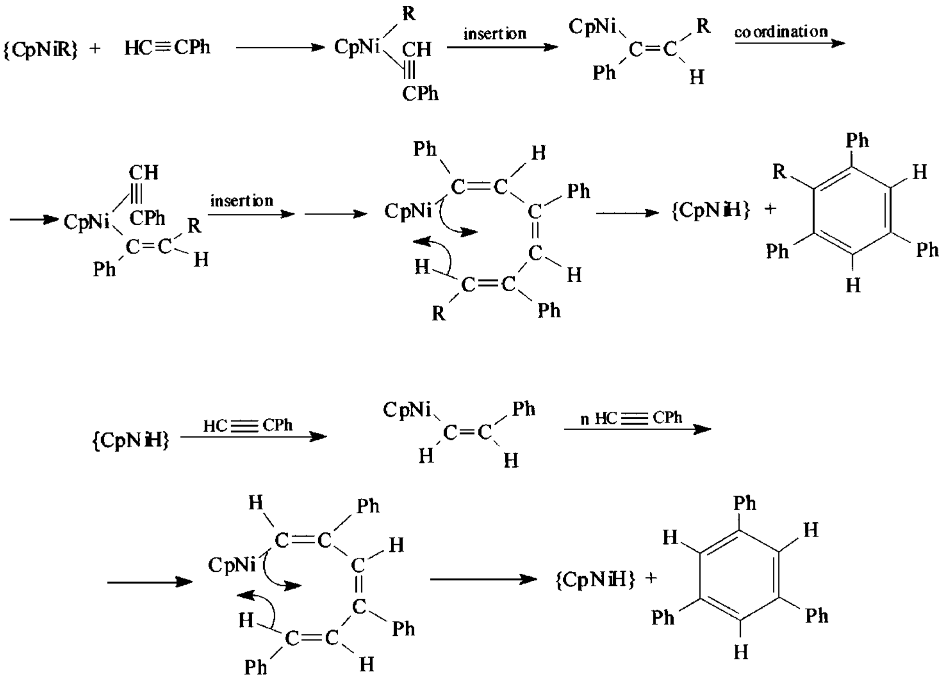
The MALDI-TOF-MS spectrum of polyphenylacetylene ({$CpNiPh \cdot CH{\equiv}CPh$} as catalyst) exhibited four sets of signals. The most intense signals corresponded to polymers with two hydrogen atoms as end groups (average MW 613, adduct with H^+). The MW was in the range corresponding to 3–13 phenylacetylene molecules in the chain. The three remaining sets of signals had much lower intensity. The first of them (average MW 600, adduct with K^+) had two phenyl end groups and contained from four to nine phenylacetylene molecules in the chain. The second set (average MW 626, adduct with K^+) corresponded to the polymer with phenyl and hydrogen as end groups, containing from 3 to 11 molecules of phenylacetylene. The least intense set of signals corresponded to the polymer with the hydroxy group and hydrogen as end groups (average MW 672, adduct with K^+).

The above results suggest that polymerization of phenylacetylene in the presence of nickelocene-based catalysts led to the formation of linear polymers containing from 4 to 14 phenylacetylene molecules and of cyclic (mainly benzene derivatives) and linear oligomers (see Scheme 2). MALDI-TOF-MS measurements showed that the polymers formed contained the following end groups: R, derived from the catalyst used; H, from {CpNiH} formed in the course of the reaction; OH, introduced during hydrolysis of the reaction mixture.

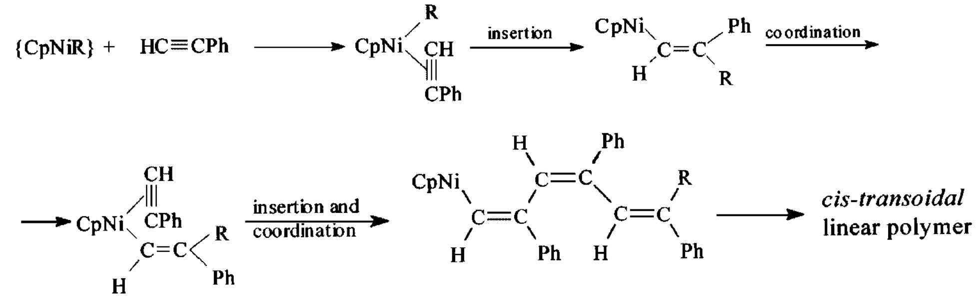
As the structure of the catalytic complex is known, we were able to propose the mechanism of polymerization and cyclization of the monomers investigated on the basis of the reaction products formed, GPC and MALDI-TOF-MS data.



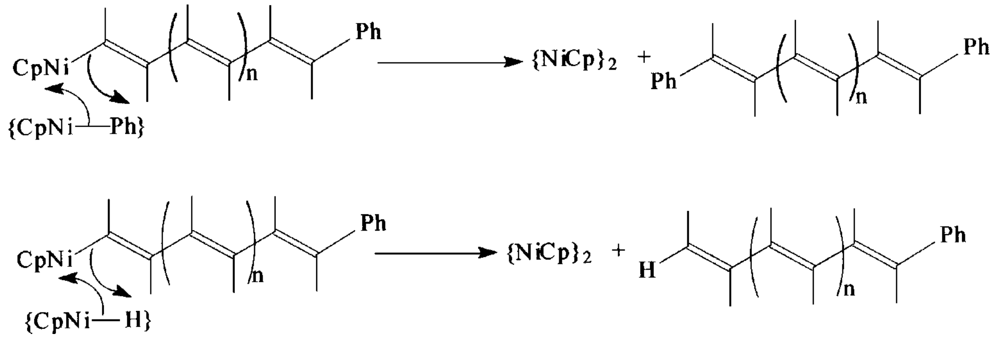
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

Polymerization of diphenylacetylene on cyclopentadienylnickel catalyst proceeded according to a well-known coordination–insertion mechanism, leading to high-molecular polymer regardless to R-group present in the catalyst (Scheme 1).

Phenylacetylene reacted similarly, but in this case both linear polymers and cyclic trimers were formed. The mechanism of cyclization with the formation of benzene derivatives is presented in Scheme 2.

Whether the cyclic trimer is formed is determined by the mode of the first insertion step. If the first phenylacetylene molecule inserts then that hydrogen and R group are bonded to the terminal carbon atom and the conformation of the 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 the mode of the first insertion step (Scheme 2).

If the first insertion step occurs as shown in Scheme 3, then only linear polymers are formed.

Based on MALDI-TOF-MS analysis, we have found that linear polymers of phenylacetylene contained R as end groups, with R being dependent on the {CpNiR} catalyst used (R=CH_3, Ph, C≡CPh). The other end groups were OH and H. For example, in polymerization of phenylacetylene on {CpNiPh} the end groups were hydrogen and phenyl. This could be explained by coupling of the growing chain with phenyl or hydrogen from catalysts {CpNiPh} or {CpNiH} (Scheme 4).

The above coupling reactions led to the formation of $(NiCp)_n$ compounds 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.

Acknowledgements

We thank the Ministry of Scientific Research and Information Technology for financial support of this work (grant no. 4 T09A 012 25).

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