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Reactivity of isopropenylacetylene, H—C≡C—C(CH_3)=CH_2, in the presence of the complex [Ni(NCS) {C≡C—C(CH_3)CH_2}(PPh_3)$_2$]

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The reactivity of isopropenylacetylene (IP) in the presence of [Ni(NCS){C≡C—C—(CH_3)=CH_2} (PPh_3)$_2$] has been examined. 1,2,4-Tris(isopropenyl)benzene (1,2,4-TIB), two isomeric tetramers formed by reaction of 1,2,4-TIB with IP, and polymeric fractions have been separated and characterized by IR, NMR and mass spectra. Stability of reaction products towards oxygen and humidity has also been investigated.

Keywords: Isopropenylacetylene, tetramers, polymers, nickel(II) catalysts

INTRODUCTION

For many years nickel complexes have been known to be active catalysts for the polymerization of acetylene[1–3] and the oligomerization or polymerization of substituted acetylenes;[2–5] cyclization reactions can also occur, giving rise to various cyclic polyenes.[6]

In preceding investigations we have examined the catalytic activity of a series of [NiX_2L_2] complexes (X = halogens, NCS; L = phosphine) in reactions with phenylacetylene[7] and 2-methylbut-3-yn-2-ol;[8] we have compared the activity of the above-mentioned catalysts with one of a series of [Ni(NCS)(C≡C—R)L_2] complexes (L = PPh_3, PBu_3),[9] which were prepared by us[10] in order to investigate influence of the pre-existence of Ni–C σ-bonds on the catalytic activity of such complexes. The nickel monoacetylides were found to be more active than the corresponding [NiX_2L_2] complexes. Polymers, cyclic trimers or linear oligomers were obtained, depending mainly on the R group of the H—C≡C—R monomer; for instance, 2-ethynylcyclohexan-1-ol (H—C≡C—$C_6H_{10}OH$) gave a linear trimer[11] while isopropenylacetylene [H—C≡C—C(CH_3)=CH_2] gave a polymer (PIA)[12] (see below).

Interest in the synthesis of polymers analogous to polyacetylene has increased markedly in the last few years owing to their peculiar electrical properties. Also recently, catalysts obtained from η-allylmetal nickel complexes were tested by other authors for the preparation of polyphenylacetylene.[13]

We have found that the conductivity of undoped and iron(III) chloride ($FeCl_3$)-doped polyphenylacetylene (PPA) and polyisopropenylacetylene (PIA) increases with increase of relative humidity.[14] These polymers might therefore find a practical application in the preparation of humidity sensors.

Both PPA and PIA are soluble polymers, whilst the majority of conducting polymers such as polyacetylene, polythiophene and polyaniline are unsoluble in most organic solvents, exhibit low processability and are rather difficult to characterize. The structural characterization of conducting polymers is an important tool because some fundamental aspects, such as the importance of π delocalization, the planarity of conjugated systems, the role of crosslinking between different chains and the interactions with oxygen, are not completely defined yet.

Therefore, we considered it interesting to investigate in more detail the polymerization reactions of isopropenylacetylene (IP) carried out in the presence of nickel complexes which give the polymer PIA and related oligomers. We have studied the low-molecular-weight soluble fractions because small molecules, correlated to monomers which give rise to polymerization reactions, are suitable model compounds for the study of the polymer structure.[15] An aspect of this work is the investigation of the reaction mechanism that involves IP and nickel(II) complexes, leading to the formation of a cyclic trimer, isomeric tetramers and oxidized polymer fractions. The reaction mechanism that is proposed should give a better insight into the problem of monomer enchainment for monosubstituted acetylenes.

EXPERIMENTAL

Apparatus

IR spectra were run on Perkin–Elmer model 577 or model 580B spectrophotometers. Molecular weights were measured on an Knauer model 11 osmometer at 60°C in dioxane. Mass spectra were carried out with an H.P. 5930 A MS spectrometer. NMR spectra were run on C-60 JEOL and on W.P. 80 SY Bruker spectrometers. Gas-chromatographic analyses were carried out on a Perkin–Elmer model 900 gas chromatograph by using columns of 2 m, i.d. 2.5 mm, filled with SE 30 silicon grease at 10% on Chromosorb 60/80 mesh. For the chromatographic separations of reaction mixtures, columns of 60 cm, i.d. 4 cm, filled with Merck 70/230 mesh ASTM silica were used.

Reagents

Reagent-grade solvents were used without further purification. Isopropenylacetylene (IP, Fluka) was distilled under vacuum before use. Nickel complexes were prepared according to literature methods.[10]

Reaction procedures

(a) Reactions in benzene

In 15 cm^3 of benzene, 200 mg of complex $[NiX_1X_2L_2]$, $[(X_1 = X_2 = NCS, Cl; L = PBu_3, PCy_3, PPh_3;\ X_1 = NCS;\ X_2 = C{\equiv}C{-}C(CH_3){=}CH_2]$, $L = PBu_3]$ and 5 cm^3 of IP (density 0.68 g l^{-1}, 3.4 g, 51 mmol) were refluxed for different periods, depending on the activity of the catalysts (see Table 1). The amount of the unreacted IP was determined by gas-chromatographic analysis under the following conditions:

Injector/column/detector temperatures, 60/30/60°C;

Carrier gas nitrogen, 1 dm^3 h^{-1};

Standard, methyl tertiary butylether.

Table 1 Reaction of isopropenylacetylene in the presence of nickel complexes. Reactions in benzene at reflux; catalyst/monomer ≈ 1 : 100

Complex	Time (h)	Unreacted monomer (%)
$[NiCl_2(PPh_3)_2]$	20	69
$[Ni(NCS)_2(PPh_3)_2]$	17	78
$[Ni(NCS)_2(PBu_3)_2]$	20	72
$[Ni(NCS)_2(PCy_3)_2]$	23	56
$[Ni(NCS)(C{\equiv}C{-}R)(PBu_3)_2]^a$	21	58
$[Ni(NCS)(C{\equiv}C{-}R)(PPh_3)_2]^a$	1	Traces

[a] $R = {-}C(CH_3) = CH_2$

(b) Reactions in bulk

Portions of 100 mg of complexes $[NiX_1X_2L_2]$ were added to 10 cm^3 of IP (b.p. 36°C) and the mixtures were refluxed. The complexes are insoluble in the monomer and no reaction occurred even after long reaction periods.

(c) Reactions in the presence of the complex $[Ni(NCS)\{C{\equiv}C{-}C(CH_3){=}CH_2\}(PPh_3)_2]$ (complex A)

To 60 cm^3 of benzene 500 mg 1.13 mmol) of complex **A** and 20 cm^3 (13.6 g, 0.21 mol) of IP were added. The mixture was refluxed for 1 h and the gas-chromatographic analysis revealed the complete conversion of IP. At this stage two different procedures were followed:

Procedure (i)

The reaction solvent was removed under vacuum and the oily brown residue was chromatographed on a silica column (see below) by using n-hexane, benzene and methyl t-butyl ether as eluents.

The gas-chromatographic analyses of the eluted fractions were carried out in the following conditions:

Carrier gas nitrogen, 3 dm^3 h^{-1};

Injector/column/detector temperatures:

(1) Fractions eluted with n-hexane: 180–200/160/190–220°C;
(2) Fractions eluted with benzene: 200–220/180/210–230°C.

The first fraction eluted with n-hexane (designated ES, yield about 30% on the monomer) and the second fraction eluted with benzene (**B**) were purified by subsequent chromatography on silica columns until single peaks were found in the gas chromatograms. By evaporation of solvents, liquid products ES and **B** were obtained. In the fractions eluted by methyl t-butyl ether no peak could be observed in the gas chromatograms even by increasing the injector and column temperatures. The elimination of solvent under vacuum gave brown vitreous films.

Procedure (ii)

After removal of the reaction solvent under vacuum, n-hexane or methanol was added to the oily brown residue; a yellow polymeric powder (PIA) separated. From the filtered solution further solid products were obtained. The total yield of solids was about 70% on the monomer.

Hydrogenation reactions of B

In a typical experiment 700 mg of **B** was dissolved into 50 cm^3 of dioxan (dried on sodium and distilled under nitrogen) and 50 mg of PtO_2 was added.

In 3 h, 145 cm^3 of hydrogen (under normal conditions) were adsorbed. The reaction products were chromatographed on a silica column. By elution with chloroform two fractions were separated: in the first one the unreacted **B** and in the second one the hydrogenated **B** (HB, see below) were present.

RESULTS AND DISCUSSION

Reactions with various catalysts were carred out in benzene (Table 1) and in bulk. No reaction occurred in bulk owing to the low solubilities of the various complexes in the monomer and to the low boiling point of IP (36°C). In the reactions carried out in benzene the best results were obtained in the presence of the complex $[Ni(NCS)(C{\equiv}CR)(PPh_3)_2]$ (**A**).

We therefore examined in detail the reactivity of isopropenylacetylene (IP) in the presence of complex **A**.

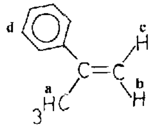
Characterization of reaction products

(a) Fraction eluted with n-hexane (ES)

The product ES eluted with n-hexane was found to be 1,2,4-tris(isopropenyl)benzene (TIB). Analysis: ($C_{15}H_{18}$) Calcd: C, 90.91; H, 9.09; Found: C, 90.85; H = 8.85%. MW (osmometric), 198 a.m.u.

UV and IR spectra are consistent with the literature.[16]

The ^{1}H NMR spectrum (Fig. 1(a)) of 1,2,4-tris(isopropenyl)benzene (1,2,4-TIB) is characterized by a signal at 2.05 ppm (9H, CH_3 groups) two multiplets at 5.1 and 5.35 ppm (6H, CH_2 groups) and a series of signals at δ = 7.2–7.35 ppm (3H, protons of the benzene ring). For comparison we have carried out also the spectrum of 1,3,5-tris(isopropenyl)benzene (1,3,5-TIB)[16] (Fig. 1(b)). The spectrum is consistent with the higher symmetry of the molecule. It can be interpreted similarly to that of α-methylstyrene:[17]



δ_H(ppm): a = 2.10, b = 5.01, c = 5.31, d = 7.10–7.52

The ^{13}C spectrum of 1,2,4-TIB is given in Fig. 1(c). Here are two signals at 21.8 and 23.9 ppm (CH_3 groups), two signals at 112.3 and 115.3 ppm ($=CH_2$ groups), and three signals at 124.5, 126.2, 129.9 ppm (CH of benzene ring). The six signals between 140.4 and 147.1 ppm are typical of the quaternary carbon atoms of the ring and of the isopropenyl groups.

The ^{13}C NMR spectrum carried out by the DEPT (Distortionless Enhancement by Polarization Transfer) technique confirms the previous attributions (Fig. 1(d)).

(b) Fraction eluted with benzene (B)

After four subsequent chromatograph runs with benzene on a silica column, the gas-chromatographic analysis showed a single peak for the fraction **B**.

The elemental analysis of **B** is consistent with the formula $(C_5H_6)_n$ (Found: C, 89.83; H, 9.81%).

In the mass spectrum the molecular peak is at 264, corresponding to four monomer units. The fragmentation of **B** (Table 2) gives the highest peak at 198, i.e. at a value corresponding to the mass of a trimer of isopropenylacetylene; by considering that the fragmentation of **B** below 198 is very similar to the one of 1,2,4-TIB, we can assume for **B** the structure of a tetramer obtained from the reaction of cyclic 1,2,4-TIB with one more molecule of the monomer.

The IR spectrum of **B** is given in Fig. 2(a). The bands at 2100–2200 cm^{-1} can be assigned to stretching vibrations of $C{\equiv}C$ groups and the band at 3300 cm^{-1} to stretching vibrations of ${\equiv}C{-}H$ groups. The UV spectrum of **B** (not shown) exhibits a maximum at 253 nm and two

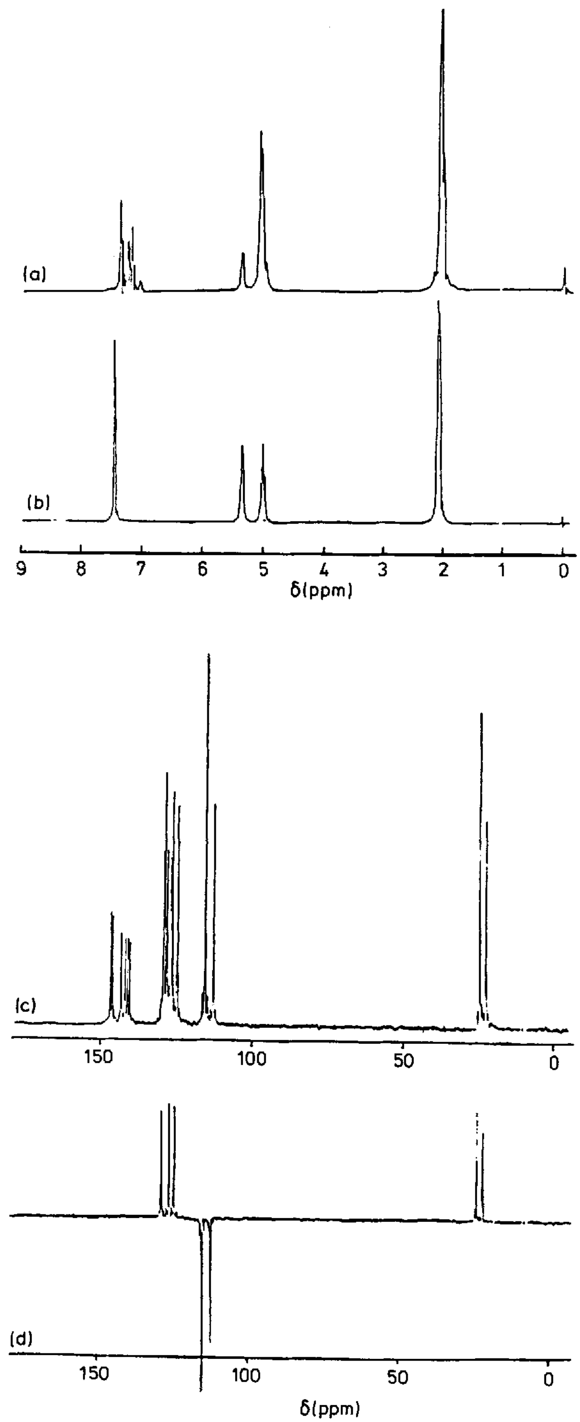


Figure 1 NMR spectra (reference TMS for ^{1}H NMR). (a) ^{1}H NMR of neat 1,2,4-TIB; (b) ^{1}H NMR of neat 1,3,5-TIB; (c) ^{13}C NMR of 1,2,4-TIB in C_6D_6; (d) ^{13}C NMR DEPT of neat 1,2,4-TIB.

Table 2 Relative abundances of the *m/z* peaks[a] from the mass spectra of 1,2,4-tris(isopropenyl)benzene (1,2,4-TIB), of fraction **B** and hydrogenated **B** (HB)

m/z	1,2,4-TIB	**B**	HB
39	20.8	13.3	13.7
41	21.2	9.0[b]	28.7
43	—	—	46.0
45	—	—	25.2
50	—	12.9	2.0
51	10.7	15.5	3.4
52	—	10.7	—
55	—	—	18.3
63	11.9	5.9	3.1
73	—	—	19.2
77	11.2	24.8	4.2
91	12.8	6.0	18.7
115	37.6	8.9	9.1
127	14.6	4.4	3.9
128	46.2	14.5	11.6
129	18.7	6.5	7.8
139	10.4	3.2	1.7
141	42.5	13.5	11.7
142	40.8	12.7	12.1
143	44.8	10.4	29.2
152	26.4	12.9	6.3
154	14.2	12.1	5.1
155	62.3	17.1	9.5
157	11.5	5.8	42.2
165	16.0	19.3	7.6
167	—	12.9	6.8
168	30.9	8.1	4.3
183	100.0	66.5	7.9
184	—	10.4	2.7
185	—	1.5	16.1
198	62.4	100.0	8.1
199	—	16.8	20.5
200	—	1.9	100.0
264	—	15.7	—
270	—	—	20.1

[a] In general, values of relative abundance higher than 10% have been reported. [b] Values of relative abundance lower than 10% have been reported by comparison between the three spectra.

inflections at 280 and 300 nm, suggesting a conjugated π-system in the molecule.

The ^{1}H NMR spectrum, however, exhibits slightly resolved multiplets which can indicate that the fraction **B** is not a single product but rather a mixture of isomers. The signals are in the range 0.76–2.10 ppm, at 4.95–5.20 ppm and at 7.20 ppm (Fig. 3(a)). The integrals of the signals at 4.95–5.20 and 7.20 ppm are in a 1:1 ratio; those of the signals at 0.76–2.10 ppm and

7.20 ppm are in a 2 : 1 ratio. The great number of signals in the ^{13}C NMR and ^{13}C DEPT NMR spectra (Fig. 3(b), (c)) also confirms the hypothesis of the presence of isomers. The signals at $\delta_C = 32.7$, 34.2 and 52.2 ppm, which are negative in the DEPT spectrum, must be related to saturated CH_2 groups. The signals at $\delta_C = 91.8$ and 69.02 ppm can be assigned to a $C{\equiv}C{-}H$ group (see the IR spectrum). From these spectral data we suggest for the components of the fraction **B** two different structures, **B I** and **B II** (Fig. 4), due to a reaction with hydrogen transfer between 1,2,4-TIB and isopropenylacetylene.

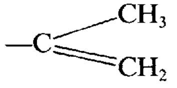
Hydrogenation reaction of fraction **B**

In the hydrogenation reactions of **B** about 2–3 mol of hydrogen per mole of **B** (considered as a mixture of two isomers) was adsorbed. The hydrogenated mixture, chromatographed on Florisil, eluent chloroform gave unreacted **B** and the hydrogenation products of **B** (HB). The mass spectrum of HB exhibits a molecular peak at 270, i.e. 3 moles of hydrogen had reacted with **B**. The most intense peak is at 200. These results can be interpreted assuming that the hydrogenation reactions occur on the chains of **B I** and **B II** (Fig. 4), which are derived by reactions between isopropenylacetylene and one of the isopropenyl groups of 1,2,4-TIB; no hydrogenation takes place to the other isopropenyl groups of **B I** and **B II**. In fact the fragmentations below 200 correspond to the mass spectrum of 1,2,4-TIB (Table 2).

(c) Fraction eluted with methyl t-butyl ether (ET)

After the complete elution of fraction **B**, methyl t-butyl ether separates a yellow band, from which, after evaporation of the solvent under vacuum, a solid (ET) is obtained. ET is soluble in acetone and can be precipitated as a yellow powder by addition of methanol.

The IR and ^1H NMR spectra are given in Figs. 2(b) and 3(d). As in the ^1H NMR spectra of fraction **B**, broad signals are observed which indicate the complexity of the structure of ET. The molecular weight (osmometric) of ET was found to be about 2000. The elemental analysis was: C, 74.07; H, 7.64%, nearly corresponding to a general formula $(C_5H_6O)_n$ (Calcd. C, 73.17; H, 7.32%). We think therefore that ET is an oxidized polymer of isopropenylacetylene. Isopropenylacetylene is probably in part linearly polymerized in the presence of the $[Ni(NCS)\{C{\equiv}C{-}C(CH_3){=}CH_2\}(PPh_3)_2]$ complex as it was observed by us in analogous reactions with other monosubstituted acetylenes.[9,12] The presence of



pendant groups on the main chain renders the polymer very reactive and reactions with oxygen, water, 1,2,4-TIB or **B I** and **B II** can occur. In fact bands at 1680–1720 cm^{-1} are due to stretching vibrations of $C{=}O$ groups; OH groups must be responsible of the broad band in the range 3200–3600 cm^{-1}; the signals at about 7–7.5 ppm in the ^1H NMR spectrum indicate the presence of cyclic structures in ET.

Products similar to ET are obtained as solid fractions (PIA) directly from the reaction mixture if the reaction solvent is removed under vacuum and n-hexane is added (see the Experimental section). If the solutions are maintained in the air, and the precipitation procedure is repeated, new fractions of PIA separate from the solution, probably because oxidation and crosslinking reactions decrease the solubility of pristine products. The IR spectrum obtained with this procedure is given in Fig. 2(c). The spectrum is similar to that of ET. The elemental analyses of the various fractions of PIA are in the range C, 61–65; H, 6–6.5%. These values indicate a deep oxidation of the starting products.

Only small amounts of 1,2,4-TIB and **B I** and **B II** could be identified, when the reaction mixtures were treated as reported above. Therefore 1,2,4-TIB and **B** are involved in further reactions (oxidation and crosslinking) if the reaction mixture is maintained in the air for long periods.

Investigation of the stability of 1,2,4-TIB and B

1,2,4-TIB was maintained in a sealed NMR tube for two months and no variation of the ^1H NMR spectrum was observed. However, we observed a continuous variation of the IR spectra of 1,2,4-TIB samples maintained *in the air* at room temperature for the same period. After two months the product is viscous. The IR spectrum (Fig. 2(d)) reveals intense absorptions in the range 1600–1800 cm^{-1} as well as in

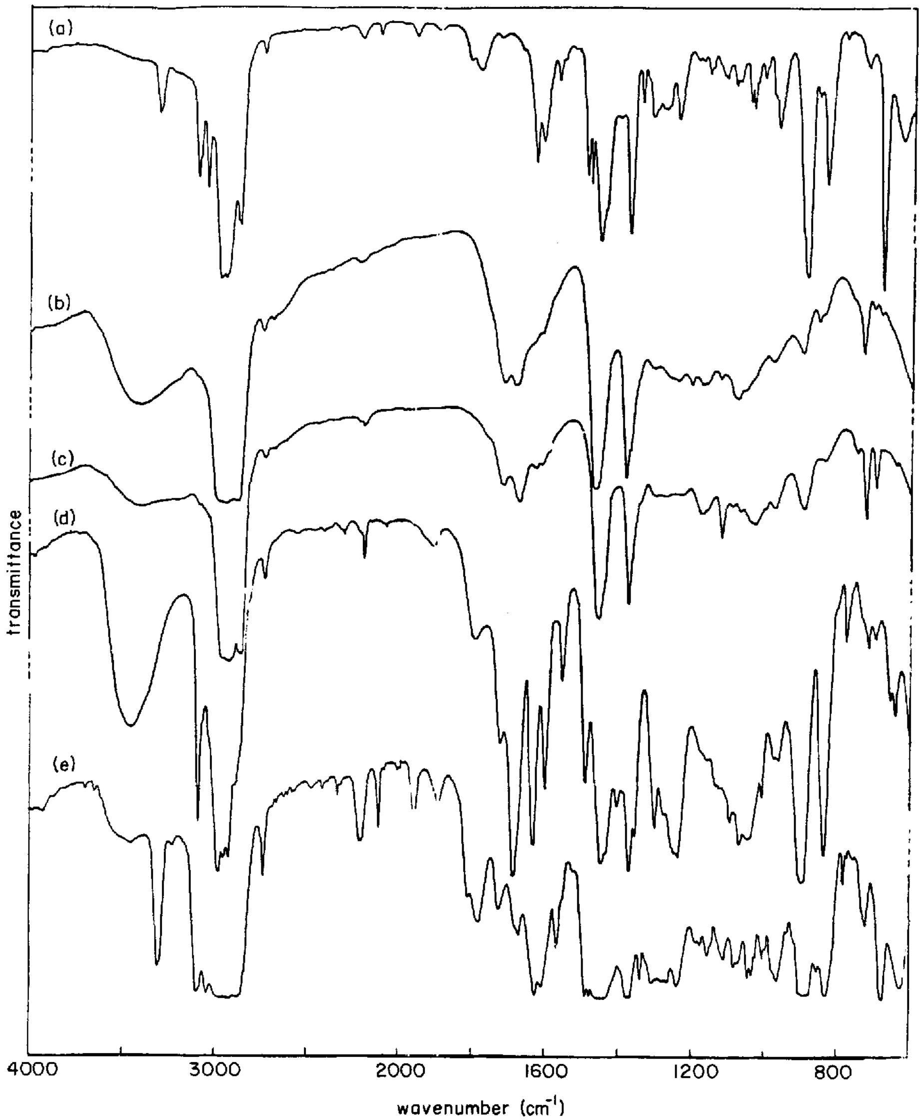


Figure 2 IR spectra (nujol mulls): a, fraction **B**; b, fraction ET; c, solid fractions PIA obtained by direct precipitation with n-hexane from the reaction solution; d, 1,2,4-TIB after exposure to the air for two months; e, fraction **B** after exposure to the air for two months.

the range 3400–3500 cm^{-1}. 1,2,4-TIB undergoes a spontaneous oxidation and crosslinking reaction which increases its viscosity. Water is also involved in these reactions, probably by addition to the double bonds (bands at 3400 and 3500 cm^{-1} in the IR spectrum); alcoholic groups are formed, which can then give rise to intermolecular etherification reactions. Bands in the 1060–1150 cm^{-1} region are characteristic of —CH$_2$—O—CH$_2$-groups in aliphatic ethers; adsorptions at 1070–1140 cm^{-1} are present in spectra of cyclic ethers and bands at 1250 cm^{-1} are observed in the IR spectra of products containing epoxy groups; C=O groups of ketones and aldehydes absorb in the range 1600–1800 cm^{-1}. Bands in these regions of the spectrum of oxidized 1,2,4-TIB indicate that isopropenyl groups interact with oxygen and moisture giving rise to various oxidized species.

The elemental analysis of 1,2,4-TIB maintained

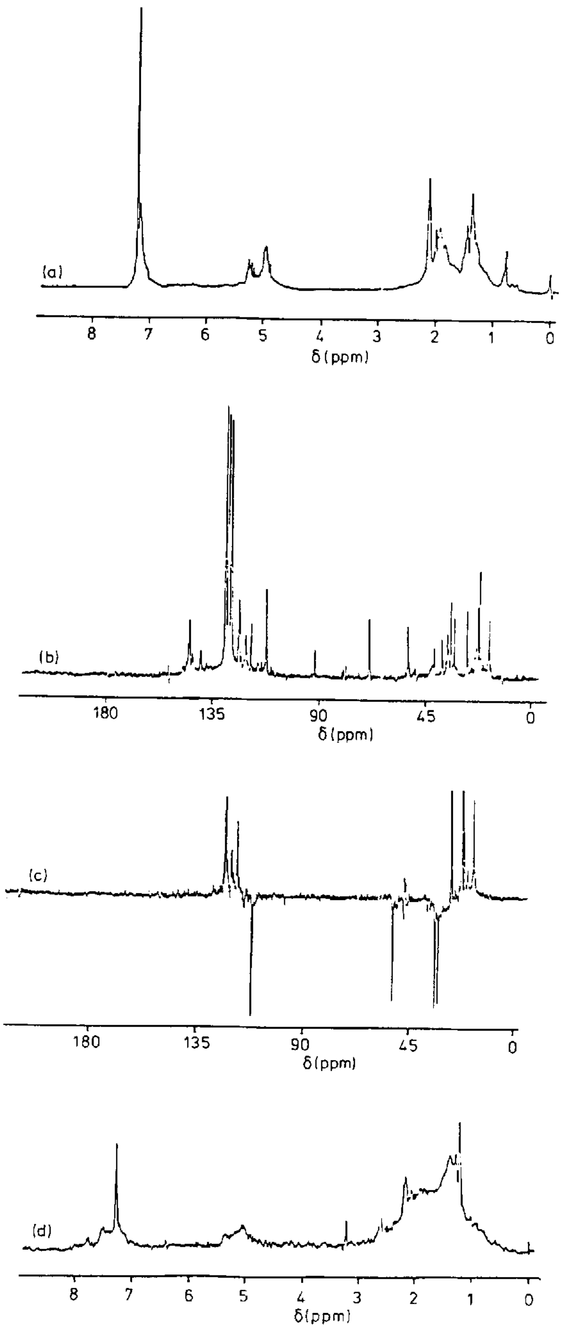


Figure 3 NMR spectra (reference TMS for ^1H NMR). (a) ^1H NMR of fraction **B** in CCl_4; (b) ^{13}C NMR of fraction **B** in C_6D_6; (c) ^{13}C NMR DEPT of neat fraction **B**; (d) ^1H NMR of oxidized polymer ET in CCl_4.

in the air for several months was C, 72.92; H, 7.37%. This corresponds to the addition of three oxygen atoms to each 1,2,4-TIB molecule.

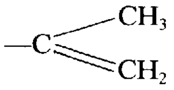
After several months, 1,2,4-TIB becomes a transparent glasslike solid, insoluble in the common organic solvents.

The mixture of **B I** and **B II** (**B**) exhibits an analogous behaviour. It is stable in an inert atmosphere for a few months at room temperature. In the air, addition of water and oxidation takes palce and **B** becomes viscous and then a glasslike solid as for 1,2,4-TIB. The IR spectrum of a viscous sample of **B** after two months is given in Fig. 2(e) (Analysis: C, 76.44; H, 7.73%, in agreement for the formula $C_{20}H_{24}O_3$). 1,2,4-TIB and **B** are stable for long periods at −40°C.

CONCLUSIONS

In the reactions with IP the complex $[Ni(NCS)\{C{\equiv}C{-}C(CH_3)CH_2\}(PPh_3)_2]$ is more active than the complex $[Ni(NCS)_2(PPh_3)_2]$, as was previously seen for phenylacetylene.[9]

The induction period is reduced and probably the growth of the chain takes place by insertion of the molecules of IP into the Ni–C σ-bond. A *cis–cis*oidal orientation of the growing chain leads to the formation of the cyclic trimer: the unsymmetrical isomer is formed and no 1,3,5-tris (isopropenyl) benzene was identified among the reaction products. This seems to be a general trend in nickel(II)-catalysed reactions; also for phenylacetylene in the presence of a similar catalytic system we found that the 1,2,4-isomer was the major product.[9] The suggested reaction mechanism which leads to 1,2,4-TIB and tetramers **B I** and **B II** is given in Fig. 4. The molecules of IP can be coordinated to the metal in the intermediate stages throughout the triple bond, giving 1,2,4-TIB (Fig. 4, stages a, b, c, d). However, the π-coordination to nickel of a



$$-C(CH_3){=}CH_2$$

group of a monomer molecule can activate an interaction between this double bond and the double bond of the third monomer unit in the growing chain. Also, in this case, ring closure occurs giving a 1,2,4-substituted benzene; hydrogen transfer from C_2 to C_4 (solid arrow) or from C_3 to C_1 (broken arrow) with subsequent bonding between C_2 and C_3 (stage e), leads to the formation of isomers **B I** and **B II**. Hydrogen transfer reactions of olefins are known to occur in

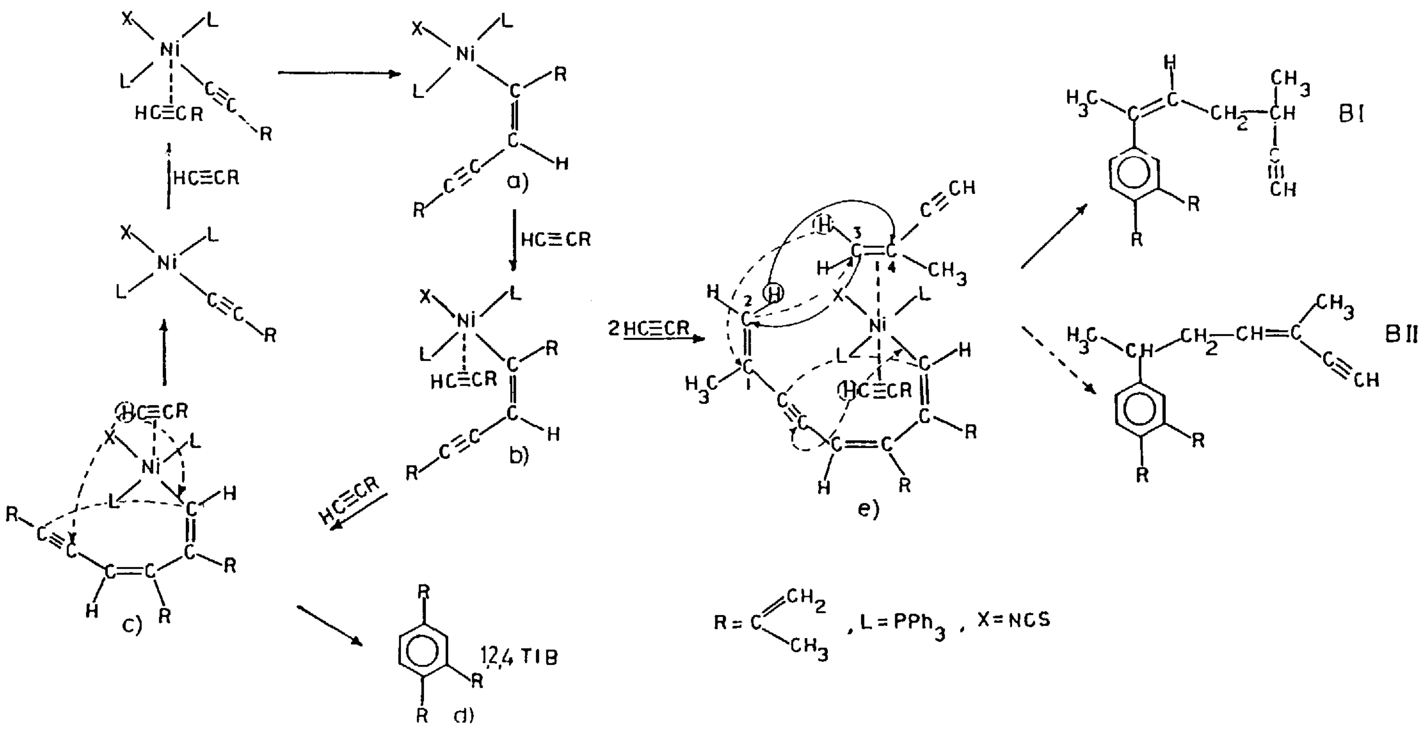


Figure 4 Proposed reaction mechanism.

palladium-mediated processes of olefin dimerization or trimerization with diphenylacetylene.[18] Therefore the products obtained here in the reactions of IP are not only cyclic trimers, and linear polyene polymers, as we have observed in reactions with other monosubstituted acetylenes.[9]

The presence of unsaturated radicals bonded to the benzene ring or as pendant groups in the polyenic chain renders the reaction products more reactive than similar products obtained with other monosubstituted acetylenes.

Despite oxidation and crosslinking when PIA is doped with iodine (75% w/w) or with $FeCl_3$ (50% w/w), its conductivity increases from $10^{-12}\,\Omega^{-1}\,cm^{-1}$ (undoped PIA) to $\sim 10^{-4}\,\Omega^{-1}\,cm^{-1}$.

This study shows the complexity and variety of products that can be obtained from a single catalytic polymerization reaction. Although in this case the structure of some oligomers (tetramers) could be elucidated, further investigations are needed for a better insight of the polymer structure. However we have demonstrated that an increase in conductivity can be observed also when oxidized polymer materials are doped and humidity can be considered in some cases as a doping species, as we have stated in our previous investigations.[14]

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