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Poly(*N*,*N*-dimethylpropargylamine): a π-conjugated polymer as macromolecular ligand

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The reaction between *N*, *N*-dimethylpropargylamine (DMPA) and a Ni(II) complex $Ni(NCS)_2(PPh_3)_2$, leads to the formation of a π-conjugated polymer (PDMPA) and to the interaction of the nickel atom of the complex with the nitrogen atoms of the pendent groups; a polymer–metal complex, PDMPA–Ni(II), is obtained. Reactions have been carried out using various complex/monomer molar ratios: the yield of the reaction and the nickel content of the polymer–metal complexes increase by increasing the amount of $Ni(NCS)_2(PPh_3)_2$. Reactions of DMPA with a Rh(I) complex have also been studied for comparison; this catalyst induces only the linear polymerization of the monomer. The structure of PDMPA and of its complexes with Ni(II) has been studied by means of infra-red, nuclear magnetic resonance and X-ray photoelectron spectroscopies; a change in the stereochemistry of nickel, passing from $Ni(NCS)_2(PPh_3)_2$ to the PDMPA–Ni(II) complexes, has been demonstrated.

(Keywords: polymer–metal complexes; π-conjugation; macromolecular ligand)

INTRODUCTION

Polymer–metal complexes have attracted the interest of a great number of researchers; the thermodynamics of polymer–metal complex formations and their ligand exchange reactions have been widely studied. The catalytic and electrochemical properties of these materials have been investigated and they have also been used to simulate metal-containing enzymes[1,2]. A lot of work has been done on phtalocyanine-type systems[3].

π-Conjugated polymers and, particularly, polymers analogous to polyacetylene have been studied owing to their electrical properties, which make them promising materials for molecular electronics. Akopyan and co-workers, for instance, studied the polymerization of many propargyl derivatives[4] obtaining semiconductive paramagnetic polymers. They also synthesized some dipropargyl- and monopropargyl-amines[5]; in the latter case, linear polymers were obtained. Some poly(mono-substituted) acetylenes show reversible and reproducible changes in their electrical conductivity when they are exposed to vapours of various chemical substances; polyphenylacetylene, for example, has been used to prepare resistive-type[6,7] or surface acoustic waves (SAW)-type[8] humidity sensors.

Recently, some complexes between polymers having a π-conjugated backbone and various metals have been prepared and their electrical and optical properties have been studied. Agh-Atabay *et al.*[9] reported the preparation of cobalt complexes with two different soluble poly-diacetylenes, in which the metal coordinates the polymer through the triple bonds of the polymeric chain; the polymer–metal complexes showed third-order non-linear optical properties. Nishihara *et al.*[10] prepared organo-metallic π-conjugated polymers by reacting alkyl-substituted polyphenylenes with molybdenum and chromium carbonyl complexes; coordination of the metal atoms to the benzene rings of the polymeric chains led to the formation of arene–metal complexes, and the metal-containing polymers showed a higher conductivity than the pristine materials.

This paper describes the preparation and characterization of a new polymer–metal complex, PDMPA–Ni(II), formed by a π-conjugated polymer having an amine function in the pendent group, poly(*N*,*N*-dimethylpropargylamine) (PDMPA) and Ni(II).

EXPERIMENTAL

Materials

All the solvents were reagent grade (Carlo Erba) and were used without any further purification, except the toluene used for the polymerization reactions, which was dried over P_2O_5 and distilled before use.

N,*N*-Dimethylpropargylamine (Fluka) was freshly distilled before use.

$Ni(NCS)_2(PPh_3)_2$ was prepared by the published method[11]; $[Rh(cod)Cl]_2$ (Fluka) is a commercial product and was used without further purification.

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Table 1 Reactions of DMPA with Rh(I) complexes

Catalyst	Catalyst/monomer ratio	Solvent	Reaction time (h)	Yield[a] (%)
$[Rh(cod)Cl]_2$	1:80	C_6H_6	8	25
$[Rh(cod)Cl]_2$	1:200	bulk	7	10
$[Rh(cod)Cl]_2$	1:80	$C_6H_5CH_3$	20	20
$[Rh(cod)Bpz]_2PF_6$	1:200	C_6H_6	10	5
$[Rh(cod)Bipyam]_2PF_6$	1:200	C_6H_6	20	10
$[Rh(cod)Bipy]_2PF_6$	1:200	C_6H_6	20	8

[a] Referred to the solid reaction product

Table 2 Reactions of DMPA with $Ni(NCS)_2(PPh_3)_2$

Catalyst/monomer ratio	Reaction time (h)	Complex weight (mg)	Monomer weight (mg)	Yield (solid) (mg)	Insoluble fraction (%)	Elemental analysis: Soluble fraction (%)	Elemental analysis: Insoluble fractions (%)	MW (a.m.u.): Osmometric	MW (a.m.u.): g.p.c. M_n	MW (a.m.u.): g.p.c. M_w
1:320	26	100	4×10^3	200						
1:130	26	100	1.55×10^3	200		C 64.53, H 8.74, N 9.51		3.300		
1:65	24	200	1.55×10^3	400		C 63.64, H 8.01, N 11.24, P 2.58, S 6.00		3.500	16.000	70.000
1:32	24	400	1.55×10^3	500		C 61.2, H 7.71, N 10.38		3.600	14.000	68.000
1:9	20	1.5×10^3	1.55×10^3	1.45×10^3	30	C 61.16, H 6.49, N 9.30, S 6.33, P 3.05	C 50.57, H 5.94, N 10.82, S 7.89, P < 1	5.000	13.000	66.000
1:4	16	500	250	320	80		C 48.4, H 5.30, N 11.20, S 10.20, P < 1			

Polymerization reactions

Polymerizations carried out in different reaction conditions are reported in *Table 1*. The complexes, $[Rh(cod)Bpz]_2PF_6$, $[Rh(cod)Bipyam]_2PF_6$, $[Rh(cod)Bipy]_2PF_6$ (cod = *cis,cis*-cycloocta 1,5-diene, Bpz = 2,2′-bipyrazine, Bipyam = 2-2′-bipyridylamine, Bipy = 2,2′-bipyridine) were synthesized by means of literature procedures[12].

Reactions of DMPA with $[Rh(cod)Cl]_2$. In a typical reaction procedure, 180 mg of $[Rh(cod)Cl]_2$ (M_w = 493.08 u.m.a., 0.375 mmol) were dissolved in 20 ml of benzene; 3 ml of DMPA ($d = 0.784\ g\ ml^{-1}$, M_w = 83.14 u.m.a., 28.3 mmol, catalyst/monomer ratio = 1:80) and 1 ml of a 0.2 N solution of NaOH in MeOH were added. The reaction mixture was refluxed for 8 h and then concentrated under reduced pressure. When n-hexane was added, a brown solid precipitated and was filtered and dried under vacuum; by evaporating the solvent from the mother liquor, a viscous brown oil (oligomers) was obtained. PDMPA obtained from the $[Rh(cod)Cl]_2$ catalyst is soluble in many organic solvents, e.g. C_6H_6, $CHCl_3$, CH_2Cl_2, CH_3COCH_3. Yield (solid product): 25%.

Reactions of DMPA with $Ni(NCS)_2(PPh_3)_2$ leading to PDMPA–Ni(II) polymers. Weighed amounts of complex were dissolved in toluene under Ar atmosphere and the monomer was added, according to the complex/monomer molar ratios shown in *Table 2*; about 5 ml of solvents were used for 1 ml of monomer. The reaction mixtures were refluxed for the time shown in *Table 2*, then they were slowly cooled and n-hexane was added. A solid product precipitated, which was filtered, washed with hot n-hexane and dried under vacuum.

When the catalyst/monomer ratio used is 1:320, PDMPA–Ni(II) is soluble in organic solvents, such as $CHCl_3$ and CH_2Cl_2. By evaporating the solvent from the mother liquor of the reaction, oily fractions, analogous to the oligomers found in the reaction with $[Rh(cod)Cl]_2$, are obtained.

In the case of reactions carried out with complex/monomer molar ratios 1:4 or 1:9, when the crude product was treated with $CHCl_3$, an insoluble fraction and a solution were obtained. The insoluble fraction was filtered, washed with $CHCl_3$ and dried under vacuum; when the solvent was removed from the solution under vacuum, a further solid fraction was obtained, washed with hot n-hexane and dried under vacuum.

Reactions of the oily fractions with $Ni(NCS)_2(PPh_3)_2$

Portions (200 mg) of oily fractions (2.4 mmol of monomer units) were refluxed in $CHCl_3$ with 200 mg of $Ni(NCS)_2(PPh_3)_2$ (0.286 mmol; complex/monomer molar ratio 1:8.3). After 1 h the solution was concentrated under reduced pressure and n-hexane was added; a solid precipitated and was filtered, washed with n-hexane and dried under vacuum.

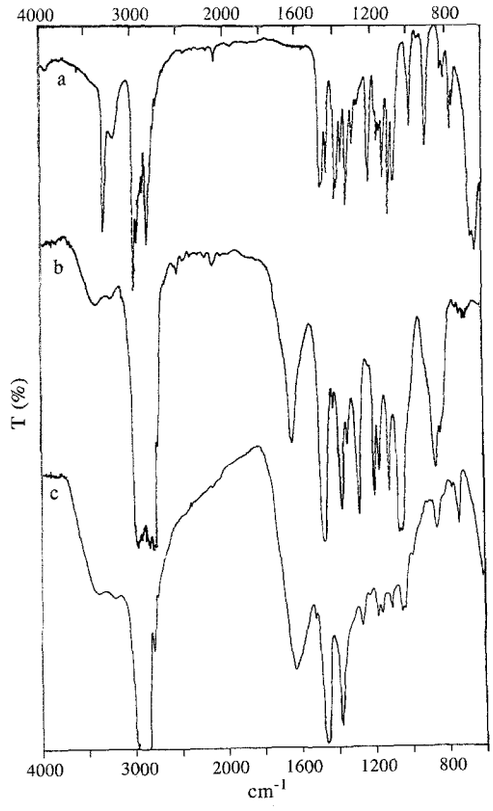

Figure 1 I.r. spectra: (a) DMPA (liquid film); (b) PDMPA from $[Rh(cod)Cl]_2$ oily fractions (liquid film); (c) PDMPA from $[Rh(cod)Cl]_2$ solid fractions (nujol mulls)

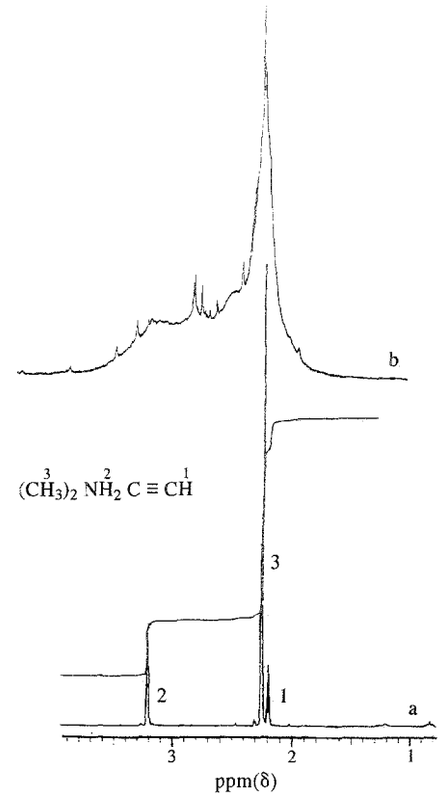

Figure 2 N.m.r. spectra ($CDCl_3$): (a) DMPA: (b) PDMPA (solid fraction from $[Rh(cod)Cl]_2$)

Methods and instrumentation

I.r. measurements were carried out using a Perkin-Elmer 1700 FTIR spectrometer; samples were prepared as nujol mulls or liquid films, using NaCl (4000–600 cm^{-1}) or CsI (600–400 cm^{-1}) optical cells. Far-infrared (f.i.r.) spectra were recorded with a Perkin-Elmer 1700 FIR, using polyethylene optical cells.

Nuclear magnetic resonance (n.m.r.) spectra were run on a AM 500 Bruker spectrometer in $CDCl_3$. X-ray photoelectron spectroscopy (X.p.s.) measurements were carried out on a VG ESCA 3 MK1 instrument, using a non-monochromatized $MgK\alpha_{1,2}$ source ($h\nu$ = 1253.6 eV). The typical vacuum in the analysis chamber was 10^{-9} torr. The spectra of the complex $Ni(NCS)_2(PPh_3)_2$ were energy referenced to the binding energies (b.e.) of the C1s signal of the aromatic carbons, positioned at 285.0 eV. Due to the presence in large amount of C–N bonds, which are probably predominant with respect to the C=C and C–C carbons, the spectra of the PDMPA–Ni(II) complexes were calibrated to the S2p signal of the NCS group, taken at a binding energy of 163.0 eV as in the pristine complex, making the assumption that sulfur binding energy is not modified upon complexation. The calibration results used are assumed to be correct and give C1s b.e. values of ~ 286.0 eV for the complexes, which is a reasonable value for C–N bonds. The P2p b.e. values were ~ 132.7 eV, which again is a rather good value for phosphorus in $OPPh_3$.

Quantitative evaluation of atomic ratios was made by using Scofield's atomic cross-section values[13] and assuming the $E_k^{1/2}$ dependence of the mean-free-path values. Further adjustment was made by experimentally determined factors.

Molecular weights were measured with a Knauer osmometer model 11 at 30°C, using $CHCl_3$ as the solvent. Gel permeation chromatography (g.p.c.) measurements were performed using a Perkin-Elmer instrument, with an LC 250 binary pump, an LC 10 oven and an LC 10J UV detector; an analytical PL-GEL column 10 μm mix, with micropore diameter of 10 μm, and $CHCl_3$ as the solvent were used. Data were collected with the program Chromatographics 2 and calculations were performed with the program GPC 5, both from Perkin-Elmer.

Elemental analyses were carried out by the Laboratorio di Microanalisi, Università di Pisa, Italy.

RESULTS

Reactions with Rh(I) catalysts

The synthesis of PDMPA by linear polymerization of the corresponding monomer using Rh(I) complexes as catalysts has been performed with the aim of preparing a stereoregular polymer like polyphenylacetylene[6,7]; the results of the reactions are shown in *Table 1*. The yield of solid product never exceeded 25%; however, in all the studied reactions, brown and viscous oily fractions consisting mainly of oligomers, were also obtained.

The i.r. spectra of the monomer DMPA and of the oily and solid products of the polymerization reactions are shown in *Figures 1a–c* respectively. In the spectrum of the monomer (*Figure 1a*), the bands at 3300, 2098 and

651 cm^{-1} are attributed, respectively, to the C–H stretching mode of a terminal alkyne group, to the C≡C stretching and to the C–H bending of the alkyne group; the bands between 1462 and 818 cm^{-1} are correlated with the presence of the amine pendent group. In the i.r. spectrum of the oily fractions (*Figure 1b*), a new band at 1625 cm^{-1} appears, due to C=C stretching modes of the polymeric chain, and the bands connected with the pendent group do not show significant modifications; these data indicate a linear polymerization, proceeding via opening of the triple bond, while the structure of the pendent group remains unchanged. Comparing the spectrum of the solid fractions (*Figure 1c*) with that of the oily fractions, no significant modification can be seen, confirming the hypothesis that the only difference between the solid and the oily fractions is the molecular weight; however, a wide band at 3370 cm^{-1} (O–H stretching) indicates the presence of water adsorbed on the polymer. Results of elemental analysis of PDMPA are significantly different from calculations.

Comparing the ^{1}H n.m.r. spectra of the monomer (*Figure 2a*) and of the polymer (*Figure 2b*), an increase in the width of the signals of methylic ($\delta = 2.25$ ppm) and methylenic ($\delta = 3.2$ ppm) protons can be seen; this is probably due to different chemical environments of the protons of the pendent groups in the disordered polymeric chain. Signals of the C=C–H protons in the backbone should appear in the 4–7 ppm range; however, in the spectra of poly(monosubstituted)acetylenes with disordered structure, the resonances are masked under broad unresolved signals. ^{13}C n.m.r. spectra are not reported because the low solubility of the polymer does not allow significant information to be obtained.

The spectral results indicate that when DMPA is reacted in the presence of Rh catalysts, a non-stereoregular linear polymer (solid) and oligomers (oily fraction) are obtained.

Reactions with $Ni(NCS)_2(PPh_3)_2$

The synthesis of PDMPA in the presence of the complex $Ni(NCS)_2(PPh_3)_2$ was also studied, because this catalyst is known to be active in the polymerization of propargyl derivatives[14]; however, the materials obtained from these reactions are quite different from the polymer synthesized using Rh complexes.

In *Table 2* the results of the reactions between DMPA and $Ni(NCS)_2(PPh_3)_2$, with complex/monomer ratios ranging from 1 : 320 to 1 : 4, are shown. The yield in solid product increases with increasing the amount of complex, but at low complex/monomer molar ratios oily fractions are obtained, similar to the oligomers found in the reactions carried out with the Rh catalysts.

The elemental analysis reveals the presence of phosphorus and sulfur in the polymers, indicating that the complex used as catalyst is present in the reaction products. The quantity of sulfur in the reaction product increases with increasing complex/monomer molar ratio. In the soluble fractions, phosphorus and sulfur are found at a molar ratio of 1 : 2. When the complex/monomer ratio used is ≥ 1 : 9, an insoluble fraction, containing a higher amount of sulfur and a reduced quantity of phosphorus, is obtained.

Figure 3 shows the i.r. spectra of the crude reaction products obtained using various complex/monomer ratios (1 : 320, 1 : 65 and 1 : 4).

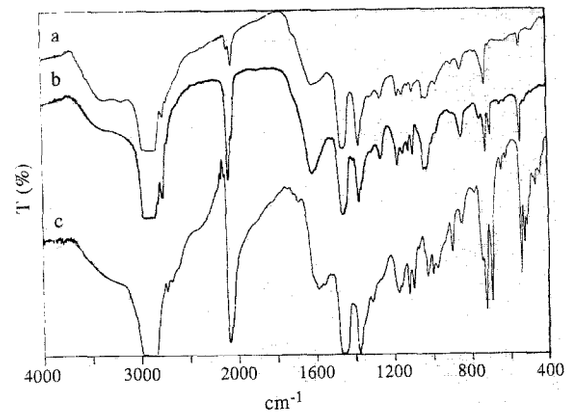

Figure 3 I.r. spectra (nujol mulls) of crude reaction products, obtained in the reaction between DMPA and $Ni(NCS)_2(PPh_3)_2$ using complex/monomer molar ratios: (a) 1 : 320; (b) 1 : 65; (c) 1 : 4

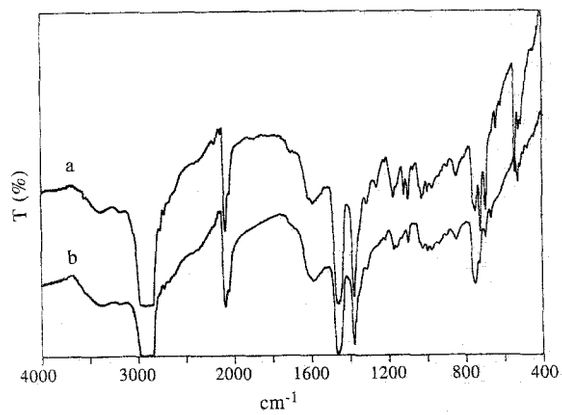

Figure 4 I.r. spectra (nujol mulls) of the PDMPA–Ni(II) polymers from catalyst/monomer ratio 1 : 9; (a) soluble fraction; (b) insoluble fraction

A band at 2087 cm^{-1} is present in all the reported spectra and in the spectrum of the pristine complex, and can be attributed to NCS groups; bands at 1120, 722, 695 and 542 cm^{-1} are due to the triphenylphosphine oxide, $OPPh_3$[15], i.e. to the oxidized form of the PPh_3 ligand. The intensity of all these signals increases by increasing the complex/monomer ratio. Other bands (1260, 1096, 1030, 844 cm^{-1}) are typical of the amine pendent group and similar to those of PDMPA synthesized in the presence of $[Rh(cod)Cl]_2$. A band at 3400 cm^{-1}, due to the stretching mode of OH groups, is slightly evident in the spectra of polymers from complex/monomer ratios 1 : 65 and 1 : 4, but still present when a complex/monomer ratio of 1 : 320 is used; therefore polymers obtained using larger amounts of complex tend to be less hygroscopic.

Figure 4 compares the i.r. spectra of the soluble and insoluble fractions of the polymer obtained when the catalyst/monomer ratio 1 : 9 is used. In both spectra the intense band at 2087 cm^{-1}, due to the NCS group, is present. The bands connected with the triphenylphosphine oxide, intense in the i.r. spectrum of the soluble fraction, are almost absent in the spectrum of the insoluble fraction (see, for comparison, the elemental analysis of the two samples).

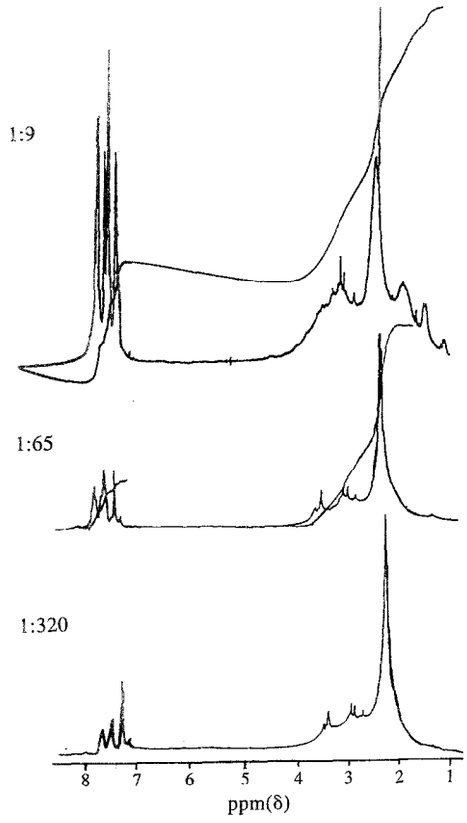

Figure 5 ^{1}H n.m.r. spectra ($CDCl_3$) of the soluble fractions of PDMPA–Ni(II) polymers from various catalyst/monomer ratios

Low-frequency i.r. spectra of various PDMPA–Ni(II) samples have been compared with the spectra of $Ni(NCS)_2(PPh_3)_2$. In the f.i.r. spectrum of $Ni(NCS)_2(PPh_3)_2$, bands at 443 and at 278–255 cm^{-1} are attributed to the bending of the NCS group (δ_{NCS}) and to the stretching of the Ni–NCS bond (ν_{Ni-NCS}) respectively[16]. The polymers also show bands at 440–450 and at 260–240 cm^{-1} due to NCS groups, as in the pristine complex.

In *Figure 5* the ^{1}H n.m.r. spectra of the soluble fractions obtained using increasing complex/monomer molar ratios are presented. Resonances in the range 2–4 ppm are due to the protons of the pendent group, as in the spectrum of PDMPA synthesized with Rh complexes. New signals appear in the range $\delta = 7.45$–7.67 ppm, the same position as the protons resonances of $OPPh_3$; the intensity of these signals increases by increasing the complex/monomer molar ratio. The ^{13}C n.m.r. spectrum of PDMPA–Ni(II) obtained using catalyst/monomer molar ratio 1:65 confirms the presence of aromatic species (resonances at 128 and 132 ppm) in the PDMPA–Ni(II) complexes. In the ^{31}P n.m.r. spectrum only one signal at 21.4 ppm is present; the signal is in the same position as the ^{31}P signal of triphenylphosphyne oxide, but appears broad (linewidth = 30 Hz), indicating the possible presence of paramagnetic species in solution.

X.p.s. measurements

To gain a better insight into the structure of PDMPA–Ni(II) complexes, both soluble and insoluble fractions

Table 3 X.p.s. measurements of Ni(II) complex, $Ni(NCS)_2(PPh_3)_2$, and soluble and insoluble fractions of PDMPA–Ni(II) complexes

Complex/ monomer ratio	Fraction	Core level	B.e. (eV)	*FWHM* (eV)	Stoichiometry (number of atoms/1Ni)	
					Experimental	Calculated
Ni(II) complex		C1s	285.0	2.1	36.8	38
		N1s	398.7	1.9	2.1	2
		S2p	163.0	2.5	2.3	2
		P2p	131.7	2.2	2.0	2
		$Ni2p_{3/2}$	855.6	2.0	1	1
1:65	Soluble	C1s	286.0	3.1	76	
		N1s	400.0	2.8	13.1	
		S2p	163.0	2.7	1.6	
		$Ni2p_{3/2}$	855.9	3.0	1	
		P2p	132.5	2.8	1.3	
1:9	Soluble	C1s	286.0	3	78.3	
		N1s	400.1	2.7	11.8	
		S2p	163.0	2.7	2.0	
		$Ni2p_{3/2}$	855.8	3.1	1	
		P2p	132.7	2.7	1	
1:9	Insoluble	C1s	285.8	3	40	
		N1s	399.7	3.1	7	
		S2p	163.0	3.1	1.7	
		$Ni2p_{3/2}$	856.6	3.6	1	
1:4	Insoluble	C1s	285.8	3.3	23.7	
		N1s	399.7	3.7	4.7	
		S2p	163.0	3.2	1.8	
		$Ni2p_{3/2}$	856.6	3.6	1	

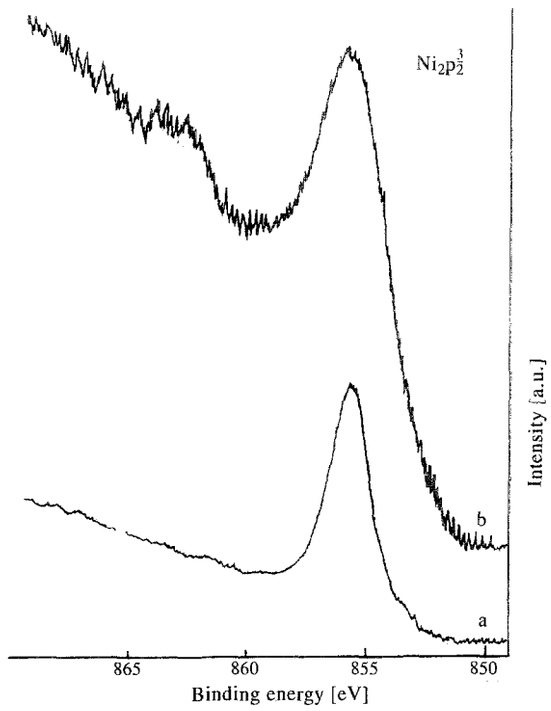

Figure 6 $Ni2p_{3/2}$ X.p.s. spectra of: (a) $Ni(NCS)_2(PPh_3)_2$; (b) PDMPA–Ni(II) polymers from catalyst/monomer ratio 1 : 9; soluble fraction

prepared using complex/monomer ratios 1 : 65, 1 : 9 and 1 : 4 have been studied by means of X.p.s. The reported X.p.s. data are the average of many measurements performed on different samples of PDMPA–Ni(II) prepared with the same procedure. For the purpose of comparison, the pristine complex, $Ni(NCS)_2(PPh_3)_2$, has also been analysed and the results are shown in *Table 3*.

Concerning the $Ni(NCS)_2(PPh_3)_2$ complex it should be remarked that the b.e. values found for $Ni2p_{3/2}$, P2p, N1s and S2p core levels are in perfect agreement with the values reported by Tolman *et al.*[17]. The X.p.s. spectra of the soluble and insoluble fractions of PDMPA–Ni complexes confirm the presence of Ni in all the examined samples.

Comparing the b.e. values of the $Ni2p_{3/2}$ core-level signal in the spectra of PDMPA–Ni(II) complexes with that of the pristine complex, we notice that while for the nickel in the soluble fraction the $Ni2p_{3/2}$ b.e. value is the same, within experimental error (±0.2 eV), we detect a slight shift towards higher b.e. values by ≈1.0 eV for nickel in the insoluble fractions. Literature data[17] regarding nickel complexes report an increase in the $Ni2p_{3/2}$ b.e. of about 2 eV when the oxidation number of the nickel atom changes from 0 to +2, and of about 5 eV when the oxidation number changes from +2 to +4. Therefore, from the analysis of our data, the conclusion is that on going from the pristine complex to PDMPA–Ni(II) complexes, the formal oxidation number of the nickel atom remains the same.

In *Figure 6* the $Ni2p_{3/2}$ core-level spectrum of a PDMPA–Ni(II) complex is compared with the spectrum of the square-planar, diamagnetic pristine complex $Ni(NCS)_2(PPh_3)_2$. The $Ni2p_{3/2}$ signal of the PDMPA–Ni(II) complex shows a larger full width at half-maximum (*FWHM*), is positioned on a sloping background, and shows a shake-up satellite at higher b.e. from the main line. According to Matienzo *et al.*[18,19], paramagnetic, octahedral or tetrahedral complexes of Ni(II) can be distinguished from square-planar diamagnetic complexes by analysing the $Ni2p_{3/2}$ core-level spectra. The $Ni2p_{3/2}$ spectra of paramagnetic complexes show a shake-up satellite assigned to $3d \rightarrow 4s$ transitions, which are forbidden by symmetry for diamagnetic complexes; moreover, the $Ni2p_{3/2}$ signal results are significantly broader (about 0.7 eV) in paramagnetic than in diamagnetic complexes, because of $d \rightarrow d$ transitions occurring simultaneously with the main photoemission process. Tolman *et al.*[17] also refer that, for paramagnetic Ni(II) complexes, $Ni2p_{3/2}$ core-level signals tend to be less intense, larger and positioned on a sloping background.

Literature results[19,20] further report that the b.e. of the $Ni2p_{3/2}$ in Ni(II) complexes is influenced by the coordination number of the nickel atom and by the stereochemistry of the complex, and increases in the series: square planar < tetrahedral < octahedral. The b.e. value of the $Ni2p_{3/2}$ signal is about 0.6–1.0 eV higher in energy for the insoluble fractions than for the soluble ones (*Table 3*). By comparison with the literature data, the X.p.s. spectra of DMPA–Ni(II) indicate a change in the stereochemistry and in the magnetic properties of the Ni(II) complexes; while the pristine Ni(II) complex is square-planar and diamagnetic, the PDMPA–Ni(II) complexes must be paramagnetic, tetrahedral or octahedral, the latter coordination state being more likely in the insoluble fractions than in the soluble ones.

Considering the phosphorus X.p.s. spectra we observe a P2p signal at 131.7 eV for the pristine Ni complex attributable to the PPh_3 group (*Table 3*). For the soluble fraction of the PDMPA–Ni(II) complex we find a P2p signal shifted towards higher energies at 132.7 eV, corresponding to the value already reported in the literature[21] for $OPPh_3$. Therefore, the X.p.s. spectra confirm the presence of $OPPh_3$, suggested also from i.r. and n.m.r. spectra. For the insoluble fraction of the PDMPA–Ni(II) complexes no P2p signal has been detected, therefore the amount of phosphorus present is lower than the limit of detection by X.p.s.

Analysis of the N1s spectra shows an increase in the b.e., taken at the maximum of the signals, for the nickel polymer complexes PDMPA–Ni(II) compared with $Ni(NCS)_2(PPh_3)_2$. For the catalyst we find N1s b.e. = 398.7 eV while for the polymer a N1s b.e. of ~ 400.0 eV is detected for both the soluble and the insoluble fractions. For the PDMPA–Ni(II) complexes the N1s peaks are much broader than for the pristine Ni complex, with $FWHM \approx 3$ eV.

Three different types of nitrogen atoms can be present in all the studied samples: nitrogen atoms of the NCS ligands, aminic nitrogen of the free pendent groups, and aminic nitrogen that can coordinate the Ni atoms. The b.e. of the N1s electrons for aminic nitrogens is reported to increase by about 1 eV upon coordination to Ni(II)[22]. Unfortunately, in our case we do not have good resolution of the N1s spectra and the different nitrogen core level contributions cannot be resolved since they give rise to convolute broad signals asymmetric on the tail at lower b.e., where the contribution from the NCS nitrogen atoms is expected.

DISCUSSION

In previous investigations we found that Rh complexes give highly stereoregular poly(phenylacetylene)[6,7]. Nickel complexes, NiX_2L_2 (X = halogen, L = phosphines), have also been used as catalysts in the polymerization of monosubstituted acetylenes $H-C\equiv C-R$[14,23,24], and cyclic trimers or polymers were obtained, depending on the R substituent, and on the ligands around the Ni atom. $NiX(C\equiv C-R)L_2$ (X = halogen, NCS) complexes are probably the active catalysts in these reactions: in fact in the presence of $Ni(NCS)_2(PPh_3)_2$ and of $Ni(NCS)(C\equiv C-Ph)(PPh_3)_2$ complexes, phenylacetylene gives the same final reaction products, but with the last complex, the induction time, that is the time in which the first Ni–C σ bonds are formed, is shortened[25]. The chain grows by insertion of the activated monomer molecules in the Ni–C σ bond.

We considered it of interest to investigate the polymerization of an acetylenic monomer containing the $N(CH_3)_2$ group, to see the influence of functional groups on the properties of polymers. It is not easy to polymerize monomers containing functional groups because deactivation of catalysts often occurs. In fact the yields of polymers of DMPA obtained in the presence of Rh catalysts are rather low (*Table 1*); Rh catalysts can give conversions of phenylacetylene of about 100%.

The reactions with the $Ni(NCS)_2(PPh_3)_2$ complex (*Table 2*) show the influence of the dimethylamino pendent group. By increasing the catalyst/monomer ratio from 1:320 to 1:4 the yield of products increases. This is due to a reaction of the molecules of Ni complex with the $N(CH_3)_2$ groups of the polymer chain. The Ni complex has two roles: to induce the polymerization of the DMPA and to give polymer complexes. The structure of the reaction products was characterized by elemental analysis, i.r., n.m.r. and especially by X.p.s. spectra. The elemental analyses (*Table 2*) indicate the presence of phosphorus and sulfur in a ratio of 1:2. The i.r. spectra (*Figures 3 and 4*) indicate a band at 2087 cm^{-1}, due to NCS groups, and bands of $OPPh_3$. These data suggest that $Ni(NCS)_2(PPh_3)_2$ groups are bonded to the chain.

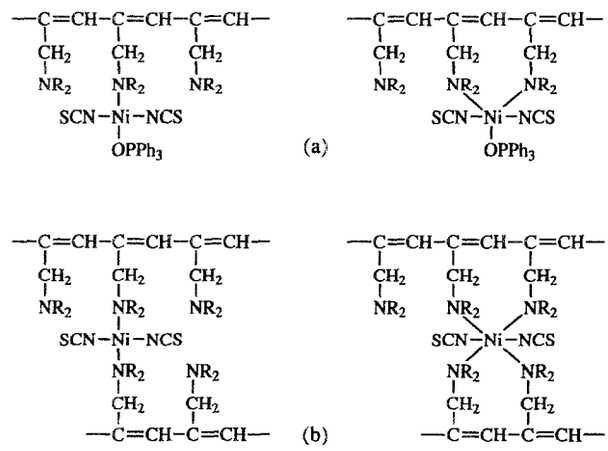

Figure 7 Proposed structures of the soluble (a) and insoluble (b) fractions of PDMPA–Ni(II) polymers

According to literature data[26,27], in the i.r. spectrum of $OPPh_3$ an intense band at 1195 cm^{-1} is attributed to the P=O stretching mode; in transition metal complexes with the triphenylphosphine oxide ligand, the position of this band shifts to lower wavenumbers as a consequence of the coordination of the oxygen atom of $OPPh_3$ to the transition metal. In our spectra, we find the P=O band at about 1170–1175 cm^{-1}, overlapping with other bands due to the $-CH_2N(CH_3)_2$ pendent group; these data indicate that $OPPh_3$ is bound to the nickel atom.

The ^1H and ^{31}P n.m.r. spectra confirm the presence of $OPPh_3$ in the reaction products. Therefore an oxidation of the PPh_3 ligands of the nickel complex occurs even in the Ar atmosphere used during the polymerization procedure. Dissolved oxygen is easily activated and bonded to the phosphorus atom giving $OPPh_3$ as ligand.

The atomic ratios determined by X.p.s. (*Table 3*) are in good agreement with the elemental analysis data: the insoluble fractions show a higher nickel and sulfur content and a reduced phosphorus content compared to the soluble ones. In the soluble fractions nickel, sulfur and phosphorus are present in atomic ratios of ~1 : 2 : 1; in the insoluble fractions the nickel/sulfur atomic formula ratio is ~1 : 2 while the phosphorus signal has not been detected, indicating a release of the phosphine ligands according to the elemental analyses reported in *Table 2*.

From the analysis of these results it is evident that the $Ni(NCS)_2(PPh_3)_2$ complex acts as a catalyst towards DMPA, giving oily linear polymers $[-CH=CR-]_n$, of low molecular weight; the $N(CH_3)_2$ groups of the polymer chain can react with the Ni atom of the complex $Ni(NCS)_2(PPh_3)_2$ by substitution of one or two PPh_3 ligands (which are present in the polymer complex as $OPPh_3$). By increasing the number of $N(CH_3)_2$ groups bonding Ni atoms, the yield of reaction products increases, and two fractions – the soluble and insoluble one – are obtained.

When only one triphenylphosphine molecule is eliminated, a soluble fraction is formed, showing a sulfur/phosphorus molar ratio 2:1 (elemental analysis and X.p.s. spectra); in the other case, the two phosphine ligands can be substituted by two amine groups in two different polymer chains, and cross-linked insoluble fractions are obtained. The polymer probably also acts as a chelating agent (*Figure 7*). It is noteworthy that the triphenylphosphine molecule bound to the nickel is oxidized to triphenylphosphine oxide.

Polymerization of the monomer and interaction of the polymer with the nickel complex take place when high catalyst/monomer ratios are used, leading to the formation of polymer–metal complexes PDMPA–Ni(II). When the oily fractions, consisting mainly of oligomers, are treated with $Ni(NCS)_2(PPh_3)_2$, solid fractions, having the same spectroscopic characteristics of PDMPA–Ni(II), are found. These results confirm that linear polymerization of the monomer and interaction of the amine groups of the polymer with the pristine complex are two independent processes.

From the elemental analysis and the integrated ^1H n.m.r. resonances of the soluble samples of PDMPA–Ni(II) (catalyst/monomer ratio 1:65 and 1:9, respectively), the presence of one $Ni(NCS)_2(OPPh_3)$ group

Table 4 Measured and calculated atomic ratios for PDMPA–Ni(II)

Complex/ monomer ratio	Fraction	Elemental analysis (%)	X.p.s. measured atomic ratios	Proposed structures[a]	Calculated atomic ratios	Calculated elemental percentages
1:65	Soluble	C 63.64, H 8.01, N 11.24, S 6.00, P 2.58	$C_{76}N_{13.1}S_{1.6}P_{1.3}Ni$	$\{[CH=C-CH_2N(CH_3)_2]_{10}Ni(NCS)_2(OPPh_3)\}$	$C_{70}N_{12}S_2PNi$	C 65.48, H 8.18, N 13.1, S 5.0, P 2.42
1:9	Soluble	C 61.16, H 6.49, N 9.30, S 6.33, P 3.05	$C_{78.3}N_{11.8}S_2P_2Ni$	$\{[CH=C-CH_2N(CH_3)_2]_8Ni(NCS)_2(OPPh_3)\}$	$C_{60}N_{10}S_2PNi$	C 64.47, H 7.79, N 12.53, S 5.74, P 2.77
1:9	Insoluble	C 50.57, H 5.94, N 10.82, S 7.89	$C_{40}N_7S_{1.7}Ni$	$\{[CH=C-CH_2N(CH_3)_2]_5Ni(NCS)_2\}$	$C_{27}N_7S_2Ni$	C 57.07, H 8.02, N 16.65, S 9.57
1:4	Insoluble	C 48.4, H 5.3, N 11.2, S 10.2	$C_{23.7}N_{4.7}S_{1.8}Ni$	$\{[CH=C-CH_2N(CH_3)_2]_4Ni(NCS)_2\}$	$C_{22}N_6S_2Ni$	C 52.09, H 7.1, N 16.65, S 12.6

[a] The structures are determined on the basis of ^1H n.m.r. and X.p.s. data

about every 8–12 monomer repeat units can be estimated. However, there is no evidence for the binding of the $Ni(NCS)_2(OPPh_3)$ moiety occurring at regular chain length intervals because ^1H n.m.r. data show only a statistical ratio between coordinating moieties and pendent groups.

Since a subunit of the polymer corresponds, on average, to $[CH=CCH_2N(CH_3)_2]_{10}Ni(NCS)_2(OPPh_3)$ ($M_w = 1282$ u.m.a.), and the measured g.p.c. M_n values are in the range 1.6×10^4 to 1.3×10^4 for samples of PDMPA–Ni with catalyst/monomer ratios of 1:65 and 1:9 respectively, the enchainment of about 10–12 subunits in the polymer chain can be evaluated.

If we attempt, from the X.p.s. data, a calculation of the number of repeat units relative to the nickel atoms in the polymeric chain, the trend is that the nickel content increases by increasing the complex/monomer molar ratio. In the soluble fractions the coordinating moiety bound to the $N(CH_3)_2$ aminic group is $Ni(NCS)_2(OPPh_3)$, i.e. $NiC_{20}H_{15}N_2S_2PO$, while in the insoluble fractions it is mainly $-Ni(NCS)_2-$, i.e. $NiN_2C_2S_2$, phosphine oxide being absent as already discussed.

In *Table 4* the elemental analysis data and the X.p.s. measured atomic ratios are compared with the calculated values for the proposed structures. For the soluble fractions obtained from 1:65 and 1:9 catalyst/monomer ratio, the experimental data are very similar to each other and in fairly good agreement, within experimental error, with a ratio of 1:8 to 1:10 between the coordinating moiety $Ni(NCS)_2(OPPh_3)$ and the monomer repeat units $CH_2=C-CH_2N(CH_3)_2$, thus confirming the results obtained from the proton n.m.r. spectra. The excess of carbon atoms detected by X.p.s. is due to carbon contamination, always present on the surfaces.

For the insoluble fractions, X.p.s. measured ratios between the Ni, S and N atoms indicate that one coordinating group, $Ni(NCS)_2$, can be found roughly every five monomer units and every three to four monomer units for the samples obtained using, respectively, 1:9 and 1:4 catalyst/monomer ratio. The elemental analysis data, however, are not in good agreement with the X.p.s. results. The low contents of nitrogen and carbon in the studied samples can be explained by water adsorption on the polymer surface and/or by a partial hydrolysis of the amino group, $-CH_2N(CH_3)_2$, to yield a hydroxy group $-CH_2OH$. An $-OH$ stretching band of low intensity was detected in the i.r. spectra, and the polymer was found to be hygroscopic. It should be remarked that the structures proposed in *Figure 7* are simplified models of the Ni coordination sites which are randomly distributed in the polymeric matrix.

CONCLUSIONS

The reactivity of the complex $Ni(NCS)_2(PPh_3)_2$ towards DMPA has been investigated. The complex behaves as a polymerization catalyst that induces the growth of a π-conjugated $[-CH=CR-]_n$ polymeric backbone. The pendent groups $R=CH_2N(CH_3)_2$ coordinate to the Ni(II) atom of the complex, giving organometallic polymers in which the metal is surrounded by the NCS, $OPPh_3$ and R ligands in tetrahedral or octahedral configuration; in this latter case the phosphinic ligands are almost completely removed and crosslinking between adjacent chains occurs. The coordination between PDMPA and Ni(II) proceeds ranging from a catalyst/monomer ratio of 1:320 up to 1:4. Rh(I) complexes, which were successfully tested in the synthesis of highly stereoregular polyphenylacetylene[28], give non-stereoregular PDMPA in low yield.

Studies on the electrical and magnetic properties of PDMPA–Ni(II) polymeric complexes are in progress.

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