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Organometallic polymers from *N,N*-diethylpropargylamine containing Ni coordination centers

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The reaction of *N,N*-diethylpropargylamine with increasing amounts of the complex $[Ni(NCS)_2(PPh_3)_2]$ leads to π-conjugated organometallic polymers containing Ni(II). XPS measurements show the presence of paramagnetic metal centers, which coordinate two NCS ligands, one phosphine and NEt_2 pendant group of the polyenic chain. The number of Ni-bonded atoms increases by increasing the complex/monomer molar ratio. The organometallic polymers are promising materials for humidity sensors, giving reproducible results for various subsequent cycles of relative humidity variations in the range 60–90%. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polymers with π-electron delocalised systems have been largely investigated because their conductivity increases by many orders of magnitude by doping[1]. More recently, one-dimensional conjugated polymers were considered of interest because of their non-linear optical properties (NLO)[2]. Conducting polymers have been used in the fabrication of light-emitting diodes (LEDs) with different luminescence emission, depending on the chemical structure of the polymer[3,4]. Organometallic polymers, containing transition metal centers in the conjugated chain, have been synthesised in view of their liquid crystalline behaviour[5,6] and of their NLO properties[2]. Polymers in which metal centers were coordinated to π-systems of the polymeric chain were also prepared, showing conductivity higher than the pristine materials[7].

Recently we have investigated the reactivity of some functionalised monosubstituted acetylenes $H{-}C{\equiv}C{-}R$ ($R = CH_2N(CH_3)_2$, CH_2OH, $Si(CH_3)_2$) towards Ni and Pd complexes[8–10]. We found that, by increasing the amount of transition metal complex, the yield of organometallic polymers, in which the metal centers are in part inserted in the main chain and in part coordinated to the pending groups or to the double bonds of the chain, increases.

In this paper we will discuss the reactivity of *N,N*-diethylpropargylamine (DEPA) with the $[Ni(NCS)_2(PPh_3)_2]$ complex. The present results will be compared with those of our previous investigations.

EXPERIMENTAL

Materials

N,N-Diethylpropargylamine (Fluka) was distilled, dryed over Na_2SO_4, maintained at −30°C, and redistilled under reduced pressure before use. All solvents, reagent-grade commercial products, were dried and carefully degassed by fluxing argon before use.

The complex $[Ni(NCS)_2(PPh_3)_2]$ was synthesised according to the literature method[11] (m.p. 184°C). The novel $[Ni(NCS)(C{\equiv}C{-}CH_2{-}NEt_2)(PPh_3)_2]$ complex was prepared following the method proposed for the synthesis of analogous complexes[12]: 0.62 ml (0.5 g) of DEPA (d = 0.804 g/ml) are added to 1 g of $[Ni(NCS)_2(PPh_3)_2]$ in 20 ml of $NHEt_2$. The mixture is refluxed for about 2 h. By cooling the reaction vessel, first a red solid separates from the reaction mixture. This product was characterised by i.r. spectroscopy and elemental analysis; it corresponds to $[Ni(NCS)_2(NHEt_2)_2]$ which is formed in a side reaction.

$$[Ni(NCS)_2(PPh_3)_2] + 2NHEt_2 \rightarrow [Ni(NCS)_2(NHEt_2)_2] + 2PPh_3$$

After separation of this solid product and subsequent concentration of the resulting reaction solution to about 5 ml, addition of MeOH induces the precipitation of yellow crystals of $[Ni(NCS)(C{\equiv}C{-}CH_2{-}NHEt_2)(PPh_3)_2]$. Yield: 20–30%, m.p.: 136–138°C. Elemental analysis: exp. (calcd.): C 70.2% (70.5); H 5.6% (5.3); N 3.8% (3.7); S 3.6% (4.3); P 8.1% (8.3). The complex is soluble in CH_3COCH_3 and $CHCl_3$, while it is insoluble in toluene, benzene and ethanol.

Polymerisation reactions

In a typical experimental set-up (catalyst/monomer ratio 1/50) 200 mg of $[Ni(NCS)_2(PPh_3)_2]$, 2.0 ml (1.6 g) of DEPA and 5 ml of toluene are introduced into a reaction vessel and the mixture is degassed by means of a vacuum line connected to a rotary pump. A dried atmosphere is created by argon. The outgassing procedure is repeated at

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Table 1 Polymerization reactions of DEPA in the presence of the complex $[Ni(NCS)_2(PPh_3)_2]$

				Elemental analysis (%)				Atomic ratios			Molecular weights		
Sample	Cat/mon ratio	Time (h)	Yield (%)	C	N	H	S	C/N	C/H	C/S	M_n (a.m.u)	M_w (a.m.u.)	$p = M_w/M_n$
P500	1/500	60	2	57.4	8.1	6.7	3.8	8.3	0.71	40.3	54400	206800	3.8
P100A	1/100	20	7	60.8	8.2	6.7	5.9	8.7	0.76	27.5			
P100B	1/100	40	14	60.7	6.3	7.0	3.5	11.2	0.72	46.2	8500	18400	2.17
P50A	1/50	20	12	57.6	6.7	6.1	6.8	10.0	0.79	22.5			
P50B	1/50	40	10	60.4	9.3	7.9	6.0	7.6	0.64	26.8	5100	7800	1.05
P30A	1/30	20	21										
P30B	1/30	40	21										
P30C[a]	1/30	72	43	59.6	9.5	8.0	6.2	7.3	0.62	25.6			
P10A	1/10	20	20										
P10B	1/10	45	24										
P10C[a]	1/10	72	60	56.3	9.2	6.4	7.7	7.1	0.72	19.5	13500	41200	3.0

Calculated values for $C_7H_{13}N$: C 75 6%; N 12.6%; H 11.7%. C/N ratio = 7; C/H ratio = 0.54

[a] The reaction mixture was worked up after 72 h

least three times. The mixture is then warmed up to about 70–80°C for different times, as reported in *Table 1*. After about 15 min the colour of the solution turns to brown. The catalyst is insoluble in toluene, but at the end of the reaction no unreacted catalyst has been found. The reaction mixture is cooled at room temperature and, upon addition of *n*-hexane or petroleum ether, a dark brown powder separates from the reaction mixture. The solid is washed with hot *n*-hexane to eliminate $OPPh_3$, which separates from the catalyst during the reaction. The resulting black solution is concentrated under reduced pressure, and a second fraction of polymeric material is obtained. This second fraction is an oil or a powder, depending on the reaction catalyst/monomer ratio.

The brown polymer is completely soluble in DMF, and partially soluble in $CHCl_3$, DMSO, THF, CH_3COCH_3, C_6H_6, EtOH and MeOH. It is also soluble in acidic water. The polymer warmed at 150–160°C decomposes, leaving a carbon residue.

Doping procedures

Polymers of DEPA (PDEPA) were homogeneously or heterogeneously doped with I_2, $FeCl_3$ and HCl. After doping, shiny black powders were always obtained, independently on the doping procedure. The black powders are soluble in DMF, and insoluble in most common solvents.

Doping with I_2 was carried out by dissolving 200 mg of polymer in a small amount of THF and by adding a solution of 200 mg of I_2 in 10 ml of THF. The mixture was stirred for about 30 min and mantained at room temperature for about 12 h. By elimination of the solvent under vacuum, a black powder is obtained.

An analogous procedure was followed to dope the polymer with $FeCl_3$, but in this case the mixture was mantained under argon atmosphere, because the system exhibits a strong tendency to adsorb water.

Doping with HCl was performed by exposing finely powdered PDEPA to vapours of HCl ($C = 37\%$ in weight) in a closed vessel for about 10 days. The HCl uptake was determined after leaving the doped polymer under vacuum for several hours to eliminate the excess of HCl not directly bonded to the polymer. The weight increase of the polymer was about 20%.

Films of PDEPA have been prepared by casting from DMF or $CHCl_3$ solutions of doped or undoped polymers.

Instrumentation

IR spectra were recorded on a 1700 Perkin-Elmer FTIR spectrophotometer as nujol mulls or on liquid films. U.v. spectra were run on a Perkin-Elmer Lambda 5 spectrophotometer, using $CHCl_3$ as solvent. ^1H and ^{13}C n.m.r. spectra were recorded on a Varian XL300 spectrometer in $CDCl_3$ or in deuterated DMF, using the solvent signals for calibration. XPS measurements were performed on a VG ESCA3 MK1 spectrometer, using the Al $K\alpha_{1,2}$ radiation ($h\nu = 1486.6$ eV). The typical vacuum in the analysis chamber was 2×10^{-9} Torr. The core level signals were energy referenced to the binding energies (BE) of the C1s signal of aromatic/aliphatic carbon atoms, positioned at 285.0 eV. Quantitative evaluations of atomic ratios were made by using Scofield's atomic cross-section values[13] and assuming $E_k^{1/2}$ dependence on a mean free path value. Further adjustments were made by experimentally determined factors. Composite signals were analysed with a curve-fitting program.

Molecular weights were determined by gel permeation chromatography (g.p.c.), using a Perkin-Elmer apparatus, with an LC 250 binary pump, an LC oven and an LC10J UV detector. Polystyrene standards were used for calibration. Data were analysed by Chromatographics 2 and GPC5 Perkin-Elmer programs. The solvent used was DMF at a 0.8 ml min^{-1} flux.

Elemental analyses were carried out at the Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, Italy.

Conductivity measurements were performed on pellets ($\varnothing = 1$ cm, $h = 0.15$ cm) prepared with a Specac P/Y 150 hydraulic press at 10 tons or on films (thickness 1 μm) obtained by casting from DMF or $CHCl_3$ solutions. The films were supported on a silica substrate, where Al interdigitated structures were previously photolithographically defined (50 Al fingers: 0.8 cm × 20 μm; spatial periodicity, 20 μm). The resistance measurements were carried out at 30°C in an Angelantoni UY150 chamber, in which the humidity was varied step by step up to 90% (the uncertainty on the relative humidity was ± 3%; on the temperature it was ± 1%). The resistance values were measured with a Keithley 616 electrometer.

RESULTS

Features of the reactions

Polymerisation reactions of DEPA were carried out in the presence of the [Ni(CNS)$_2$(PPh$_3$)$_2$] complex by varying the complex/monomer ratio from 1/500 to 1/10, in similar way as in our preceding investigations on analogous systems[8-10]. Results are reported in *Table 1*. Also in this case the yield of products increases by increasing the amount of complex used in the reaction. The elemental analysis reveals the presence of sulfur in the reaction products even when the catalyst monomer ratio is 1/500. The sulfur content increases by increasing the complex amount, as was found in our previous investigations on the reactivity of *N,N*-dimethylpropargylamine (DMPA)[9]: therefore the reaction is expected to follow a similar pathway.

The reaction time has a significant importance on the yield of products. In the case of a complex/monomer ratio of 1/10, a yield of about 60% on the total weight of the reactants is obtained, if the reaction mixture is worked up after 3 days (experiment P10C); after 20 h the reaction yield was 20% and after 45 h it was about 24% (experiments P10A and P10B, respectively). Analogous variations of yields were found for the other catalyst/monomer ratios used here (*Table 1*).

The reaction products are organometallic polymers containing Ni, as shown by the XPS, i.r. and n.m.r. spectra, which will be discussed in following sections.

When the polymers are washed with hot *n*-hexane, OPPh$_3$ is released. The presence of OPPh$_3$ in the polymeric complexes was also found in our previous investigations[8-10]. The PPh$_3$ ligand is oxidised during the polymerisation reactions, in a parallel reaction activated by the Ni or Pd atom of the catalysts. The oxidation occurs, even when the polymerisations are carried out in an deoxygenated atmosphere. The oxidation can occur also at the end of the polymerisation, when the polymer is separated from the reaction solvent. The OPPh$_3$ species is only weakly bonded to the Ni atom in the polymeric complex. Thin-layer chromatography on polymer samples washed with *n*-hexane does not indicate the presence of free OPPh$_3$ which, however, is found in the *n*-hexane used for washing.

The elemental analyses show variations of both C/N and C/H ratios in the polymers, if compared with the theoretical ratios of the monomer (C/N = 7 and C/H = 0.54). A release of the NMe$_2$ groups was found to occur in the polymerisation of DMPA[10] under similar reaction conditions; probably also the NEt$_2$ groups of DEPA are in part hydrolysed during the polymerisation reactions. The hydrolysis reaction can be activated by the transition metal present in the complex polymeric molecule.

Upon concentration of the solution by evaporation of the reaction solvent under vacuum, oily fractions are obtained. If a further amount of complex is added to these oily fractions, and the mixtures are warmed, new solid products are formed, showing i.r., n.m.r. and XPS spectra similar to those of the first polymeric fractions.

Polymerisation reactions have been carried out also in the presence of the complex [Ni(CNS)(C≡C–CH2–NEt$_2$)(PPh$_3$)$_2$]. The monoacetylide complex was found to increase noticeably the reaction rate in the cyclisation and polymerisation reactions of phenylacetylene[14]. However, in the reactions with DEPA we did not find an increase in the reaction rate, or an increase in the yield of products. The reaction products showed the same properties of polymers obtained using the [Ni(NCS)$_2$(PPh$_3$)$_2$] complex. Therefore, the monoacetylide was not used for the synthesis of the organometallic polymers of DEPA.

The molecular weights of PDEPA are reported in *Table 1*. Values in the range 10000–200000 were found for the various polymers, the highest M_w being the one of the polymer obtained with the complex/monomer ratio of 1/500. In all the measured chromatograms, two peaks corresponding to OPPh$_3$ and to PPh$_3$ were observed. Probably these ligands are released from the Ni atoms of the polymer, by the action of the DMF used as solvent for the g.p.c. determinations.

I.r., n.m.r. and u.v. spectra.

The i.r. spectra of PDEPA polymers (*Figure 1*) show an absorption band at 2085 cm^{-1}, whose intensity increases by increasing the complex/monomer ratio, as we have already found in the previous investigations with DMPA, in the presence of the same complex. This band is due to

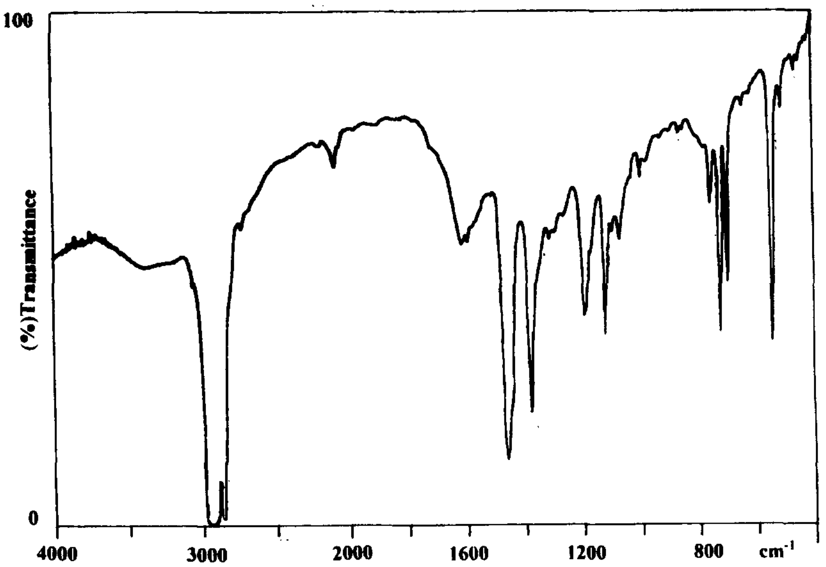

Figure 1 FT-i.r. spectrum of PDEPA polymer (P50)

Table 2 XPS data of reference complexes and of organometallic PDEPA polymers

		C1s	C1s	$Ni2p_{3/2}$	N1s	N1s	S2p	P2p
$[Ni(NCS)_2(PPh_3)_2]$	BE	285.0		855.6	398.7		163.1	131.7
	FWHM	1.9		2.2	2.1		2.2	2.3
$[Ni(NCS)(C{\equiv}C-CH_2NEt_2)(PPh_3)_2]$	BE	285.0		855.3	398.6		163.2	131.9
	FWHM	2.0		2.7	2.7		2.8	3.0
$[Ni(NCS)_2(NHEt_2)_2]$	BE	285.0	286.0	855.9	398.9	402.1	163.3	
	FWHM	1.8	1.9	2.4	2.0	1.9	2.5	
P100	BE	285.0		855.1	399.0	402.0	162.6	132.6
	FWHM	2.6		2.9	2.6	2.0	3.0	2.4
P50	BE	285.0		855.5	399.0	401.9	162.5	132.4
	FWHM	2.7		3.0	2.7	2.1	2.7	2.5
P30	BE	285.0		855.5	399.0	402.2	162.5	132.5
	FWHM	2.6		3.5	3,2	1.7	3.0	2.7
P10	BE	285.0		855.5	398.9	401.8	162.3	132.4
	FWHM	2.8		3.5	3.3	2.2	2.6	2.6

BE and FWHM are given in eV

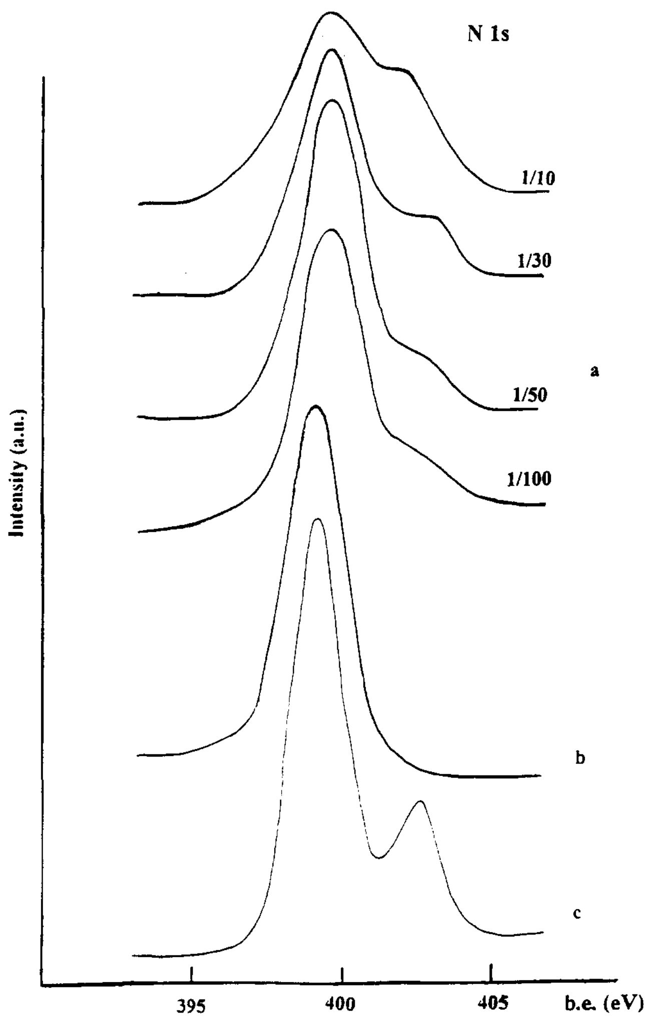

Figure 2 Core level N1s spectra of PDEPA polymers and of reference Ni complexes: (a) N1s spectra of PDEPA polymers at increasing complex/monomer ratio (i.e. 1/100, 1/50, 1/30, 1/10); (b) N1s spectrum of $[Ni(NCS)_2(PPh_3)_2]$; (c) N1s spectrum of $[Ni(NCS)_2(NHEt_2)_2]$

the NCS group of the complex which is still present in the polymer. Bands at 3306 and 650 cm^{-1}, due to the stretching and bending modes, respectively, of the acetylenic C–H bond of the monomer, are absent. The absorption band at 1613 cm^{-1} is attributed to the presence of conjugated double bonds formed in the polymerisation reaction of the acetylenic monomer. The band observed at 542 cm^{-1} is due to $OPPh_3$. This band is also present in the spectra of the other organometallic polymers[8–10], obtained by using increasing amounts of Ni or Pd bistriphenylphosphine complexes. The metals act as catalysts for the oxidation reaction of PPh_3, which occurs as already found in the case of Rh complexes[15]. The band revealed at 1185–1190 cm^{-1} is due to the $OPPh_3$ group bonded to the Ni atom. The absorption band at 459 cm^{-1}, which is present also in the i.r. spectrum of the $[Ni(NCS)_2(PPh_3)_2]$ complex, is attributed to the Ni–P stretching vibration, and indicates the presence in the polymers of some PPh_3 molecules bonded to the Ni atoms.

In the ^1H n.m.r. spectrum of PDEPA (deuterated DMF as solvent), broad signals at 1.04 (CH_3), 2.5 (CH_2 of NCH_2CH_3), and 3.3 ppm (CH_2 of $=C-CH_2N$) are observed. Signals at 7.72 and 7.61 ppm indicate the presence of phosphines in the polymer, as was found in the case of PDMPA obtained in the presence of Ni or Pd complexes with PPh_3 as ligand. The signals due to hydrogens bonded to the carbon double bonds of the chain are not clearly shown. The absence of these signals in the ^1H n.m.r. spectra of substituted polyacetylenes is attributed to the irregular structure of the chain and to the low solubility of polymers. As a consequence of the low solubility of the PDEPA, in the ^{13}C n.m.r. spectra we observed only signals of very low intensity at the expected δ values for the aliphatic carbons (12.6 (CH_3), 48 (CH_2 of NCH_2CH_3), and 61 ppm (CH_2 of $=C-CH_2N$)) and signals in the range 130–135 ppm, due to the phosphine ligands.

The u.v. spectra of PDEPA in $CHCl_3$ show an increasing continuum of absorption from about 500 nm, with a shoulder at 300 nm.

XPS investigations

XPS is an important technique for the investigation of the structure of these complex and poorly soluble materials. Measurements have been carried out on powders of PDEPA obtained at various complex/monomer ratios. For the purpose of comparison, the spectra of some reference molecules have also been measured: $[Ni(NCS)_2(PPh_3)_2]$, $[Ni(NCS)(C{\equiv}CCH_2NEt_2)(PPh_3)_2]$ and $[Ni(NCS)_2(NHEt_2)_2]$.

Table 3 XPS atomic ratios for the organometallic PDEPA polymers

Sample	Ni	C	N-bonded	N-free	S	P	C/N[a]	N_b/Ni	N_f/Ni	N_f/N_b	P/Ni
P100	1	120	1.7	11.4	2.9	1.0	9.0	1.7	11.4	6.7	1.0
P50	1	90	1.5	9.0	2.2	1.0	8.2	1.5	9.0	6.0	1.0
P3O	1	89	1.7	8.9	2.4	1.3	7.6	1.7	8.9	5.2	1.3
P10	1	56	1.5	6.4	2.2	0.6	7.3	1.5	6.4	4.3	0.6

[a] The C/N ratio is related to the monomer units in the chain: the carbon atoms bonded to Ni as PPh_3 or as $OPPh_3$, the C and N atoms of NCS groups are subtracted to the total of carbon and nitrogen atoms

Table 4 XPS atomic ratios for reference complexes

	$Ni2p_{3/2}$		C1s		N1s		S2p		P2p	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$[Ni(NCS)_2(PPh_3)_2]$	1	0.8	38	44.0	2	2.0	2	2.0	2	2.0
$[Ni(NCS)(C{\equiv}C{-}CH_2NEt_2)(PPh_3)_2]$	1	1.0	44	47.2	2	2.3	1	1.5	2	2.1
$[Ni(NCS)_2(NHEt_2)_2]$	1	1.0	10	10.6	3	2.6	2	2.4		

Table 5 Conductivity values (σ, Ω^{-1} cm^{-1}) of films (1 μm) of undoped PDEPA

	Relative humidity (%)			
	90	80	70	60
Conductivity (a)	4.03×10^{-9}	1.47×10^{-9}	5.95×10^{-12}	1.47×10^{-12}
Conductivity (b)	3.57×10^{-9}	1.07×10^{-9}	3.94×10^{-12}	1.47×10^{-12}

The conductivity values are referred to cyclic increase (a) and decrease (b) of the relative humidity

XPS data are reported in *Table 2*. All the energies are calibrated to the C1s signal of aromatic/aliphatic carbons positioned at 285.0 eV binding energy (BE).

The C1s signals are symmetrical in the spectra of the different polymers, although the full width at half maximum (FWHM) is larger than that of the C1s signals of the pristine Ni complexes. The broadening of the spectra of polymers is thought to be due to the presence of CH_2 and CH_3 carbons of the Et groups of the monomer units in different chemical environments.

The N1s signals show two components in the spectra of PDEPA, the first component is found at 399.0 eV, the second one at higher BE at about 402 eV. The intensity of the N1s signal at 402.0 eV increases by increasing the complex/monomer ratio in the PDEPA (*Figure 2a*). It is noteworthy that in the monoacetylide complex $[Ni(NCS)(C{\equiv}C{-}CH_2NEt_2)(PPh_3)_2]$ only one N1s signal was found (BE = 398.6 eV) (*Figure 2b*), but with a FWHM larger than that observed in the N1s spectrum of the $[Ni(NCS)_2(PPh_3)_2]$ complex (BE = 398.7 eV) (*Table 2*). Therefore, in the case of the monoacetylide complexes, the signal due to the nitrogen atom of the NEt_2 group, which is not bonded to the metal atom, shows a BE close to that measured for the NCS. In the PDEPA spectra the larger difference in the N1s BE values indicates that the NEt_2 pending groups of the polymeric chain are, at least in part, bonded to Ni atoms. A similar N1s signal was found in the XPS spectrum of the complex $[Ni(NCS)_2(NHEt_2)_2]$, which was obtained as a secondary product in the synthesis of the monothiocyanate monoacetylide complex. In this complex the N atoms of the $NHEt_2$ groups are bonded to the metal and give rise to a N1s spectrum with two components at 398.9 and 402.1 eV, due to the presence of NCS and $NHEt_2$ groups, respectively (*Figure 2c*).

The $Ni2p_{3/2}$ core level signal exhibits the same BE either in the complexes or in the PDEPA spectra. However the nickel signals measured for PDEPA are broader and show shake up satellites at about 6 eV from the main Ni2p signal (*Figure 3*). The shake up satellites are present also in the Ni2p signal of the complex $[Ni(CNS)(C{\equiv}C{-}CH_2NEt_2)(PPh_3)_2]$. The presence of satellites in the XPS spectra of Ni complexes is indicative of an octahedral or tetrahedral structure of a paramagnetic Ni(II) complex[16,17]. Square planar complexes do not exhibit these satellites as is the case of the $[Ni(NCS)_2(PPh_3)_2]$ complex. These shake-up satellites are assigned to 3d → 4s transitions, which are forbidden by symmetry for the diamagnetic complexes. The $Ni2p_{3/2}$ signal is significantly broader in the paramagnetic complexes, as found in the PDEPA spectra, because the d → d transitions occur simultaneously with the main photoemission process.

The S2p signal in the spectra of PDEPA polymers is observed at lower energies compared to those of the two reference complexes. The signal comes from the convolution of two components, the $S2p_{1/2}$ and the $S2p_{3/2}$, with 1 eV difference in BE. Different compositions of the polymers could induce the observed variations of the BE values.

Experimental results and calculation of atomic ratios show that Ni is present in all the PDEPA polymers, and that for one Ni atom there are about two sulfur atoms (*Table 3*). By comparing these results with those related to the Ni complexes (*Table 4*), we can see that, in the polymer molecules, two NCS groups still remain bonded to the Ni atoms, as in the starting complex. Phosphorus is also present in all the examined complex polymers. The atomic ratio P/Ni is about 1/1: one phosphine molecule is lost in the reaction leaving a coordination position which is free to form new bonds on the Ni atom.

The amount of carbon atoms with respect to the Ni atoms increases, as the catalyst monomer ratio decreases. Therefore the number of Ni atoms in the polymer molecule

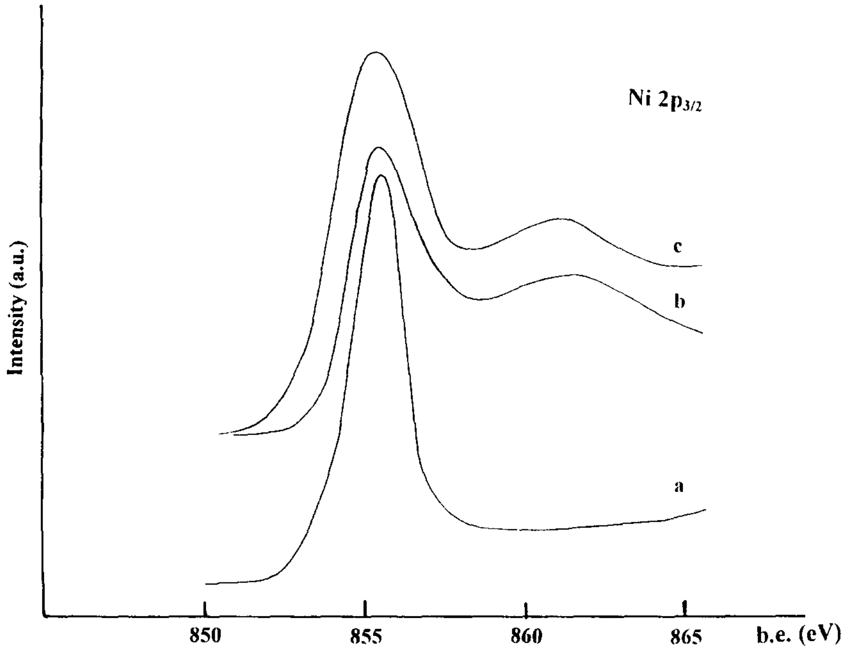

Figure 3 Core level Ni2p$_{3/2}$ spectra: (a) catalyst complex [Ni(NCS)$_2$(PPh$_3$)$_2$]; (b) reference complex [Ni(NCS)(C≡C–CH$_2$–NEt$_2$)(PPh$_3$)$_2$]; (c) PDEPA polymers

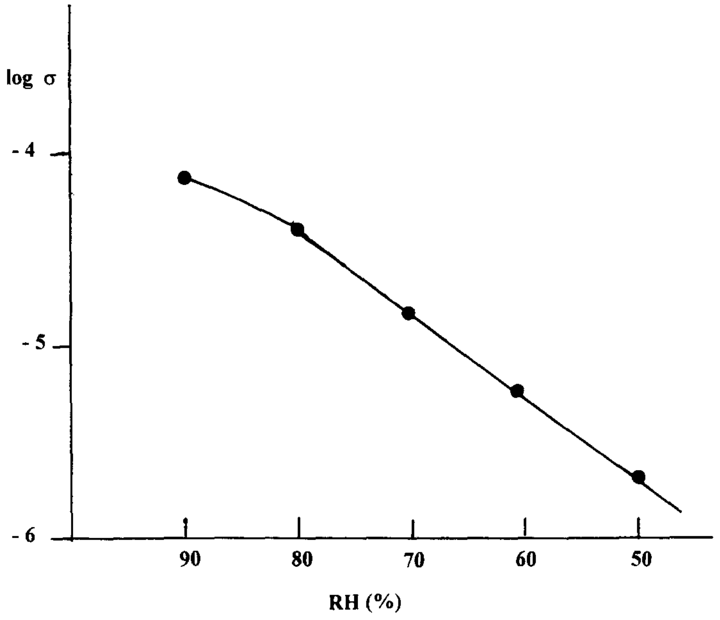

Figure 4 Electrical response (log σ) *versus* relative humidity (R.H.) variations of HCl-doped PDEPA

increases by increasing the amount of complex used in the reaction.

The C/N ratio in the monomer molecule is 7. We have calculated the atomic ratio between C and N in monomer units of the PDEPA (*Table 3*), finding that also in this case during the formation of the metal-containing polymers some NEt$_2$ groups are released, as was previously found for analogous systems[8–10] (see Section 4).

Electrical measurements

Resistance measurements of undoped or doped PDEPA have been carried out on films, cast from CHCl$_3$ or DMF solutions, or on pressed pellets.

Measurements, performed in a climatic chamber on pressed pellets of PDEPA doped with FeCl$_3$, showed low reproducibility, owing the high tendency of this system to adsorb water. The pellets ($\varnothing$ = 1 cm, h = 0.15 cm) showed, at 50% relative humidity (R.H), a conductivity $\sigma = 1.6 \times 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and, at R.H. = 80%, $\sigma = 2.8 \times 10^{-3}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. However the pressed pellets were irreversibly damaged in few days. A better stability was found for pressed pellets of undoped PDEPA; therefore measurements were also carried by casting films on an interdigitated Al electrodes system from CHCl$_3$ solutions.

Conductivity values concerning films of undoped PDEPA are reported in *Table 5*. A conductivity variation of about three orders of magnitude was found, by varying the ambient humidity from 60 to 90%. The measured values were reproducible during various cycles performed by increasing and decreasing the humidity content of the measurement chamber. At low humidity conditions the resistance was too high and could not be measured by our instrumentation.

Films of I_2-doped PDEPA samples showed resistance values of the same order of magnitude as the undoped polymers. Both the response and the reproducibility values were less good than those of undoped PDEPA films.

PDEPA polymers were doped with HCl by maintaining the powders in the presence of HCl vapours for 10 days. After elimination under vacuum of the unbonded HCl the weight increase of the PDEPA samples was about 20%. Resistance measurements were carried out on pressed pellets at different relative humidity conditions. The log σ values are reported as a function of the R.H. in *Figure 4*. The examined samples gave reproducible responses after several cycles of humidity variations. Films of PDEPA/HCl could not be obtained, owing to the insolubility of the systems in most common solvents.

DISCUSSION

DEPA reacts with $[Ni(NCS)_2(PPh_3)_2]$ giving organometallic polymers. Analogous behaviour was found for DMPA in reactions with the same complex[9] and with the $[Pd(C{\equiv}CCH_2NMe_2)_2(PPh_3)_2]$ complex[10], which gives polymers containing increasing amounts of metal by increasing the complex/monomer ratio. A different substituted acetylene propargyl alcohol ($H{-}C{\equiv}C{-}CH_2OH$) reacts in a similar way with the related bis-acetylide $[Pd(C{\equiv}CCH_2OH)_2(PPh_3)_2]$ complex[10]. These functionalised monosubstituted acetylenes are activated by the metal complex, which induces the opening of the triple bond of monomers to give polymeric chains with delocalised π systems. The metal centers lose at least one of the two phosphine ligands; the metal also catalyses the oxidation of PPh_3 to $OPPh_3$. This oxidation reaction occurs in all the examined systems, even under rigorous reaction conditions, showing the high tendency of the complexes used in these reactions to catalyse the oxidation of PPh_3 to $OPPh_3$. The obtained polymers contain the metal atoms bonded to the linear chain in different coordination sites, as can be deduced by the XPS spectra and by the elemental analyses of polymers. The metal atoms can be inserted in the chain, because the growth of the chain occurs by insertion of the monomer units in the Me–C σ bond; the metal can be also coordinated to the double bonds or to the pending groups of the polymer chain.

In the previously studied polymerisation reactions of DMPA with $[Ni(NCS)_2(PPh_3)_2]$, both soluble and insoluble polymeric fractions were obtained. The insoluble fractions do not contain phosphorus atoms, as shown by XPS. In that case, two coordination positions around the Ni atom remain free and can form new bonds with the nitrogen atoms of the chain pending groups or with the double bonds of the polymeric chains. If bonding occurs between two or more chains, crosslinked insoluble polymers are formed. Two NCS groups, however, always remain bonded to each Ni atom.

In this investigation we have found that the polymers obtained by DEPA contain Ni atoms bonding at least one $OPPh_3$ or PPh_3 molecule and about two NCS groups. The $Ni2p_{3/2}$ XPS signal of both PDMPA and PDEPA exhibit shake up satellites, which indicate the formation of paramagnetic Ni complexes. The shake up satellites are associated to tetrahedral or octahedral arrangements around the Ni atoms, the latter arrangement indicating crosslinking between polymer chains.

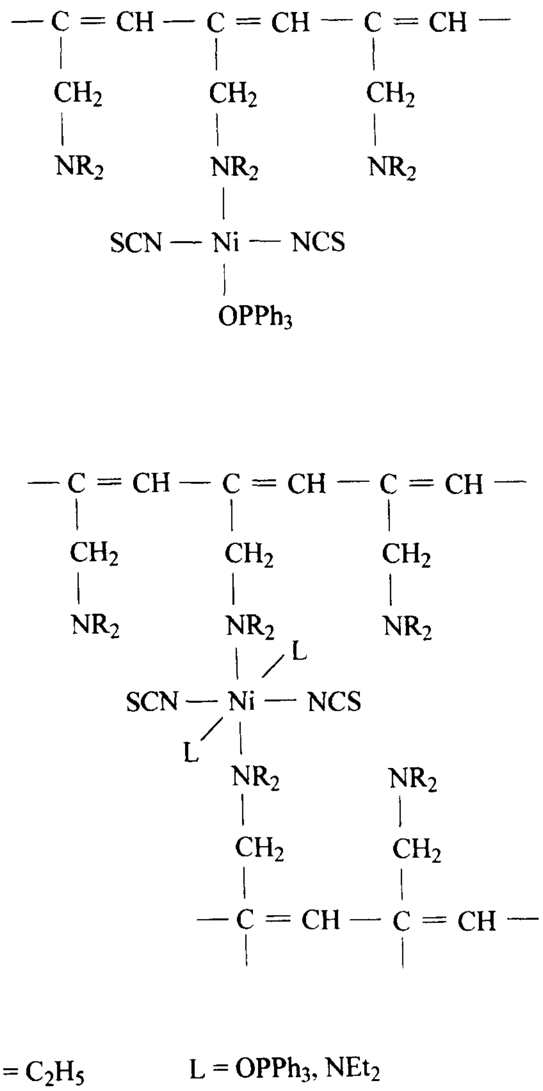

Figure 5 Proposed structures of organometallic PDEPA polymers containing tetrahedral or octahedral Ni coordination sites

From the XPS spectra it is possible to deduce the atomic ratios between the various elements in the polymer molecules (*Table 3*). Although these ratios can give only a semiquantitative estimation of the stoichiometry, it is evident that the C/N ratio, calculated by subtracting the carbon and the nitrogen atoms of the ligands, is always greater then 7 (the C/N ratio of the monomer molecule). Therefore, also in this case, some NEt_2 groups of the monomer are released, as we have already found for similar systems[8–10]; however, the secondary reactions, leading to modifications of the monomer units, occur more easily in the presence of Pd complexes. Different hypotheses have been formulated to explain the elimination of amino groups, such as catalysed hydrolysis reactions, cyclisation reactions of the chains, or crosslinking reactions[9,10].

From the data in *Table 3* we see that, for one Ni atom, there are two S, one P and more than one N bonded atoms. Therefore the coordination number of Ni is greater than 4. Bonding with NEt_2 groups of different chains can lead to crosslinked polymers.

On the basis of all these observations it is possible to propose a structure for the organometallic polymer molecules obtained by the reactions between DEPA and $[Ni(NCS)_2(PPh_3)_2]$ (*Figure 5*). The depicted structure is drawn from an average of experimental results.

CONCLUSIONS

Our investigations have shown that monosubstituted acetylenes, containing functionalised pending groups, can be polymerised in the presence of some metal complexes, which act as polymerisation catalysts but react also with the functionalised groups of the monomer, giving organometallic polymers. The chemical structure and the nature of the Ni coordination sites have been elucidated by XPS studies. In the PDEPA, paramagnetic Ni(II) is found in both tetrahedral and octahedral configurations. The octahedral Ni(II) is bonded to two NCS, one $OPPh_3$, and to NEt_2 ligands of the polymer chain pending groups. Interaction of Ni with the polymer C=C bonds may also occur.

Electrical measurements indicate the possible use of these materials in the preparation of gas sensors. Doped PDEPA are shown to be sensitive to humidity variations in the 50–90% relative humidity range, giving reproducible conductivity values in cyclic measurements. The doped PDEPA is poorly soluble. The aim of future investigations will be to prepare new organometallic polymers with similar properties and increased solubility, in order to obtain films which could be used for electronic applications.

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