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Synthesis and X.p.s. characterization of organometallic Pd containing polymers from monosubstituted acetylenes

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Organometallic polymers containing Pd atoms in different co-ordination sites were obtained and characterized. The reactions were performed in a wide range of complex/monomer molar ratios. Functionalized monosubstituted acetylenes, namely propargyl alcohol (POH) and N,N-dimethylpropargylamine (DMPA) undergo co-ordinative polymerization in the presence of the corresponding bis(triphenylphosphine)bis(acetylide) Pd(II) complexes, $[Pd(PPh_3)_2(C{\equiv}C-CH_2OH)_2]$ and $[Pd(PPh_3)_2(C{\equiv}C-CH_2N\,(CH_3)_2)_2]$. The complexes are active catalysts for the activation of the C≡C bond of acetylenic monomers, leading to a π-conjugated C=C backbone. By increasing the complex/monomer ratios, interaction of Pd with the C=C double bonds of neighbour chains and with the polymer pendant groups also occurs. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Previous investigations on the catalytic activity of bis(triphenylphosphine)Ni (II) complexes in reactions with monosubstituted acetylenes, showed that different reaction products can be obtained depending on the ligands around the Ni atom and on the R groups in the H–C≡C–R monomer. Some catalysts gave regiospecific cyclization of acetylenic alcohols[1–4], others led to the formation of linear trimers[5] or mixtures of cyclic trimers and linear polymers[6,7]. More recently the $[Ni(NCS)_2(PPh_3)_2]$ complex was used as catalyst for the polymerization of $H-C{\equiv}C-CH_2N(CH_3)_2$ and polymers containing increasing amounts of co-ordinatively bonded Ni were obtained, by increasing the complex/monomer ratio[8].

Pd complexes were also found to be active catalysts in polymerization reactions of some acetylenes[9,10]. However, $H-C{\equiv}C-Si(CH_3)_3$ reacts in the presence of *trans*-$[Pd(PPh_3)_2(C{\equiv}C-Si(CH_3)_3)_2]$ giving Pd containing polymers[11].

Now we have investigated the reactions of $[Pd(PPh_3)_2(C{\equiv}C-R)_2]$ where R is CH_2OH and $CH_2N(CH_3)_2$, with the corresponding acetylenes $H-C{\equiv}C-CH_2OH$ and $H-C{\equiv}C-CH_2N(CH_3)_2$. The characterization of the reaction products was mainly accomplished by the X.p.s. technique. The polymerization of the $[Pd(PPh_3)_2(C{\equiv}C-R)_2]$ complexes was also investigated.

EXPERIMENTAL

Materials

Propargyl alcohol (POH = 2-propyn-1-ol) and N,N-dimethylpropargylamine (DMPA = 3-dimetylamino-1-propyne) (Aldrich, Italy) were dried on Na_2SO_4 and distilled prior to use. All the solvents were reagent grade (Carlo Erba, Italy), dried on Na_2SO_4 and distilled before use.

The *cis*-$[Pd(PPh_3)_2Cl_2]$ complex was prepared and purified according to the literature method[12].

The synthesis of *trans*-$[Pd(PPh_3)_2(C{\equiv}C-CH_2OH)_2]$ (Pd-POH) was carried out as previously reported[13].

Synthesis of *trans*-$[Pd(PPh_3)_2(C{\equiv}C-CH_2N(CH_3)_2)_2]$ (Pd-DMPA): 1 g of $[Pd(PPh_3)_2Cl_2]$ (1.4 mmol) and 0.5 ml of DMPA (4.2 mmol) with a molar ratio 1/3 were dissolved in 20 ml of Et_2NH and 5 mg of CuI were added. The mixture was cooled at 0°C and stirred for 15 min. The white product was filtered off and quickly washed with Et_2NH and MeOH, in order to eliminate HCl which may remain bonded to the amine groups of the acetylene:

$$[Pd(PPh_3)_2Cl_2] + 2H-C{\equiv}C-CH_2N(CH_3)_2 \xrightarrow{Et_2NH/CuI}$$
$$[Pd(PPh_3)_2(C{\equiv}C-CH_2N(CH_3)_2)_2] + 2Et_2NH{\cdot}HCl$$

The complex is soluble in chlorinated solvents, alcohols and ether and insoluble in DMF and DMSO. It is unstable in solution giving black products. Elemental analysis found (calculated): C% = 68.95 (69.50); H% = 6.00 (6.00); N% = 3.72 (3.50); P% = 7.30 (7.60). P.F. = 125–128°C. Yield 96%. U.v. spectrum in $CHCl_3$ $\lambda_{max} = 277$ nm. I.r. spectrum: bands at 2107 cm^{-1} (C≡C stretching). ^1H n.m.r. data: $\delta = 1.57$ ppm (CH_3); $\delta = 2.60$ ppm (CH_2); and at $\delta = 7.7, 7.4, 7.3$ ppm (aromatic protons).

Instruments

I.r. spectra have been carried out on a Perkin–Elmer 1400 *FT*i.r. spectrophotometer as Nujol mulls or as cast

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Table 1 Polymerization reactions of POH with Pd-POH

Sample[a]	Complex/ monomer ratio	Yield (%)	Elemental analyses[b]		G.p.c. analyses	
			C%	H%	M_w (amu)	M_n (amu)
Pd-PPOH(A)	1/1300	90	63.7	7.3	77 600	52 800
Pd-PPOH(B)	1/100	98	65.3	7.0	51 000	35 300
Pd-PPOH(C)	1/70	95	65.7	6.7	53 000	36 000
Pd-PPOH(D)	1/40	75	65.0	6.5	61 000	36 500
Pd-PPOH(E)	1/10	67	58.4	5.7	75 000	41 000

[a] All reactions were carried out for 24 h at 55°C in toluene, except for Pd-PPOH(A) (bulk reaction)
[b] Theoretical values for C_3H_4O: C% = 64.4, H% = 7.1

Table 2 Polymerization reactions of DMPA with Pd-DMPA

Sample[a]	Complex/monomer ratio	Yield (%)	Elemental analyses[b]			C/N ratio	G.p.c. analyses	
			C%	H%	N%		M_w (amu)	M_w (amu)
Pd-PDMPA(A)	1/300	40	68.4	6.52	8.44	9.45	36 000	12 000
Pd-PDMPA(B)	1/200	47	66.4	6.68	8.32	9.37	45 000	15 000
Pd-PDMPA(C)	1/100	52	65.4	6.72	9.11	8.38	40 000	13 000
Pd-PDMPA(D)	1/50	50	58.7	7.28	8.62	7.89	27 000	9 300
Pd-PDMPA(E)	1/10	57	55.8	7.30	8.52	7.75	38 000	12 600

[a] All reactions were carried out for 24 h at 55°C in toluene, with exception for Pd-PDMPA (A) (48 h)
[b] Theoretical values for C_5H_9N: C% = 72.3, H% = 10.8, N% = 16.9, C/N = 5

films. The n.m.r. spectra were run on a Varian XL 300 Spectrometer using $CDCl_3$ as solvent. U.v. spectra were measured on a Perkin–Elmer Lambda 5 spectrophotometer.

Molecular weights were measured with a GPC Perkin–Elmer apparatus (binary pump LC 250, oven LC10, u.v. detector LC 10J). Polystyrene standards were used for the calibration. Data analysis was performed by the Chromatographics 2 and GPC 5 programs. The solvent flux was 1 ml min^{-1} on a PL GEL 10 μm column.

X.p.s. measurements were performed on a VG ESCA 3 MK1 spectrometer (Vacuum Generators Ltd, UK). The Al $K\alpha_{1,2}$ ($h\nu = 1486.6$ eV) radiation was used. Vacuum was 10^{-8} Torr in the preparation chamber and was in the low 10^{-9} Torr range in the analysis chamber. Samples in the form of pressed powders or films were analysed. The C1*s* BE (binding energy) = 285.0 eV was taken as a reference for the calibration of the energy scale. Curve fitting analysis of C1*s*, N1*s*, Pd3$d_{5/2}$, and I3$d_{5/2}$ signals were carried out with a Basic program.

Current and resistance measurements were carried out as a function of relative humidity and temperature variations using Keithley 616 or 595 electrometers. Pressed pellets (diameter = 1 cm, $h = 0.1$ cm) were prepared with a Specac P/N 150 hydraulic press at 10 tons. Relative humidity and temperature variations were performed in an Angelantoni UY 150 chamber (the uncertainty on the humidity values is ±3%; for the temperature it is ±1%).

Polymerization reactions

Polymerization of POH, Pd-PPOH polymers. The polymerization reactions of POH were performed by varying the complex/monomer ratio from 1/1300 to 1/10 as reported in *Table 1*. Pd-POH (240 mg; 0.32 mmol) were mixed with 2, 1.3, 0.8, 0.2 ml of POH for complex/ monomer ratios = 1/100, 1/70, 1/40, 1/10 respectively. The reaction solvent was toluene (3 ml). The mixture was held for 24 h at 55°C. The solvent was evaporated under vacuum and a black vitreous mass adherent to the reaction vessel was obtained for molar ratios from 1/100 to 1/40. When the complex/monomer ratio is 1/10, a black powder is formed. The products were washed with toluene. Molecular weights of POH polymers (Pd-PPOH) were found in the range of 10^4 a.m.u. ($\bar{M}_w$).

Table 3 Polymerization reactions of Pd-POH and Pd-DMPA complexes

Sample[a]	Yield (%)	Elemental analyses			C/N ratio
		C%	H%	N%	
PPd-POH	50	47.0	3.4	—	—
PPd-DMPA	57	69.5	6.0	4.1	14.6

[a] All reactions were carried out for 24 h at 55°C in toluene

Polymerization of DMPA: Pd-PDMPA polymers. The polymerization reactions of DMPA were carried out with complex/monomer ratios ranging from 1/300 to 1/10, as shown in *Table 2*. In a typical reaction, for the 1/100 complex/monomer ratio, 3.4 ml of DMPA (2.6 g, 31 mmol) were added to 250 mg (0.31 mmol) of Pd-DMPA, with toluene as solvent (20 ml). The mixture was stirred at 55–60°C for 24 h. The solvent was eliminated under vacuum. Hexane was added to obtain a brown powder, that was filtered off and washed with THF. Careful washing of the precipitate is necessary because $OPPh_3$, the oxidation product of the PPh_3 ligand, is released from the polymer during the reaction. The total yields are in the range 40–60%. DMPA polymers (Pd-PDMPA) are soluble in many organic solvents ($CHCl_3$, CH_2Cl_2, MeOH, DMSO, DMF) and less solu-

Table 4 Electrical responses of doped polymers (pressed pellets ⊘ ≐ 1 cm, $h = 1$ mm)

Doped sample[a]	Undoped R (ohm)	I_2/hexane R (ohm)	I_2/EtOH R (ohm)	$FeCl_3$/MeOH R (ohm)	HCl(vap) R (ohm)
Pd-PPOH(A)	10^{10}	10^{6}	—	10^{6}	—
Pd-PPOH(B)	10^{11}	10^{9}[b]	—	10^{6}	—
Pd-PPOH(C)	10^{11}	10^{9}[b]	—	—	—
Pd-PDMPA(C)	10^{12}	10^{8}	10^{6}	10^{6}	10^{4}
Pd-PDMPA(D)	10^{12}	10^{8}	10^{6}	10^{6}	10^{4}
Pd-PDMPA(E)	10^{12}	10^{7}	10^{7}	10^{6}	10^{4}

[a] Nominal dopant percentage = 50%(wt/wt)
[b] Nominal dopant percentage = 30%(wt/wt)

ble in CH_3COCH_3 and C_6H_6. Molecular weights were found in the range of 10^4 a.m.u. ($\bar{M}_w$).

Polymerization reactions of the Pd-POH and Pd-DMPA complexes. Pd-POH (240 mg, 0.32 mmol) and Pd-DMPA (250 mg, 0.31 mmol) were polymerized for 24 h in 10 ml of toluene or THF at 55°C, giving black brown powders; the reaction conditions are reported in *Table 3*. The $\bar{M}_w$ of the resulting polymers (PPd-POH and PPd-DMPA) were 18 000 and 15 000 a.m.u. respectively.

Doping procedure

Different doping processes were performed. Pd-PPOH polymers were doped with I_2 by introducing weighed amount of polymer (500 mg) into a saturated solution of I_2 in hexane. The polymers are insoluble in this solvent. However, the interaction with I_2 takes place in 24 h and black powders are separated by filtration. Doping with $FeCl_3$ was carried out by dissolving $FeCl_3$ (350 mg) in MeOH and by adding Pd-PPOH (350 mg). Doped films can also be prepared; Pd-PPOH polymers are partially soluble in MeOH and homogeneous solutions were obtained during the doping process. After 24 h a black film is obtained by evaporation of the solvent. Films of doped polymers synthesized with complex/monomer ratio 1/1300 (bulk reaction) were obtained by dissolving the dopants $FeCl_3$ and I_2 and the polymer Pd-PPOH in the monomer POH used as solvent. The reported electrical measurements (*Table 4*) were carried out on pressed pellets obtained from the powders.

Pd-PDMPA polymers are more soluble than Pd-PPOH polymers. A doping reaction is reported as an example. 300 mg of polymer were dissolved in THF or EtOH and solutions of weighed amounts of I_2 or $FeCl_3$ in the same solvents were added in order to get a dopant/polymer ratio 1/1. By stirring the solution at room temperature for 24 h, a black precipitate was obtained, filtered off and dried under vacuum. Pd-PDMPA was doped with HCl by exposition of powdered polymer to HCl vapours for one week. The doping percentage (50% wt/wt) was determined by weight increase. Pellets were prepared from the black powder.

The doping was also obtained by interaction of a solution of the polymer dissolved in EtOH with HCl vapours. By drying the solution under vacuum, black films were obtained in this case.

All the data concerning the electrical response of the polymers after doping are reported in *Table 4*.

RESULTS

Some preliminary studies on the polymerization reactions of POH in the presence of Pd-POH were carried out in our group[13,14]. It was found that when the reaction occurs in bulk (for example with a complex/monomer ratio = 1/1300) a quantitative conversion of the monomer takes place. A polymer with an elemental analysis corresponding to the theoretical one is obtained. In the experiments reported in the present paper we have

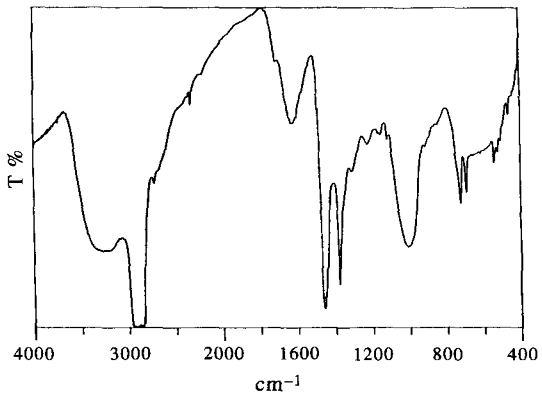


Figure 1 *FT*i.r. spectrum of the Pd-PPOH(D) sample obtained from complex: monomer ratio 1/40

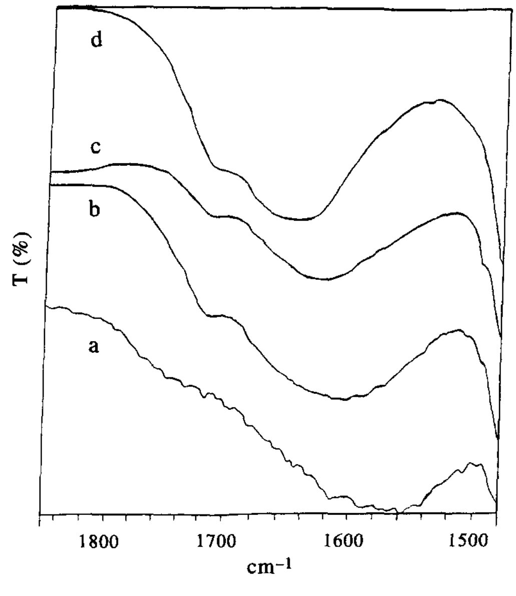


Figure 2 *FT*i.r. spectra of the polymers: (a) PPd-POH; (b) Pd-PPOH(E); (c) Pd-PPOH(E); (d) Pd-PPOH(A) obtained from the bis(acetylide) complex and from complex/monomer ratios 1/1, 1/10 and 1/1300 respectively

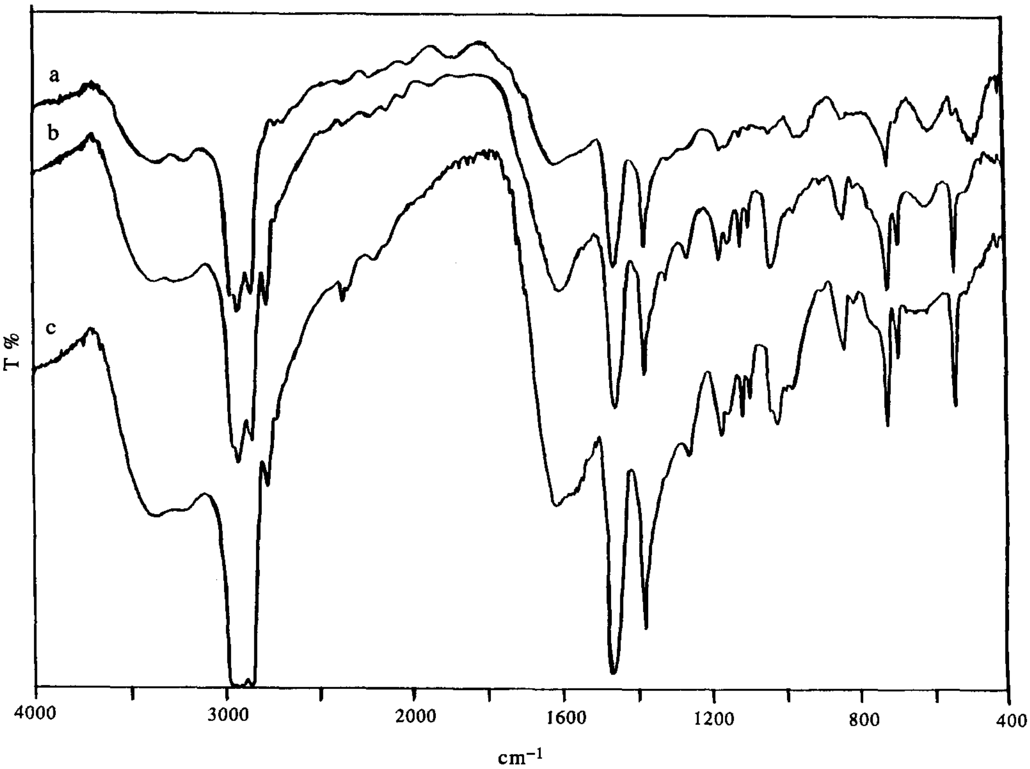


Figure 3 *FTi.r.* spectra of the polymers: (a) Pd-PDMPA(D); (b) Pd-PDMPA(C); (c) Pd-PDMPA(B)

increased the amount of the catalyst to 1/100, 1/70, 1/40 and 1/10 (reactions in toluene at $T = 55°C$) and the results are reported in *Table 1*. The elemental analysis of the Pd-PPOH polymer with complex/monomer ratio 1/10 indicates a variation of the carbon and hydrogen contents of the reaction products with respect to the calculated values for the POH polymer.

Similar polymerization reactions were also carried out with DMPA in the presence of the Pd-DMPA complex, by varying the complex/monomer ratios as reported in *Table 2*. The reaction yields are lower than the corresponding reactions of POH. The elemental analysis for the DMPA polymer does not show agreement with the theoretical values calculated for the unmodified monomeric unit C_5H_9N (C/N ratio = 5). However, by increasing the catalyst/monomer ratio a regular variation of the C/N atomic ratios for the reaction products was observed. The C/N ratio is always higher than the calculated one.

The complexes Pd-POH and Pd-DMPA have been also used in polymerization reactions without the corresponding monomers as shown in *Table 3*. These investigations were suggested by the instability of the Pd-DMPA and Pd-POH solutions, which in a few minutes change from colourless to a dark colour.

I.r. and n.m.r. spectra

The i.r spectra of Pd-PPOH are similar for all the products obtained with different complex/monomer ratios. In *Figure 1* the spectrum of the 1/40 Pd-PPOH is reported. It can be seen that the band at $2100 cm^{-1}$, characteristic of the triple bond, is absent; therefore the polymerization reaction occurs by activation of the triple bonds of the monomer molecules. The broad band at about $3270 cm^{-1}$ is due to the OH groups which are involved in intermolecular hydrogen bonds; the band at $1626 cm^{-1}$ is due to the C=C stretching mode of the chain double bonds. The position of this band is shifted to lower frequencies by increasing the complex/monomer ratio (*Figure 2*).

Examples of the i.r. spectra of Pd-PDMPA polymers at various complex/monomer ratios are reported in *Figure 3*. A band at about $1630 cm^{-1}$, due to the double bond of the chain, is present also in the spectra of these polymers and the absorbance at $2100 cm^{-1}$ is absent. They show the tendency to adsorb water from the atmosphere. By drying the samples, the band at $3300 cm^{-1}$ decreases in intensity and a decrease in the sample weight is also observed; however the band does not disappear completely. The i.r. spectra of Pd-PDMPA and Pd-PPOH show some similarities which can indicate a partial substitution of the $N(CH_3)_2$ groups of the polymer chain of Pd-PDMPA with OH groups due to a Pd catalysed hydrolysis reaction. This substitution could explain the observed decrease of the C/N ratio above discussed. The spectra of Pd-PDMPA and Pd-PPOH show also bands at 543 and $1175 cm^{-1}$. As we have discussed in previous investigations[8–11], these bands are due to $OPPh_3$ molecules formed by oxidation of PPh_3 catalysed by Pd atoms. The $OPPh_3$ molecules are bonded to the metal atoms in the polymer as shown by X.p.s. and n.m.r. spectra, that will be discussed hereafter, but the bond easily can be broken even by washing the polymers with a solvent mixture like THF/hexane.

The i.r. spectra of the polymers PPd-POH and PPd-DMPA obtained from the bis(acetylide) complexes show a great similarity with those of the Pd-PPOH and Pd-PDMPA polymers as shown in *Figures 4a, 5a* (the bis(acetylide) complexes) and *Figures 4b, 5b* (the PPd-polymers). The PPd-POH and PPd-DMPA polymers show a band due to the stretching mode of C=C bonds while the band of the triple bonds is absent

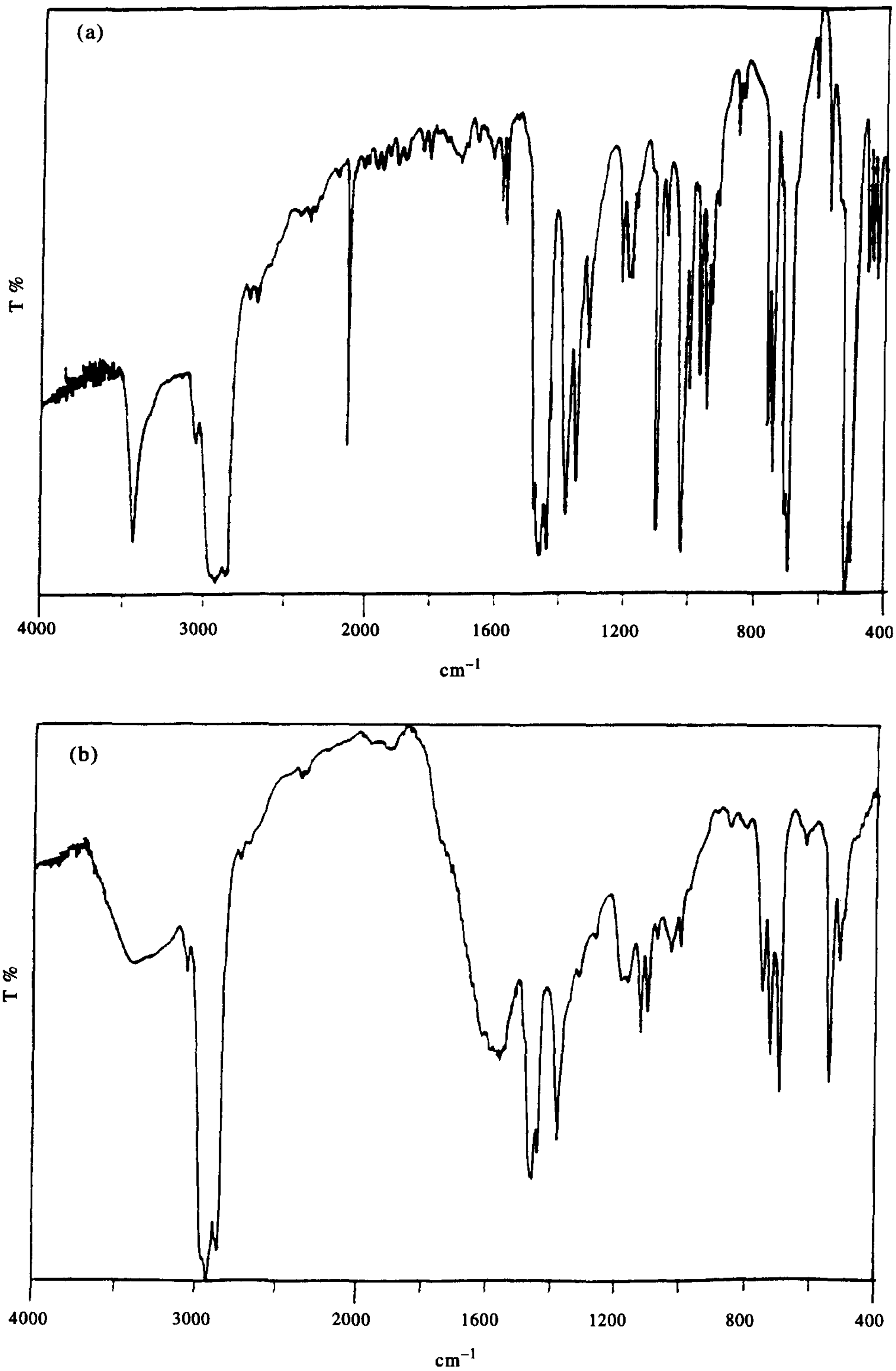


Figure 4 *FT* i.r. spectra of (a) Pd-POH bis(acetylide) complex; (b) PPd-POH polymer obtained from the polymerization of Pd-POH

(*Figures 4b*, *5b*). The phosphine ligand is transformed into $OPPh_3$ (543 and 1175 cm^{-1} bands) and in the case of PPd-DMPA a band due to the stretching mode of OH groups at 3400 cm^{-1} is also present. In *Figures 4a*, *5a* the i.r. spectra of the starting complexes are reported as a comparison.

The Pd-PDMPA are more soluble than the corresponding Pd-PPOH polymers and n.m.r. spectra could be obtained in $CDCl_3$ solutions (*Figure 6*). The spectrum of Pd-PDMPA shows a broad band in the range 1–4 ppm which indicates a disordered structure of the polymer. It is possible to distinguish signals at $\delta = 2.2$ ppm (CH_3 groups) and at $\delta = 2.8$ ppm (CH_2 groups); the resonances of the monomer appear at $\delta = 2.25$ ppm (CH_3) and $\delta = 3.20$ ppm (CH_2). The signals at about $\delta = 7.6$–7.4 ppm are absent in the spectrum of the monomer and indicate the presence of $OPPh_3$ in the polymer. The washed polymers or polymers obtained as secondary fractions (by elimination of the reaction solvents), still show the peaks at about 7.6–7.4 ppm, with a lower

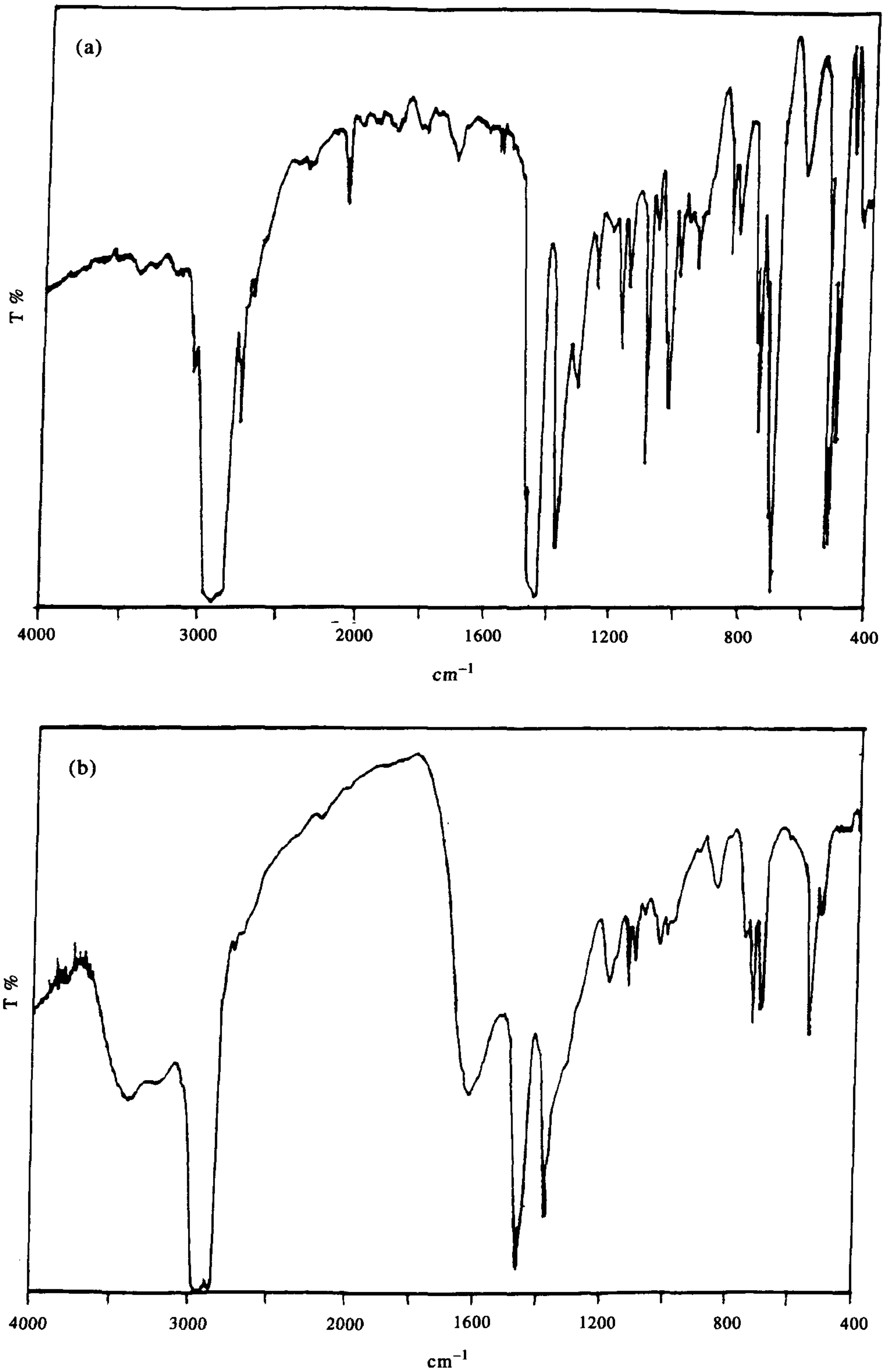


Figure 5 *FT*i.r. spectra (a) Pd-DMPA bis(acetylide) complex; (b) PPd-DMPA polymer obtained from the polymerization of Pd-DMPA

intensity. The spectra of the other Pd-PDMPA polymers show similar features.

X.p.s. spectroscopy measurements

X.p.s. is one of the most suitable tools for the investigation of insoluble polymers. Evaluation of the atomic ratios and of the electronic modifications occurring as a consequence of the polymerization reaction, can be obtained from X.p.s. spectra. The reported X.p.s. data are the average of many measurements performed on different samples. Atomic composition was determined by measuring the areas of the spectra and considering the cross section σ values, as calculated by Scofield[15].

X.p.s. of Pd-POH and Pd-PPOH

The results concerning Pd-PPOH polymers and the Pd-POH complex (considered as a reference standard for the Pd-PPOH polymers) are collected in *Table 5*. The C1*s* core level spectra of the Pd complex and of the polymers are reported in *Figure 7*. The C1*s* signal of the Pd complex (*Figure 7f*) shows a symmetric shape, centred at 285.0 eV (taken as the energy reference); the shake-up

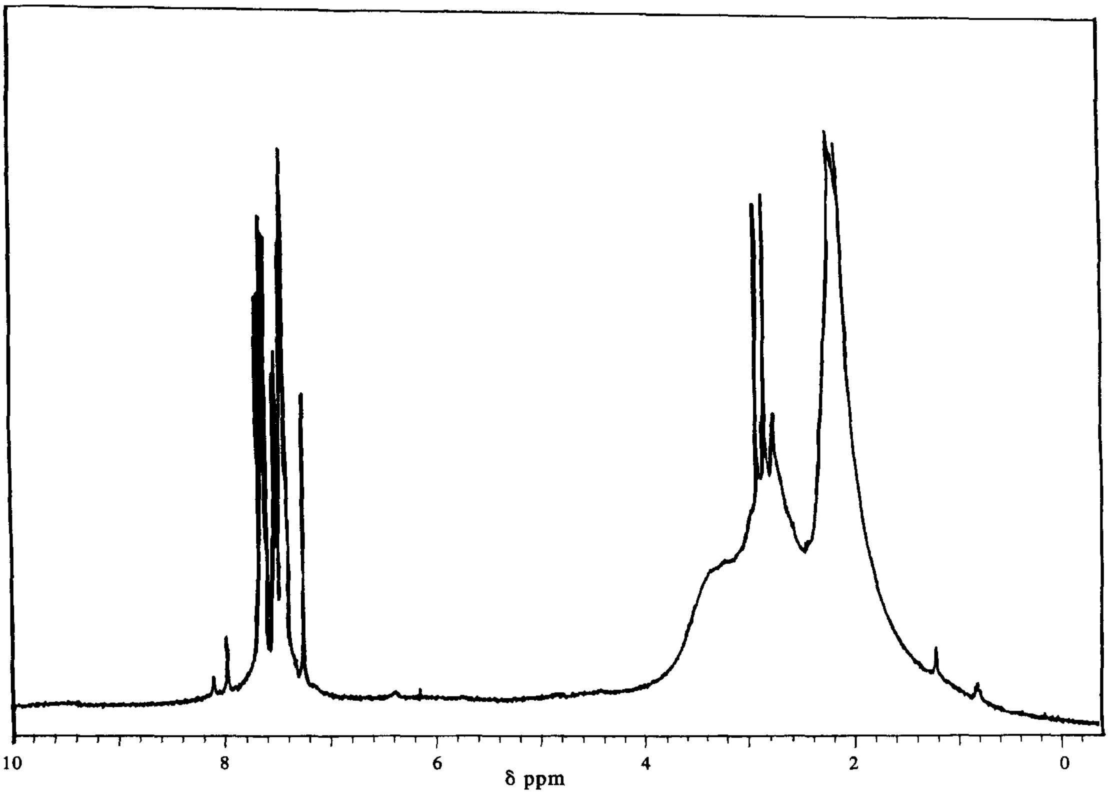


Figure 6 ^{1}H-n.m.r. spectrum of the polymer Pd-PPOH(B) obtained from complex monomer ratio 1/100

satellite at about 7.0 eV from the main C1*s* peak, is due to the $\pi \rightarrow \pi^*$ secondary transitions of the phenyl ring electrons. The evaluation of the atomic ratios agree with the calculated values.

In the case of the Pd-PPOH (A) (polymer obtained with a complex/monomer ratio = 1/1300[14]) the C1*s* spectrum (*Figure 7a*) shows a pronounced asymmetry at higher BE with respect to the main signal (BE = 285.0 eV). This is due to the presence of carbon atoms in different chemical environments: those of the main chain and those of the pendant groups $-CH_2OH$ (BE = 286.6 eV). Curve fitting of the C1*s* signal has been performed; the two C1*s* components are in the 2/1 atomic ratio. In this sample, the P2*p* and the Pd3*d* signals are absent.

As the complex/monomer ratio increases, an increase of the ratio between the two C1*s* peak components (at 285.0 and ≈ 286.6 eV) is observed together with an increase of the C1*s* $\pi \rightarrow \pi^*$ shake-up intensity as shown in *Figure 7*. Furthermore, the Pd3$d_{5/2,3/2}$ and the P2*p* signals are also observed. The first one (*Figure 8*) shows a good resolution and symmetry of the peaks shape of the two spin–orbit components, observed for the Pd3*d* signal of the complex. However the Pd3$d_{5/2}$ component of the polymers (BE = 337.0 eV) is found at lower BE (about 1.0 eV) in comparison with the corresponding Pd3$d_{5/2}$ signal of the reference complex (BE = 338.1 eV). A charge transfer from the polymer to the metal occurs; Pd reduces its positive charge, probably because interaction between Pd and the C=C π bonds of the chain occurs. The BE value of the P2*p* core level is found at 132.4 eV, as we have already found for the Pd-containing poly(trimethylsilyl-acetylene)[11] and in agreement with the data reported in the literature for $OPPh_3$[16]. The P2*p* BE value of the complex is found at 131.8 eV. These results agree with the i.r. and n.m.r. data: the PPh_3 ligand of the complex undergoes oxidation to $OPPh_3$ during the polymerization reaction.

The O1*s* core level spectra of the complex and of the polymers show a narrow signal at BE = 532.8 eV. This value is characteristic of the –OH groups covalently bonded to the carbon. In the Pd and P containing polymers, the O1*s* spectrum exhibits a slight asymmetry at lower BE with respect to the main signal (532.8 eV) due to the contribution of the oxygen of the $OPPh_3$ groups.

The X.p.s. analysis of PPd-POH, obtained from the autopolymerization of the complex $[Pd(PPh_3)_2(C{\equiv}CCH_2OH)_2]$, shows an increase of the local charge on the metal atoms. The Pd3$d_{5/2}$ signal is shifted to lower energy (about 1.0 eV) with respect to the one measured for the starting complex.

The BE of the P2*p* signal is close to the BE detected for $OPPh_3$. The atomic ratios, reported in *Table 6*, give an estimation of the monomeric unit of the polymer obtained from the complex Pd-POH, if a partial loss of $OPPh_3$ is considered. These atomic ratios were calculated in this way: from the total number of carbon atoms, the number of carbon atoms of the phenyl rings bonded to phosphorus, are subtracted (the evaluation of the number of the phenyl rings carbon atoms is calculated from the P2*p* signal); the difference gives the carbon atoms belonging to the chain units for each Pd atom.

X.p.s. of Pd-DMPA and Pd-PDMPA

The X.p.s. data concerning the complex Pd-DMPA are shown in *Table 7*. They agree both with expected theoretical values and with elemental analysis and are assumed as a reference standard for the polymers Pd-PDMPA. In *Figure 9* we report the experimental spectra

Table 5 X.p.s. measurements of Pd-POH and Pd-PPOH polymers

Sample	Core level	BE (eV)	FWHM (eV)	No. atoms/Pd experimental
Pd-POH[a]	C1s	285.0	2.2	39.5
	O1s	532.6	2.7	2.8
	Pd3$d_{5/2}$	338.1	2.6	1.0
	P2p	131.6	2.5	2.4
Pd-PPOH(A)[b]	C1s (C=C)	285.0	2.0	2.2
1/1300	C1s (C–OH)	286.6	2.0	1.1
	O1s	532.9	2.2	1.0
	Pd3$d_{5/2}$	—	—	—
	P2p	—	—	—
Pd-PPOH(B)	C1s (C=C)	285.0	2.3	160.3
1/100	C1s (C–OH)	286.6	2.3	54.2
	O1s	532.8	2.2	52.0
	Pd3$d_{5/2}$	336.9	3.1	1.0
	P2p	132.5	3.0	1.6
Pd-PPOH(C)	C1s (C=C)	285.0	2.4	128.2
1/70	C1s (C–OH)	286.7	2.4	37.2
	O1s	532.7	2.4	41.5
	Pd3$d_{5/2}$	337.1	3.2	1.0
	P2p	132.4	3.0	2.2
Pd-PPOH(D)	C1s (C=C)	285.0	2.8	99.9
1/40	C1s (C–OH)	286.8	2.9	27.3
	O1s	532.6	2.8	32.1
	Pd3$d_{5/2}$	336.8	2.9	1.0
	P2p	132.4	3.1	1.8
Pd-PPOH(E)	C1s	285.0	3.5	36.4
1/10	O1s	532.5	2.9	9.5
	Pd3$d_{5/2}$	337.3	3.3	1.0
	P2p	132.3	3.7	0.7

[a] Calculated atomic ratios, normalized to the Pd signal: $PdC_{42}P_2O_2$

[b] X.p.s. performed on the films cast from solutions of polymer in POH; the atomic ratios were calculated with respect to the O1s peak area, since no Pd signal was observed in this sample

of Pd-DMPA complex: Pd3$d_{5/2,3/2}$, C1s, P2p and N1s. The C1s core level signal is found at BE = 285.0 eV and shows a symmetric shape and the shake-up transition $\pi \rightarrow \pi^*$ signal at about 6.5 eV from the main peak. The main line has two contributions: aliphatic and aromatic carbon atoms of the phosphine phenyl rings as shown by a curve fitting analysis. The Pd atom has a formal oxidation number +2 and shows a signal at BE = 338.3 eV, with a separation between the two spin–orbit components 5/2, 3/2 of 5.2 eV. The signal due to N1s has a BE = 399.3 eV and gives a symmetric shape. The P2p line lies at 131 eV.

In *Table 7* the X.p.s. data for the polymers Pd-PDMPA obtained with complex/monomer ratios: 1/200, 1/100, 1/50, 1/10 are shown. In *Figure 10* we report the C1s, Pd3$d_{5/2,3/2}$, N1s, P2p spectra of the polymer Pd-PDMPA obtained with a complex/monomer ratio 1/200 taken as an example for all the Pd-PDMPA polymers. The C1s signal is broad and it can be seen that the shake up satellite disappears almost completely in the polymer spectrum, indicating that only a small amount of phosphine is still present in the Pd-PDMPA polymers. The fitting of the peak shows the second component at higher energy at about 2.0 eV from the main one, due to the presence of the carbon atoms bonded to N. The relative intensity of C bonded to N atoms is now enhanced with respect to that of the reference complex.

Also the N1s core level signal fitting shows the presence of two components. The main peak at 339.3 eV is due to the N bonded to C of the pendant groups and the second component at 401.6 eV is due to a positively charged nitrogen atoms[17]. The increase of the BE of nitrogen indicate a partial decrease of the electronic density around the N atom, probably due to co-ordination of Pd atoms to the pendant groups.

The Pd3d core level signal shifts toward lower BE with respect to the value detected for the complex (BE in the polymer = 337.3 eV; BE in the complex = 338.3 eV), confirming new interactions of the metal, which can occur with the double bonds of the chain and with the nitrogen atoms of the pendant group explaining the observed trend of N1s. The measured P2p signal at 132.3 eV is due to $OPPh_3$. The signal decreases in intensity after washing the polymer with THF; $OPPh_3$ is only weakly bonded to the metal also in this case. Experimental data indicate loss of nitrogen, because the C/N ratio in all the polymers is higher than the expected one as reported in *Table 7*. This ratio is equal to 5 in the monomer and we always found values in the range 7.9–9.8 for the Pd-PDMPA polymers. These values were calculated subtracting from the experimentally determined total number of carbon atoms of the polymer, the

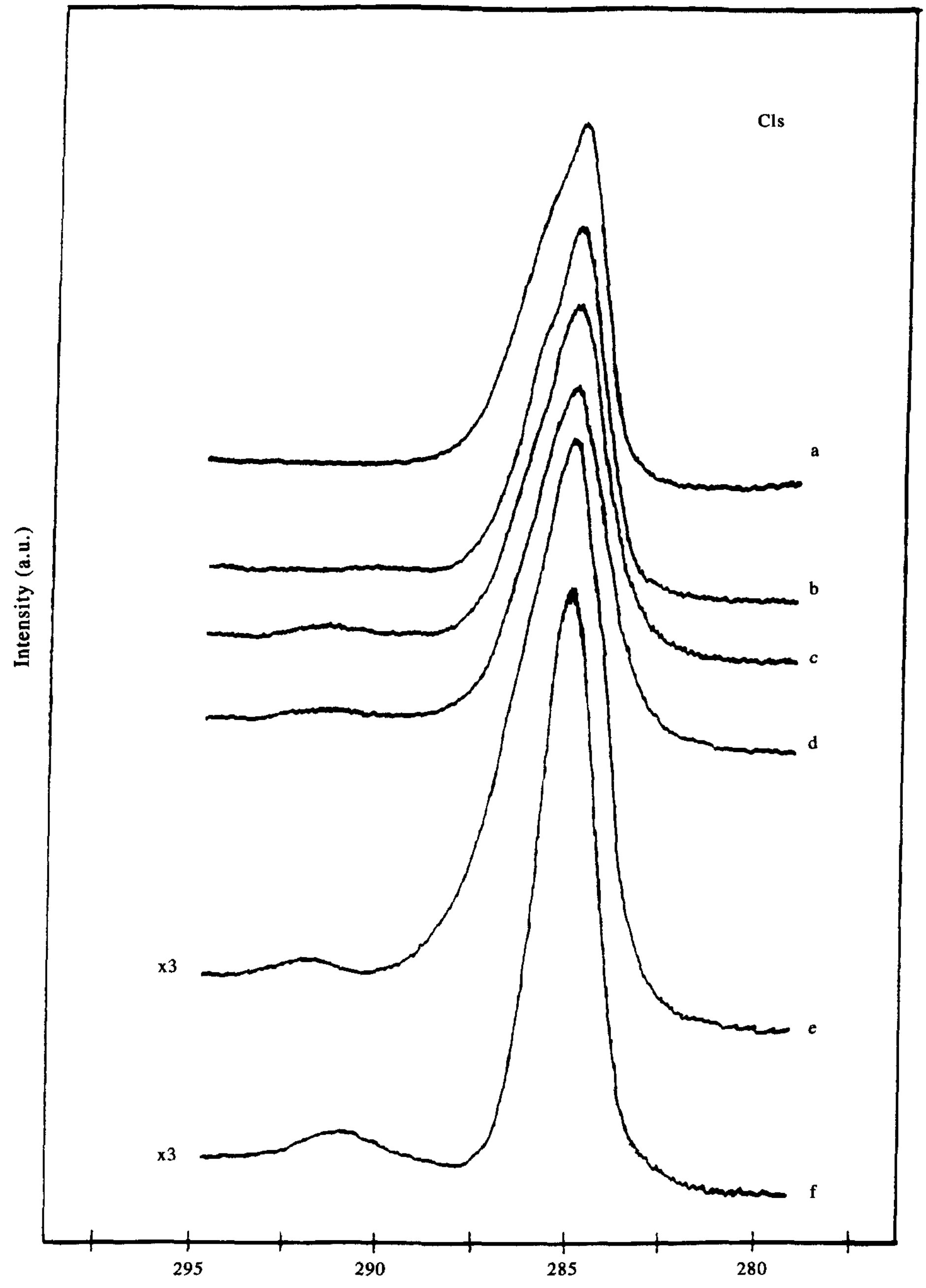


Figure 7 C1*s* core level spectra of: (a) Pd-PPOH(A); (b) Pd-PPOH(B); (c) Pd-PPOH(C); (d) Pd-PPOH(D); (e) Pd-PPOH(E) and (f) Pd-POH complex

carbon atoms of the triphenylphosphine oxide, evaluated from the P2*p* signal (to each P atom three phenyl rings are bonded). In this way, the number of carbon atoms belonging to the repeat monomer units (modified or unmodified) in the polymer chain may be obtained.

We have also investigated the PPd-DMPA polymer, obtained from the auto-polymerization of the bis(acetylide) complex $[Pd(PPh_3)_2(C{\equiv}CCH_2N(CH_3)_2)_2]$ and we found similarities with the Pd-PDMPA polymers spectra as shown in *Table 6*. The PPd-DMPA polymer loses N: we found a C/N ratio equal to 9.3. The N1*s* signal has two components (BE = 339.7 eV for the main component and BE = 401.3 eV for the N^+ component). The C1*s* signal shows a feature very similar to that of the C1*s* signal of the polymers, obtained with different complex/monomer ratios. Also in this case PPh_3 is converted into $OPPh_3$; however the bond between Pd and the ligand is weaker than in the Pd-PDMPA because the P2*p* signal (BE = 132.3 eV) does not disappear after washing. The Pd3*d* signal is found slightly shifted at 337.8 eV, about 0.5 eV higher with respect to the starting complex and about 0.5 eV lower with respect to the polymers.

Electrical responses

Previous studies on different poly(monosubstituted) acetylenes, that were successfully used as sensitive membranes for gas sensors[18], prompted us to also carry on investigations on these new materials. In *Table 4* we report preliminary results obtained for pristine and doped Pd-PPOH and Pd-PDMPA samples. We observed an increase in the conductivity of pressed pellets of doped polymers. The best result was obtained for a Pd-PDMPA polymer doped with HCl vapours. Preliminary measurements of the electrical responses to

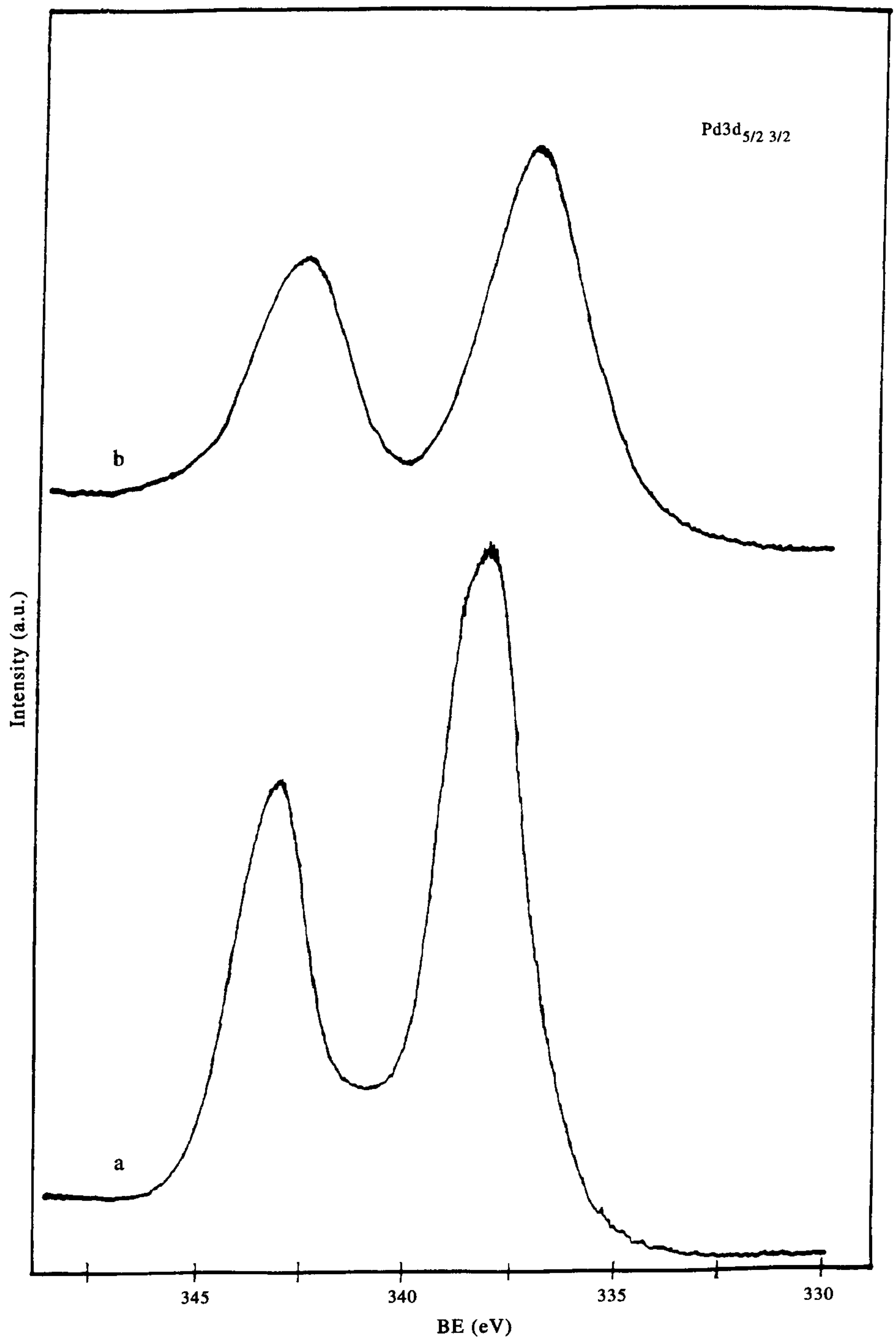


Figure 8 $Pd3d_{5/2,3/2}$ core level spectra of: (a) Pd-POH complex; (b) Pd-PPOH polymers (obtained from all the complex/monomer ratios)

Table 6 X.p.s. measurements of PPd-POH and PPd-DMPA polymers

Sample[a]	Core level	BE (eV)	FWHM (eV)	No. atoms/Pd[b] experimental
PPd-POH	C1*s*	285.0	3.0	20.5 (42)
	O1*s*	532.3	3.8	5.3 (2)
	$Pd3d_{5/2}$	337.3	3.5	1.0 (1)
	P2*p*	132.1	2.9	0.7 (2)
PPd-DMPA	C1*s*	285.0	2.2	34.0 (46)
	N1*s*	399.7	2.5	2.2 (2)
	$Pd3d_{5/2}$	337.8	1.8	1.0 (1)
	P2*p*	132.3	2.2	0.8 (2)

[a] Measurements performed on powders
[b] Calculated values for the starting complexes are given in parentheses

Table 7 X.p.s. measurements of Pd-DMPA and Pd-PDMPA polymers

Sample	Core level	BE (eV)	FWHM (eV)	No. atoms/Pd experimental[b]	C/N (calculated)
Pd-DMPA[a]	C1*s*	285.0	2.5	45.6	24
	N1*s*	399.3	2.4	1.9	
	Pd3$d_{5/2}$	338.3	2.4	1.0	
	P2*p*	131.2	2.6	2.0	
Pd-PDMPA(B)[b]	C1*s*	285.0	2.4	76.0	9.8
	N1*s*	399.7	2.5	7.7	
	Pd3$d_{5/2}$	337.5	2.0	1.0	
	P2*p*	132.4	2.2	0.2	
Pd-PDMPA(C)[b]	C1*s*	285.0	2.5	77.0	8.5
	N1*s*	399.4	2.6	9.0	
	Pd3$d_{5/2}$	337.3	2.4	1.1	
	P2*p*	132.2	2.4	0.2	
Pd-PDMPA(D)[b]	C1*s*	285.0	3.0	59.4	8.2
	N1*s*	399.6	3.0	7.0	
	Pd3$d_{5/2}$	337.2	2.8	1.0	
	P2*p*	132.3	2.6	0.2	
Pd-PDMPA(E)[b]	C1*s*	285.0	2.8	45.5	7.9
	N1*s*	399.5	2.8	5.7	
	Pd3$d_{5/2}$	337.2	2.9	1.0	
	P2*p*	132.3	2.6	0.2	

[a] Calculated atomic ratios: $PdC_{46}P_2N_2$. Measurements on the sample Pd-PDMPA(A) could not be made because of the poor yield of the purified material

[b] Measurements performed on films cast from $CHCl_3$ solutions

relative humidity (r.h.) variations were carried out on thin films of doped Pd-PDMPA and Pd-PPOH polymers. Fast and reproducible responses in the range 0–90% of r.h. (the conductivity values vary from 10^{-12} to 10^{-8} S cm^{-1}) were obtained[19].

DISCUSSION

The polymerization mechanism of the acetylenes in presence of transition metals provides for triple bond activation followed by insertion of the monomer in a metal–carbon bond. This occurs when small amounts of catalyst are used and the structure of the polymers is $[-HC{=}C(CH_2R)-]_n$, with R = OH or $N(CH_3)_2$.

The polymerization of POH and DMPA have been carried out with a progressive increasing of the complex/monomer ratio, in order to see if the functional groups and the double bonds of the chain can give rise to interactions with the metal. In both cases we found that the polymers contain the Pd and the $OPPh_3$ ligand. X.p.s. measurements suggested an increase of the electronic density on the Pd atoms in the polymers. The ligand PPh_3 is oxidized to $OPPh_3$ by an oxygen insertion catalysed by the metal[11,20] during the polymerization reaction, as confirmed by i.r., n.m.r. and X.p.s. results. The metal in the backbone may be co-ordinated to the oxygen atom of the $OPPh_3$. The new bond between Pd and $OPPH_3$ is weak; the triphenylphospine oxide can be easily released leaving free co-ordination sites on the metal, which can co-ordinate the π system of the chain. This co-ordination may also involve near chains. On the basis of these observations we can propose the polymer structures reported in *Figure 11*, where n is the number of monomeric units and x is the number of $OPPh_3$ molecules, for each Pd atom. They have been calculated for Pd-PPOH by X.p.s. (*Table 5*) and agree with elemental analyses (Pd-PPOH(B) $n = 131$, $x = 1.6$; Pd-PPOH(C) $n = 82$, $x = 1.6$; Pd-PPOH(D) $n = 68$, $x = 1.8$; Pd-PPOH(E) $n = 24$, $x = 0.7$).

For Pd-PDMPA polymers X.p.s. measurements indicate the presence of two components in the N1*s* signal. The variation of C/N ratios indicate the loss of some pendant groups. A Pd-N co-ordination occurs, which weakens the C–N bond and may be responsible for secondary catalytic processes such as the co-ordination of water and the hydrolysis of the pendant groups. The activated loss of $N(CH_3)_2$ by cyclization processes or intramolecular nucleophilic reactions, leading to the structures drawn in *Figure 12*, can also occur leading to a polymeric structure which is difficult to define.

By increasing the complex/monomer ratio we have observed a decreasing number of N atoms in the polymers, that is an increasing number of transformed pendant groups. The palladium catalyses the polymerization, but by increasing the complex/monomer ratio, the number of reaction sites increases giving rise to secondary reactions. In the case of Pd-PPOH secondary reactions are not observed; the polymerization reaction goes on giving good yields for low and high complex/monomer ratios.

In the polymerization reactions of the complexes *trans*-$[Pd(PPh_3)_2(C{\equiv}C{-}CH_2OH)_2]$ and *trans*-$[Pd(PPh_3)_2(C{\equiv}C{-}CH_2N(CH_3)_2)_2]$ new polymers PPd-POH and PPd-DMPA were obtained. Considering the reactivity of palladium complexes[21-23] an oxidative coupling between two acetylenic fragments can occur, with a corresponding reduction of the metal to Pd(0). A general scheme of an oxidative coupling of alkynes was reported by Trost[21]. This kind of reaction was also reported by Heck[23] for the preparation of disubstituted acetylenes from monosubstituted acetylenes. On the basis of these

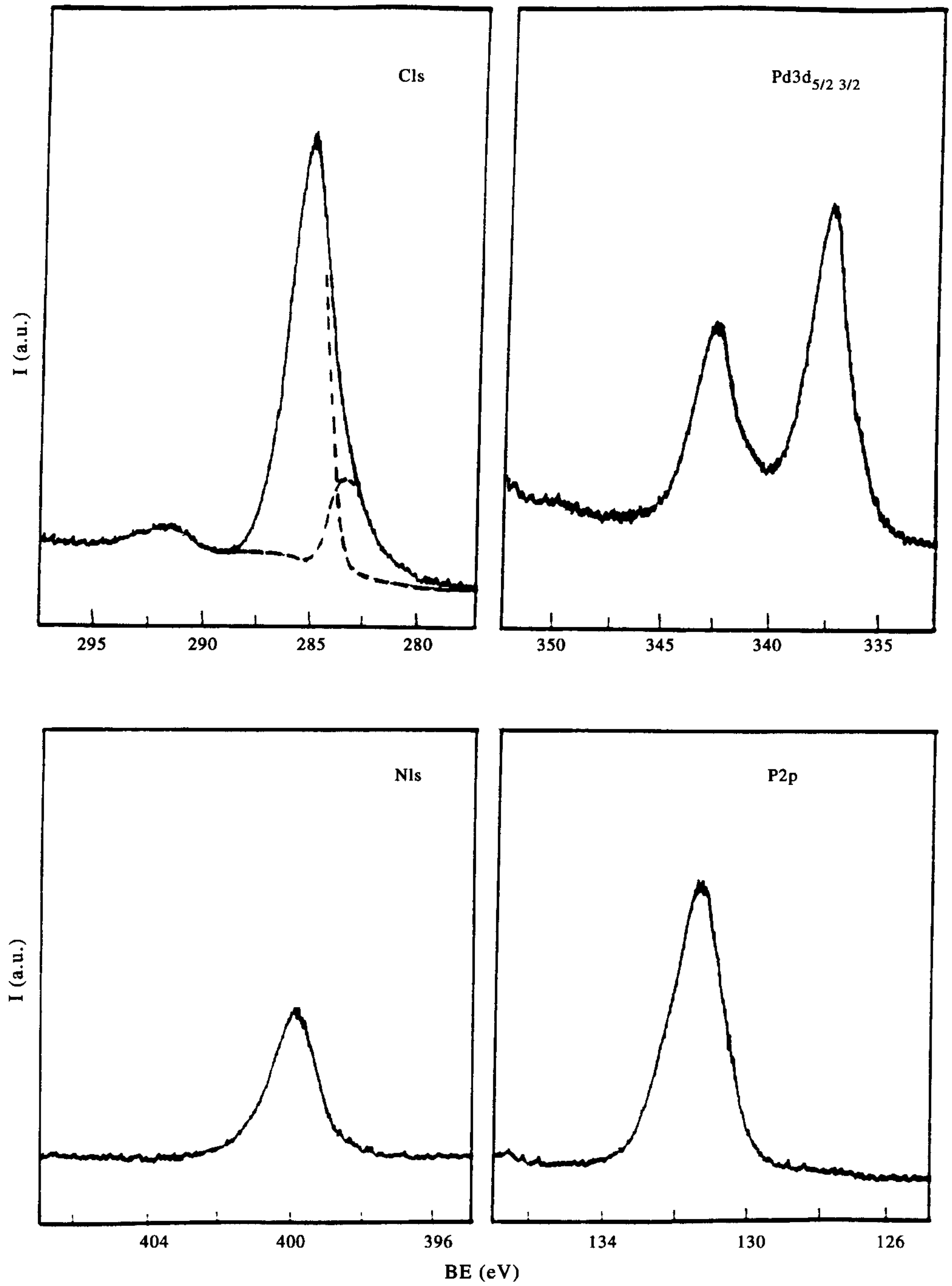
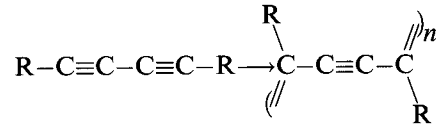


Figure 9 X.p.s. characterization of the Pd-DMPA complex; C1*s*, Pd3$d_{5/2,3/2}$, N1*s* and P2*p* core level spectra. Dotted lines indicate the curve fittings, solid lines show the experimental signals. The intensity of the signals is given in arbitrary units; the calculated atomic ratios are given in *Table 7*

observations we propose an analogous oxidative coupling mechanism for Pd-POH and Pd-DMPA. The resulting dyine polymerizes giving a backbone with alternating double and triple bonds[24,25].



$$R{-}C{\equiv}C{-}C{\equiv}C{-}R \longrightarrow \left(\overset{R}{C}{=}C{\equiv}C{-}\underset{R}{C}{=} \right)_n$$

The sequence of double and triple bonds in the chain give the possibility of linking Pd atoms, as shown by the X.p.s. spectra. Pd can co-ordinate the π system of the chain. The Pd3*d* signals show BE values that are between that of the complexes and that of palladium zero. The formation of polymers occurs as reported in the literature for the vicinal diacetylenes[26].

CONCLUSIONS

The reactivity of the complex $[Pd(PPh_3)_2(C{\equiv}C{-}CH_2OH)_2]$ towards propargyl alcohol and of the complex $[Pd(PPh_3)_2(C{\equiv}C{-}CH_2N(CH_3)_2)_2]$ towards N,N-dimethylpropargylamine has been investigated.

The catalysts induce the polymerization of the monomers as a growth of a π-conjugated $[-CH{=}CR-]_n$ polymeric

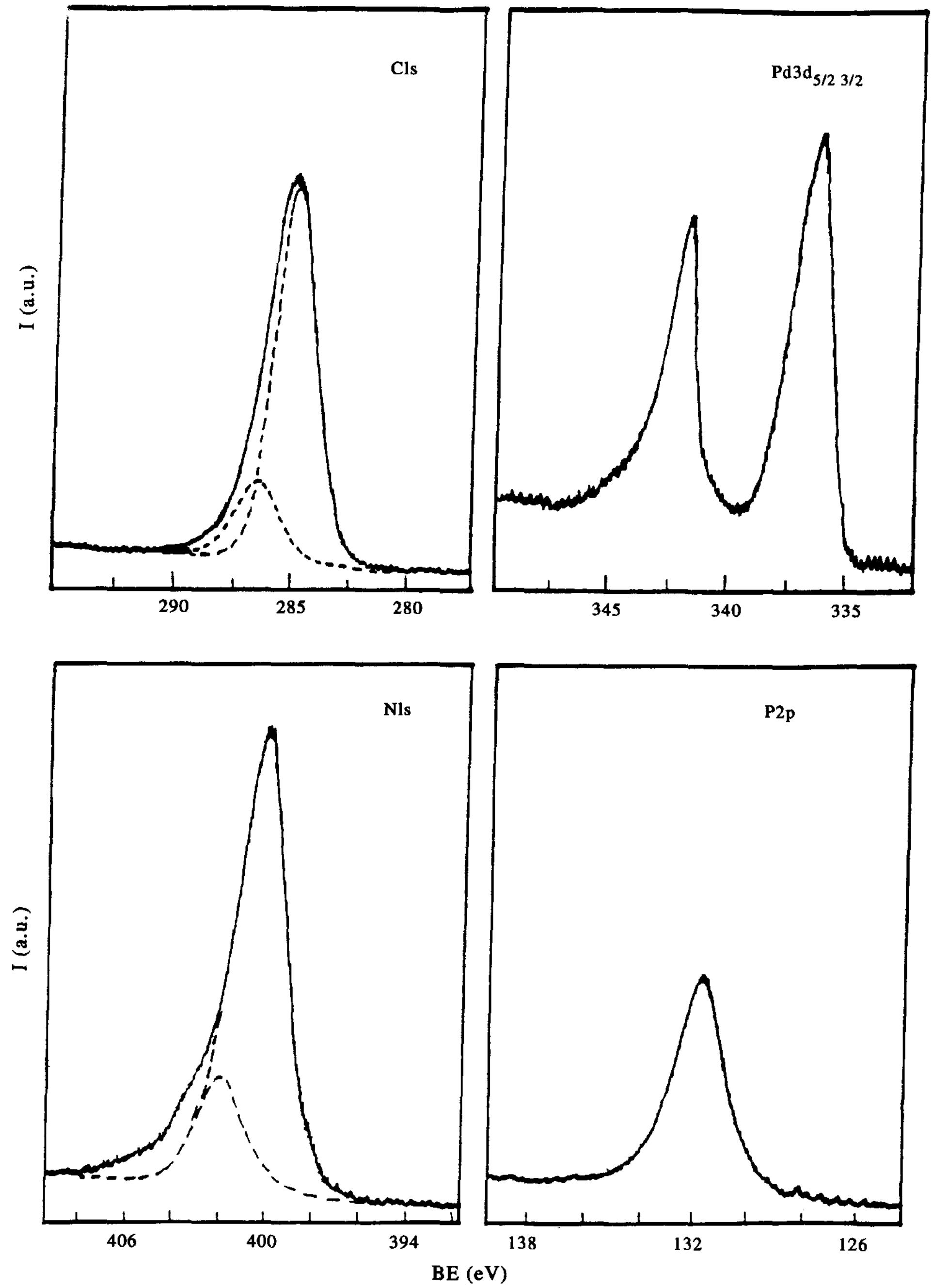


Figure 10 X.p.s. characterization of the Pd-PDMPA polymers; C1*s*, Pd3$d_{5/2,3/2}$, N1*s* and P2*p* corre level spectra. Dotted lines indicate the curve fittings, solid lines show the experimental signals. The intensity of the signals is given in arbitrary units; the calculated atomic ratios are given in *Table 7*

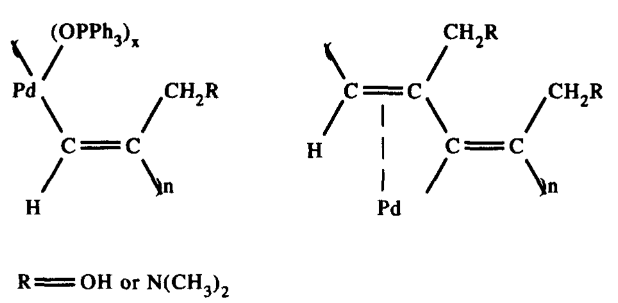


Figure 11 Structures of the polymers upon increasing the complex/monomer ratios (≥ 1/100 for Pd-PPOH and ≥ 1/300 for Pd-PDMPA)

backbone. By increasing the complex/monomer ratio metal containing polymers are formed. The catalysts play different roles: (a) activation by Pd of the triple C≡C bond of the monomer and insertion into the Pd-C σ bond; (b) oxidation of the PPh_3 to $OPPh_3$ that can be then released (c) activation of the C–N bond of the pendant groups of Pd-PDMPA polymers, leading to polymers with a lower nitrogen content. The Pd-POH and Pd-DMPA complexes give polymers through an oxidative coupling of acetylenic moieties to form a π-conjugated structure coordinated to the palladium.

X.p.s. investigation have been especially useful in the assessment of the Pd species.

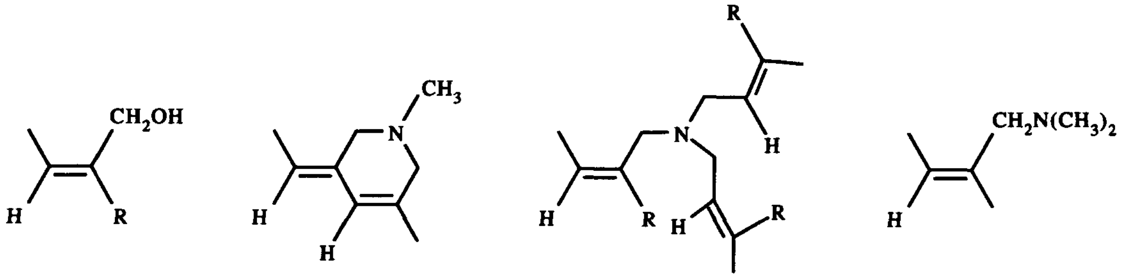


Figure 12 Modifications of the pendant groups (Pd catalysed) in Pd-PDMPA

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