Synthesis and characterization of poly(ethynyltrimethylsilane) containing Pd(II) coordination sites

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The polymerization of ethynyltrimethylsilane with $\{Pd[C \equiv C\text{-}Si(CH_3)_3)]_2(PPh_3)_2\}$ in different complex: monomer ratios has been investigated. Polymers containing Pd(II) have been isolated and characterized by means of X.p.s. and *FT* i.r. measurements. The insoluble polymers obtained contain Pd sites that are σ-bonded to the π-conjugated growth chain and coordinated to the C = C bonds of adjacent chains in a crosslinked structure. The soluble polymers isolated have a linear structure where Pd(II) coordinates through σ-bonds to the polymeric chains and to OPPh$_3$ ligands. If NHEt$_2$ is used as the polymerization solvent, substitution of Si(CH$_3$)$_3$ by N(C$_2$H$_5$)$_2$ groups occurs, catalysed by the Pd complex. Comparison of the X.p.s. and g.p.c. measurements and elemental analyses give an estimation of the number of monomer repeat units for every Pd atom. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ethynyltrimethylsilane; polymerization; Pd catalysts)

INTRODUCTION

The synthesis, characterization and catalytic activity of polymer–metal complexes have been widely investigated owing to the catalytic activities of these materials in redox and hydrogenation reactions[1]. Organometallic π-conjugated polymers have been recently prepared[2–4] with the aim of improving the electrical conductivity by enhancement of the ordering of the polymer chain throughout the insertion of a metallic site. It is known that organometallic polymers containing transition metals (Fe, Co, Ni, Cu) show strong magnetic coupling between the metal centres[5]. Poly-yne materials containing Pt and Pd in the polymeric chain have been also prepared because of interest in their potential third-order non-linear optical properties[6,7]; analogous polymers with silicon atoms in the main chain have been reported to give μ-coordinated complexes by reacting with Co$_2$(CO)$_6$[8].

In this article polymerization reactions of ethynyl-trimethylsilane (HC $\equiv$ C-Si(CH$_3$)$_3$) using the complex $\{Pd[C \equiv C\text{-}Si(CH_3)_3)]_2(PPh_3)_2\}$ are reported. The complex was used either as an initiator, or in increasing complex:monomer ratios leading to polymers with Pd incorporated in the growing polymeric chain.

EXPERIMENTAL

Instruments

FT i.r. spectra (nujol mulls) were recorded with a

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Perkin-Elmer 1700 X spectrophotometer; u.v. measurements in CHCl$_3$ were performed with a Perkin-Elmer Lambda 5 instrument; molecular weight determination was accomplished using a Perkin-Elmer GPC-HPLC instrument, using a Shodex column, eluent CHCl$_3$ and polystyrene standards. The X.p.s. measurements were performed on a VG ESCA3 MK1 instrument with a non-monochromatized Mg Kα source (1253.6 eV); vacuum in the analysis chamber was in the low 10^{-9} torr range. All the spectra were energy referenced to the C 1s binding energy (BE) signal at 285.0 eV. Quantitative evaluation of atomic ratios was achieved by using Scofield's atomic cross-sections[9]. The inelastic mean free path was considered as a function of $E_k^{1/2}$. Experimentally determined sensitivity factors were also used. Curve fitting analysis was made using an IBM PC. Elemental analyses were carried out at the Laboratorio di Micro-analisi, Facoltà di Farmacia, Università di Pisa, Italy.

Materials

All the solvents were reagent grade and freshly distilled from CaH$_2$ before use; the monomer ethynyl-trimethylsilane (ETMS) (Fluka) was also distilled under vacuum. WCl$_6$ (Fluka) was a commercial product used without any further purification.

Synthesis of the complex $\{Pt[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$. [PtCl$_2$(PPh$_3$)$_2$] (300 mg (0.38 mmol)) was refluxed with HC $\equiv$ C-Si(CH$_3$)$_3$ (0.35 ml, 2.5 mmol) in a solution of NH(C$_2$H$_5$)$_2$ (5 ml) and of CuI (5 mg, 2.6 $\times$ 10^{-2} mmol) for 1 h. The white crystalline complex which formed was

recovered by filtration, washed with fresh $NH(C_2H_5)_2$ and dried *in vacuo*. Crystallization from $CHCl_3/C_2H_5OH$ or C_6H_6/C_2H_5OH yielded white microcrystals, m.p. 260–263°C (yield, 95%). Elemental analysis: found (calc.); C = 60.34 (60.40)%; H = 5.22 (5.25)%. I.r. (nujol mull) (cm^{-1}): 2041 s(νC $\equiv$ C); 1241 s(νSi-CH$_3$); 865, 838 s(δSi-C-H); u.v. λ_{max} = 278 nm.

Synthesis of the complex $\{Pd[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$. Following the above procedure $[PdCl_2(PPh_3)_2]$ (600 mg, 0.85 mmol) was reacted with HC $\equiv$ CSi(CH$_3$)$_3$ (0.35 ml, 2.5 mmol). The solution was stirred for 10 min at room temperature; the complex precipitated as white microcrystals, which were recrystallized in the same way, m.p. 132–135°C (yield, 95%). Elemental analysis: found (calc.); C = 66.65 (66.94)%; H = 5.85 (5.82)%. I.r. (nujol mull) (cm^{-1}): 2040 s(νC$\equiv$C); 1242 s(νSi-CH$_3$); 865, 838 s(δSi-C-H); u.v. λ_{max} = 320 nm.

Polymerization reactions

The polymers were synthesized by reacting the $\{Pd[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$ complex with ETMS using C_6H_6 or $NH(C_2H_5)_2$ as solvents. In a typical polymerization reaction $\{Pd[C \equiv CSi(CH_3)_3]_2(PPh_3)_2\}$ (430 mg, 0.48 mmol) and ETMS (1.65 ml, 11.9 mmol, 1.17 g) (catalyst:monomer ratio = 1:25) were poured into $NH(C_2H_5)_2$ (5 ml) containing CuI (5 mg cocatalyst). The reaction mixture was kept at 50°C for 24 h (under argon) until solid material formed; the solvent was evaporated under vacuum, the solid crude polymeric products were treated with CH$_3$OH and two fractions (A and B) were obtained; (A) a powder which was recovered by filtration, washed with methanol and dried; after evaporation of the solvent (B), the solid residue, was washed with hot petroleum ether and dried under vacuum.

Analogous reactions carried out in the presence of $\{Pt[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$ gave no polymeric products.

Polymerizations in the presence of $[PdCl_2(PPh_3)_2]$ and PdCl$_2$ were performed under similar reaction conditions; these complexes also showed some catalytic activity. A
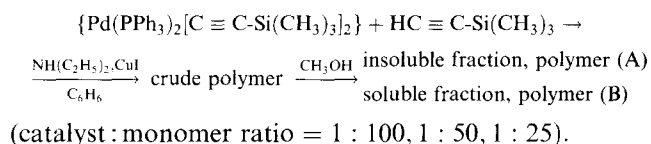
polymerization reaction using the catalyst WCl$_6$ was also carried out following the literature procedure[10] for purposes of comparison. The reaction yields and elemental analyses of representative reactions are collected in *Table 1*; the data concerning B fractions obtained in low yields are not reported.

RESULTS AND DISCUSSION

The polymerizations of ETMS and analogous alkynes leading to linear polyenic chains with Si(CH$_3$)$_3$ pendant groups have been reported to occur on initiation with Mo and W chlorides[10–12], W and Cr carbenes[13], and Ta and Nb chlorides[14,15]. No evidence of metal or catalyst insertion into the polymer chain has been reported.

Performing preliminary investigations on the reactivity of ETMS in the presence of PdCl$_2$ and $[PdCl_2(PPh_3)_2]$, we obtained polymerization products of brown or black colour, quite different from the polymers reported in the literature which are pale yellow. The bis(acetylide) complexes $\{Pd[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$ and $\{Pt[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$ have been prepared, because in previous investigations we have observed that the presence of a metal σ-bonded acetylenic ligand in the catalyst enhances the reactivity of the monosubstituted acetylenes[16,17]; however, no catalytic activity of the platinum complex was observed. Then our research was focused on the polymerization of ETMS in the presence of the Pd bis(acetylide) complex. After performing many reactions at different catalyst:monomer ratios, we found that the yield of the polymerization products increases with increasing amount of complex used as the catalyst.

The crude polymers can be separated (by treatment with CH$_3$OH) into insoluble (A) and soluble (B) fractions, see scheme below.

$\{Pd(PPh_3)_2[C \equiv C\text{-}Si(CH_3)_3]_2\} + HC \equiv C\text{-}Si(CH_3)_3 \rightarrow$

$\xrightarrow[C_6H_6]{NH(C_2H_5)_2,CuI}$ crude polymer $\xrightarrow{CH_3OH}$ insoluble fraction, polymer (A) / soluble fraction, polymer (B)

(catalyst:monomer ratio = 1 : 100, 1 : 50, 1 : 25).

Table 1 Polymerization reactions of ETMS

| Catalyst	Monomer (g)	Catalyst: monomer ratio^a	Solvent	ml	Temp. (°C)	Time (h)	Colour	Yield (mg)	Elemental analysis (%)^b			
									C	H	P	N
PdCl$_2$	1.4	1:100	Toluene	8	20	60	Brown	40	63.17	6.12	0	0
(PPh$_3$)$_2$PdCl$_2$	1.4	1:100	NHEt$_2$	5	20	24	Black	294 (A)	64.97	6.92	1.30	1.00
							Black	240 (B)	62.92	7.01	2.40	5.29
(PPh$_3$)$_2$Pd(ETMS)$_2^c$	1.17	1:25	NHEt$_2$	5	50	24	Black	300 (A)	58.97	6.58	0	4.88
							Black	200 (B)	70.79	6.23	8.10	1.28
	1.17	1:50	C$_6$H$_6$	5	50	24	Black	200 (A)	53.63	5.41	0	0
	2.34	1:100	NHEt$_2$	5	50	24	Black	250 (A)	64.64	6.42	0	6.04
							Black	100 (B)	68.57	6.54	2.54	3.77
(PPh$_3$)$_2$Pt(ETMS)$_2^c$	1.17	1:100	NHEt$_2$	5	80	100	–	0				
	1.17	1:100	C$_6$H$_6$	5	100	100	–	0				
WCl$_6$	1.17	1:50	Toluene	5	20	24	Yellow	500 (A)	58.3	9.62		

(A) Insoluble fractions
(B) Soluble fractions
^{a} Molar ratio
^{b} Calculated for [-CH = CSi(CH$_3$)$_3$-]$_n$ C = 61.6 H = 10.19
^{c} ETMS here indicates the -C $\equiv$ C-Si(CH$_3$)$_3$ ligand
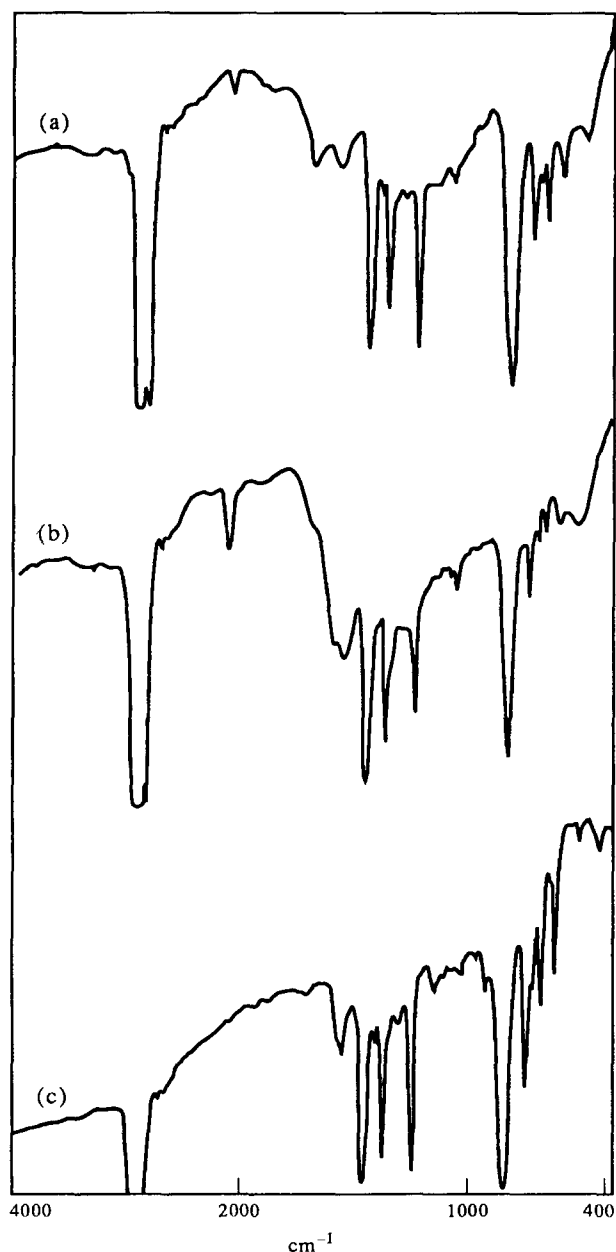
Figure 1 *FT* i.r. spectra (nujol mulls) of: (a) polymer A (Pd catalyst), prepared in C_6H_6; (b) polymer A (Pd catalyst), in $NHEt_2$; (c) polymer PETMS (WCl_6 catalyst)

Figure 2 X.p.s. spectra C1s core level for: (a) $\{Pd[C \equiv C\text{-}Si(CH_3)_3)]_2$ $(PPH_3)_2\}$; (b) polymer A prepared in $NHEt_2$; (c) polymer A prepared in C_6H_6

Comparing the elemental analyses of products obtained in reactions carried out in the presence of various catalysts (*Table 1*), it can be seen that WCl_6 gives a polymer (PETMS) with C and H contents in good agreement with the theoretical values for $\{\text{-CH} = C[Si (CH_3)_3]\text{-}\}_n$ according to literature data[18,19]. In the polymers obtained in the present study phosphorous and nitrogen are present. Phosphorous is absent in the insoluble fractions (A). When $NHEt_2$ is used as the reaction solvent, nitrogen is present both in the insoluble (A) and soluble fractions (B). The products obtained in the presence of Pd complexes are therefore different from those obtained using WCl_6 as the catalyst. The presence of phosphorous and nitrogen cannot be attributed to catalyst and solvent impurities because the analyses were performed on thoroughly washed samples.
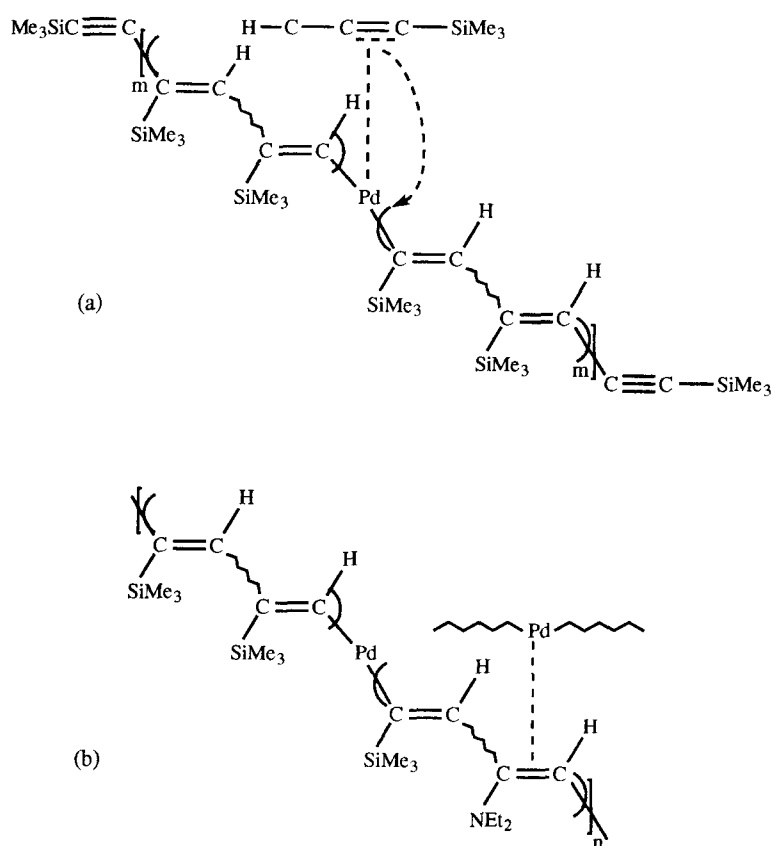
Insoluble polymers

The i.r. spectra of the insoluble polymer fractions (A) obtained in C_6H_6 or $NHEt_2$ as solvents are reported in *Figures 1a* and *b*. The bands at $1249\,\text{cm}^{-1}$ (νSi-CH_3) and $\sim 840\,\text{cm}^{-1}$ (δ-Si-C-H) are present in both spectra, as well as in the spectrum of the Masuda polymer (*Figure 1c*), indicating the presence of $Si(CH_3)_3$ groups in the polymerization products. The vibration modes of the silyl groups are more evident in the spectra of the polymers prepared in benzene. A band at $\sim 2140\,\text{cm}^{-1}$ ($\nu C \equiv C$) is still observed in our polymers, although the $\nu = $ C-H band at about $3300\,\text{cm}^{-1}$ of the monomer disappears. The $C \equiv C$ band can be correlated to the presence of some $C \equiv C$-R groups at the end of polymeric chains (-HC $= CR$-)$_n$. Two bands at ~ 1705 and $1590\,\text{cm}^{-1}$ are observed in the spectra of polymers obtained in benzene (*Figure 1a*). *Figure 1b* shows two bands at 1607 and $1559\,\text{cm}^{-1}$ for the spectra of polymers obtained in $NHEt_2$.

Since polymers A are insoluble, a suitable tool for the investigation of their structure is X.p.s. Evaluation of the atomic ratios and the electronic modifications occurring as a consequence of the polymerization reaction were obtained from the X.p.s. spectra. The results concerning polymers A (obtained in $NHEt_2$ or benzene) and the catalyst $\{Pd[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$ (considered as a

Table 2 X.p.s. measurements of insoluble A polymers

Samples	Signals	BE (eV)	FWHM	Atomic ratios[a]
{Pd[C ≡ C-Si(CH₃)₃]₂(PPh₃)₂}[b]	C 1s	285.0	2.1	45
	Si 2p	100.9	2.1	2
	P 2p	131.8	2.0	2
	Pd 3d₅/₂	338.3	1.8	1
Polymer A	C 1s	285.0	3.3	84
(solvent NHEt₂, catalyst : monomer	Si 2p	100.8	2.8	5
molar ratio 1 : 25)	P 2p			
	Pd 3d₅/₂	336.7–338.1	4.1	1
	N 1s	399.6	2.6	4
Polymer A	C 1s	285.0	2.4	47
(solvent benzene, catalyst : monomer	Si 2p	101.3	2.4	7
molar ratio 1 : 50)	P 2p			
	Pd 3d₅/₂	336.6	2.9	1

[a] Normalized to Pd
[b] Calculated atomic ratios: $C_{46}Si_2P_2Pd$

Figure 3 Scheme of the insertion reactions into the Pd-C σ-bonds leading to chain growth: (a) reactions in C_6H_6; (b) reactions in NHEt₂

reference standard) are collected in *Table 2*, where the values of representative samples belonging to the two classes of reactions (NHEt₂ and benzene) are reported.

The C 1s core level spectra of the Pd complex and of polymers A are reported in *Figure 2*. The C 1s signal of the Pd complex (*Figure 2a*) shows a symmetric shape, centered at 285.0 eV (taken as the energy reference); the shake-up satellite at $\Delta S \approx 7$ eV from the main C 1s peak is due to the $\pi \rightarrow \pi^*$ secondary transitions of the phenyl rings. The C 1s signal of polymer A (in NHEt₂) (*Figure 2b*) is broad (FWHM = 3.1 eV) and no shake-up satellite

appears; under the broad main signal two components may be detected, which can be assigned to aliphatic carbons and carbon atoms linked to nitrogen. Polymer A prepared in benzene shows a well-resolved C 1s peak (FWHM = 2.4 eV) with no shake-up satellite (*Figure 2c*). The absence in polymer A of shake-up secondary structures, due to the $\pi \rightarrow \pi^*$ transitions of the phenyl rings' electrons, is due to the absence of these chemical groups: also no P 2p X.p.s. signal is detected in this polymer.

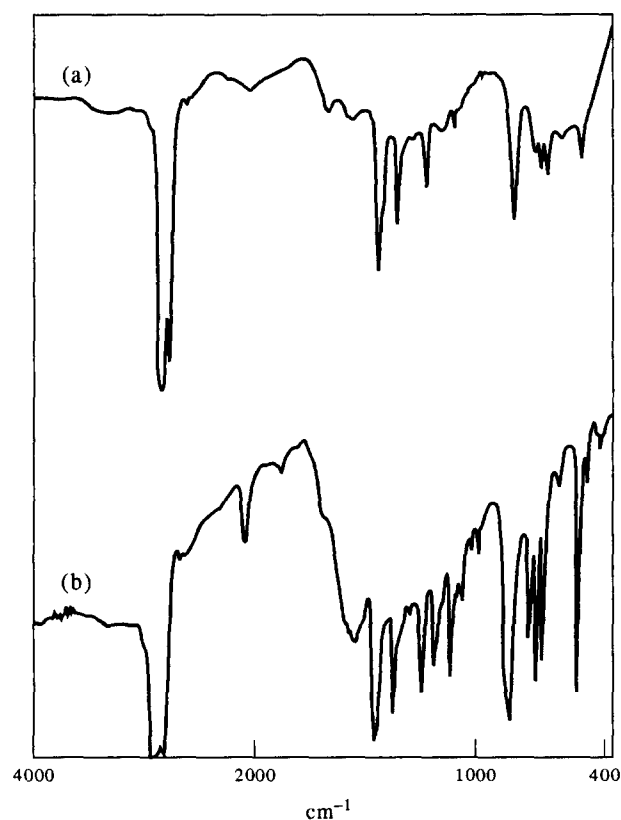In polymer A obtained using $NH(C_2H_5)_2$ as the

solvent, X.p.s. confirms the presence of nitrogen (the N 1s signal is narrow and the BE value is 399.6 eV). The substitution of some $Si(CH_3)_3$ with $N(C_2H_5)_2$ groups probably occurs during the insertion reaction of the activated $HC \equiv C-Si(CH_3)_3$ into the Pd–C bonds of the growing chain (*Figure 3a*). Pd-coordinated olefins undergo nucleophilic attack by OH^-, NHR_2 etc., giving substitution reactions more easily than the free olefins. However, in a reaction of the PETMS polymer, prepared with the WCl_6 catalyst, that is $\{-HC = C[Si(CH_3)_3]-\}_n$, with the Pd bis(acetylide) complex in the presence of $NH(C_2H_5)_2$, no substitution occurs (the $Si(CH_3)_3$ groups of the already formed polymer chain are not replaced by $N(C_2H_5)_2$); which supports our hypothesis that substitution takes place during the chain growth.

The X.p.s. spectra also reveal the presence of Pd in the polymers; the amount increases with increasing catalyst:monomer ratio. The metal is not released at the end of the polymerization reaction but remains bonded to the polymer chain as indicated in *Figure 3a*. The metal is σ-bonded to the carbon atoms of the chain. However, by releasing the phosphine ligands (phosphorous was not found by X.p.s. in these fractions), coordination of Pd to the π bonds or to the amino groups of the chain can also occur (*Figure 3b*). This
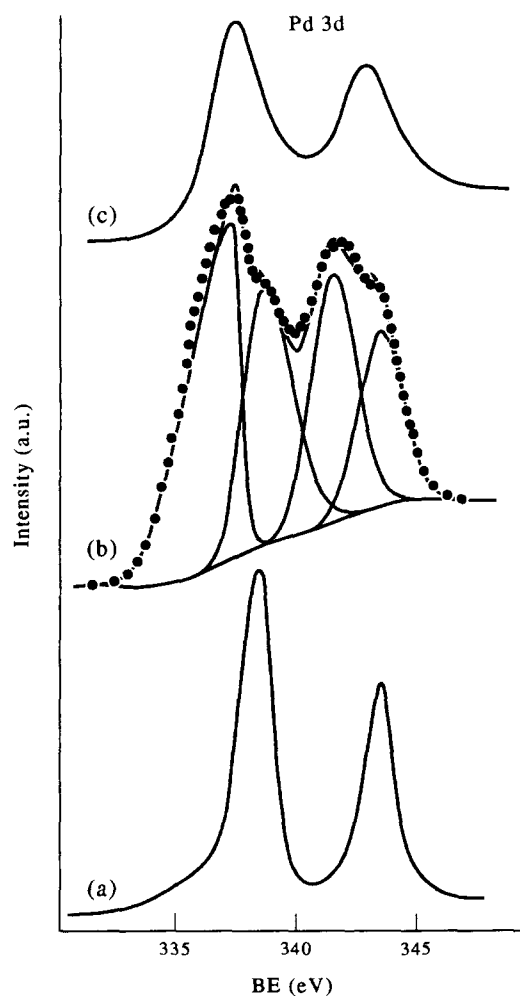
behaviour is reflected in Pd X.p.s. spectra: the Pd 3d core level signals of the Pd bis(acetylide) complex, and of polymers A (in $NH(C_2H_5)_2$ and benzene) are reported in *Figures 4a, b, c*, respectively. The Pd signal of the complex is well resolved in the two spin orbit components and no asymmetry appears (*Figure 4a*), the BE of the Pd $3d_{5/2}$ signal is found at 338.3 eV, close to the value reported for four-coordinate Pd(II) complexes[20]. Polymer A containing $N(C_2H_5)_2$ groups exhibits a Pd 3d signal where the superposition of four bands ($3d_{5/2}$, $3d_{3/2}$ of Pd in different chemical environments) can be seen (*Figure 4b*). Curve fitting shows that slightly less than 50% of Pd (Pd $3d_{5/2}$ component BE = 338.1 eV) may be considered in an electron density state analogous to that of the Pd (bis(acetylide) complex (Pd $3d_{5/2}$, component BE = 338.3 eV). The Pd $3d_{5/2}$ component at BE = 336.7 eV indicates a chemical shift of −1.6 eV in comparison with the Pd signal of the reference complex. Enhanced charge transfer from the polymer to the metal, which sensibly reduces its positive charge, probably happens because an interaction between the Pd and the C = C π-bonds of the chain occurs. The C = C double bonds with $Si(CH_3)_3$ or $N(C_2H_5)_2$ groups accept a large π-electron density through an inductive effect, which is transferred to Pd(II). Direct coordination of Pd with the nitrogen of $N(C_2H_5)$ groups might also be considered. However, the N 1s signal is narrow and its BE value (399.6) is close to that found for N,N-dimethylpropargylammine polymers (N 1s BE = 399.7 eV) where $CH_2N(CH_3)_2$ non-coordinated pendant groups are prevalent[21]; a chemical shift increase of about 1 eV has been reported for the N 1s electrons of amine nitrogen upon coordination to Ni(II)[22].
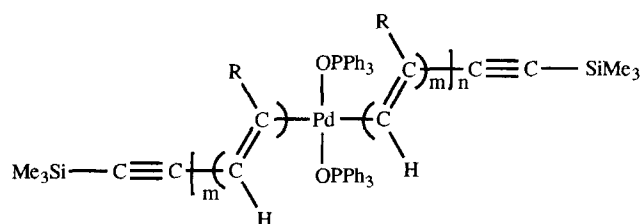

Figure 4 X.p.s. spectra of Pd $3d_{5/2,3/2}$ core level for: (a) $\{Pd[C \equiv C-Si(CH_3)_3)]_2(PPh_3)_2\}$; (b) polymer A prepared in $NHEt_2$; dotted line represents the experimental signal; (c) polymer A prepared in C_6H_6

Figure 5 FT i.r. spectra (nujol mulls) of the soluble polymers B: (a) polymer prepared in $NHEt_2$; (b) polymer prepared in C_6H_6

Polymer A obtained in C_6H_6 as the polymerization solvent, containing only $Si(CH_3)_3$ pendant groups, gives a Pd 3d spectrum well resolved in the two spin orbit components (*Figure 4c*). The little broadening of the signals indicates that Pd species in slightly different electronic and chemical environments are present. The Pd $3d_{5/2}$ component is found at BE = 336.6 eV, showing also in this case a charge transfer from the organic moiety of the surrounding polymer molecules towards the metal, as discussed for polymer A prepared in $NH(C_2H_5)_2$. The presence of Pd(0) may be ruled out since we expect a Pd $3d_{5/2}$ BE value of 334.8 eV.

Soluble polymers

The i.r. spectra of the samples B prepared in benzene and $NH(C_2H_5)_2$ are reported in *Figures 5a* and *b*, respectively. In the spectra the bands characteristic of the $Si(CH_3)_3$ groups ($\sim$1250 and 840 cm^{-1}) are present. Some bands at 1185, 1120 and 543 cm^{-1} also appear. Bands at the same frequencies have been found in the spectra of polymers obtained in the polymerization reaction of H-C $\equiv$ C-CH$_2$N(CH$_3$)$_2$ in the presence of increasing amounts of $\{Ni(NCS)[C \equiv C\text{-}CH_2N(CH_3)_2)]$ $(PPh_3)_2\}$[21]. Also in this case the complex acts as a catalyst but it can also react with the polymer chain. The PPh$_3$ ligand of the catalyst is oxidized to OPPh$_3$, which in part remains coordinated to the nickel atom and, in part, is released. An analogous reaction occurs with the $\{Pd[C \equiv C\text{-}Si(CH_3)_3]_2(PPh_3)_2\}$ complex. It is known that $[Pd(PPh_3)_n]$ complexes activate the oxidation of PPh$_3$ to OPPh$_3$[23]. This reaction may also occur during the polymerization of H-C $\equiv$ C-Si(CH$_3$)$_3$ in the presence of the $[PdX_2 (PPh_3)_2]$ complexes.

We conclude that the ligand OPPh$_3$ is bonded to the palladium atoms present in the chain because thin layer chromatography does not reveal the presence of free phosphine oxide. However, upon subsequent treatments of polymers B with hot petroleum ether, the insoluble A
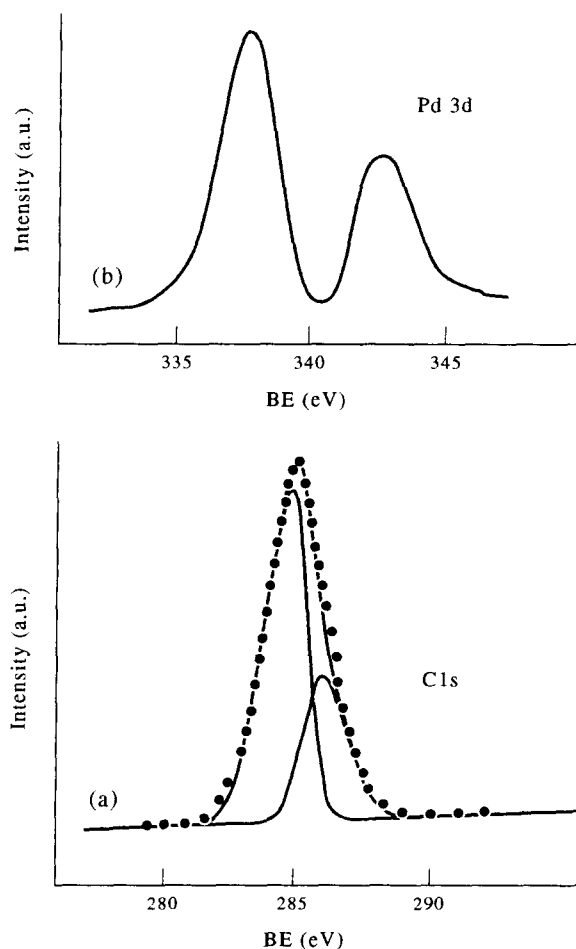
materials are formed. The oxidation of PPh$_3$ to OPPh$_3$ occurs despite the fact that the polymerizations are carried out under an argon atmosphere and with degassed solvents; probably the reaction occurs during the manipulation of the crude materials, by a mechanism analogous to that reported for Rh phosphinic complexes[24]. *Figure 6* gives the proposed structure of soluble polymers B, Pd is σ-bonded to the polyenic chains and is coordinated to OPPh$_3$.

In the i.r. spectra the signal at 2130 cm^{-1} (of medium intensity for the samples in $NH(C_2H_5)_2$ and weak intensity for the polymers in benzene) may be due to the chain end groups C $\equiv$ C-Si(CH$_3$)$_3$, while the presence of the small peak at 1700 cm^{-1} is probably due to a minor oxidation process of the C = C chain bonds.

Since the yield of the soluble part B of the polymers obtained in benzene is very small, and the polymer structure is considered to be similar to that of the soluble B samples prepared in $NH(C_2H_5)_2$ (apart from the substitution of some $Si(CH_3)_3$ groups with $N(C_2H_5)_2$), we have focused our X.p.s. investigations on the latter soluble B polymers (*Table 3*).

The C1s core level spectrum (*Figure 7a*) shows a pronounced asymmetry at higher BE energies with respect to the main signal (BE = 285.0 eV); this peak contribution at $\sim$286.6 eV may be ascribed to the

Figure 6 Proposed structure for the soluble polymers B of ETMS containing Pd(II) coordination sites: R = Si(CH$_3$)$_3$, or Si(CH$_3$)$_3$ and N(C$_2$H$_5$)$_2$ in 1 : 1 or 2 : 1 ratio; '*m*' is found in the range 5–10; '*n*' in the range 10–20; '*m*' and '*n*' are deduced from g.p.c., X.p.s. and elemental analysis data

Table 3 X.p.s. measurements of soluble B polymers[a]

	BE	FWHM	Atomic ratios[b]
C 1s	285.0	2.7	104
Si 2p	101.3	2.9	5
P 2p	132.8	2.2	2
Pd $3d_{5/2}$	337.4	2.5	1
N 1s	399.9	2.5	5

[a] Samples prepared in 1 : 25 complex : monomer ratios, solvent NH(C$_5$H$_5$)$_2$
[b] Normalized to Pd

Figure 7 X.p.s. spectra of polymer B: (a) C 1s core level; dotted line represents the experimental signal; (b) Pd $3d_{5/2,3/2}$ core level
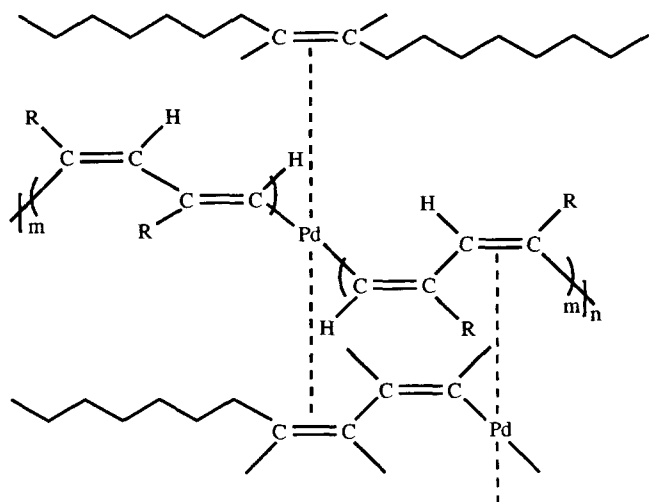
Figure 8 Proposed structure for the insoluble polymers A of ETMS containing Pd(II) coordination sites: R = Si(CH₃)₃, or Si(CH₃)₃ and N(C₂H₅)₂ in 1:1 or 2:1 ratio; 'm' is found in the range 4–8

presence of C-N or C-O groups; the shake-up satellite, clearly detected in the spectrum of the complex (*Figure 2a*), is absent here probably because the $\pi \rightarrow \pi^*$ transitions of the phenyl groups give a minor contribution, while electron delocalization of the polymeric chain double bonds is dominant.

Palladium is also found in the soluble fraction B. The Pd 3d spectrum shows a good resolution of the two spin-orbit components, symmetry of the peak shape, and broadening due to the presence of Pd atoms in slightly different chemical environments. The BE value of Pd $3d_{5/2}$ found at 337.4 eV is shifted by 0.9 eV in comparison with the Pd $3d_{5/2}$ signal of the complex at 338.3 eV; a negative charge transfer from the OPPh₃ ligands towards the metal atom is suggested (*Figure 7b*). The N 1s signal is narrow and symmetric at BE = 399.9 eV; only one nitrogen species is present. As for as the phosphorous 2p core level spectrum, the BE value is found at 132.8 eV, quite close to that reported in the literature for OPPh₃ (BE = 132.9 eV)[25], while PPh₃ gives a BE value of 131.8 eV. Then by X.p.s. measurements the presence of OPPh₃ is confirmed, also in agreement with elemental analyses (*Table 1*). The OPPh₃ molecule is linked to Pd through a coordination bond, since it has not been found 'free' in thin layer chromatography checks.

Values of $M_w = 39\,000–47\,000$ and $M_n = 20\,000–27\,000$ for samples of polymers B prepared in benzene or NH(C₂H₅)₂ show that a fairly good degree of polymerization has been achieved.

Structure of the polymers

On the basis of experimental results the structure reported in *Figure 8* is proposed for insoluble polymers A. Insolubility can be due to crosslinking between adjacent chains through the coordination of Pd atoms.

From the X.p.s. atomic ratios, calculated by the N 1s and silicon 2p normalized signal areas of various samples, it was found that in the insoluble polymers A prepared in NHEt₂, one NEt₂ group is present for every 1–2 Si(CH₃)₃ groups. The atomic ratios of N, Si, C and Pd obtained by X.p.s. signals and elemental analyses suggest that chains of 8–16 (CH = CR) units are bonded to one Pd atom, in the polymers obtained in C₆H₆ or in

NHEt₂. The number 'n' could not be determined because the samples were insoluble.

For the soluble polymers B, the evaluation of X.p.s. atomic ratios, compared with the elemental analyses performed on several samples, leads to the structure reported in *Figure 6*. From the average C:Si:N atomic ratios, the number 'm' of the repeat units can be estimated in the range 5–10, and the Si(CH₃)₃:N(C₂H₅)₂ groups ratio is 1:1 or 2:1 depending on the single examined sample (for the sample reported in *Table 3* the Si:N atomic ratio is 1:1). The number of organometallic polymeric units 'n' = 10–20 was determined from the molecular weight measurements.

CONCLUSIONS

Polymerizations of HC ≡ C-Si(CH₃)₃ carried out in the presence of the bis(acetiylide) complex {Pd[C ≡ C-Si (CH₃)₃]₂(PPh₃)₂} in 1:100, 1:50, and 1:25 catalyst: monomer ratios (solvents, benzene, NH(C₂H₅)₂) lead to the formation of soluble and insoluble materials (*Figures 6 and 8*). The catalyst plays different roles: (i) activation by Pd of the triple C ≡ C bond of the monomer and insertion into the Pd-C σ-bond with growth of the polymer chain, following the mechanism already reported for Ni(II) acetylide catalysts[16]; in the present case the complex linking the growing chain has been isolated; (ii) oxidation of PPh₃ to OPPh₃ which can then be released leaving free coordination sites on Pd, with subsequent crosslinking by means of π-interaction with the C = C bonds of neighbouring polymer chains; (iii) in the presence of NH(C₂H₅)₂, the activation of the C-Si bond also occurs during the polymerization reaction, and substitution of some of the Si(CH₃)₃ groups with N(C₂H₅)₂ has been detected.

X.p.s. investigations have been especially useful in assessment of the Pd species in the insoluble and soluble polymers.

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