

Polymerization of propargyl alcohol: comparison of the catalytic activity of Pd and Rh complexes

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The propargyl alcohol has been polymerized in the presence of $[\text{Pd}(\text{C}\equiv\text{C}-\text{CH}_2\text{OH})_2(\text{PPh}_3)_2]$ and $[\text{Rh}(\text{cod})\text{Cl}]_2$ catalysts and polymers (POHP) with different structures are obtained. By comparison with polyphenylacetylene, a *cis-transoidal* configuration of POHP prepared with the Rh(I) catalyst may be suggested. The characterization of POHP has been performed by means of i.r., n.m.r., SEM and g.p.c. measurements. Doping with I_2 , the associated isomerization process and the resistance variations are also discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: catalysts; propargyl alcohol; Pd(II) and Rh(I))

INTRODUCTION

Polymerization of propargyl alcohol (OHP) has been carried out by several authors¹. Reactions at high temperature give insoluble crosslinked polymers with elemental analyses that do not correspond to the theoretical values calculated for $(\text{C}_3\text{H}_4\text{O})_n$. Plasma polymerization produces highly hydrophilic polymer films with good coherence and transparency². Some years ago, we investigated the catalytic activity of Ni complexes $[\text{NiX}_2\text{L}_2]$ ($\text{X} = \text{I}, \text{NCS}$; $\text{L} = \text{PPh}_3$) and $[\text{Ni}(\text{NCS})(\text{C}\equiv\text{C}-\text{CH}_2\text{OH})_2(\text{PPh}_3)_2]$ ³ in reactions with OHP and polymers (POHP) were obtained in good yield³. Recently, we have studied the polymerization reaction of OHP in the presence of the complex $[\text{Pd}(\text{C}\equiv\text{C}-\text{CH}_2\text{OH})_2(\text{PPh}_3)_2]$ [Pd-C] in homogeneous conditions—a chloroform/methanol mixture in which the complex, the monomer and the resulting polymer are soluble. The influence of various parameters have been investigated and mild reaction conditions, in which POHP can be obtained, have been optimized⁴. In this paper we report new investigations on the use of Pd-C catalyst and of the complex $[\text{Rh}(\text{cod})\text{Cl}]_2$ [cod = bis-cyclooctadiene] (Rh-C) in reactions with OHP.

EXPERIMENTAL

Reagents

Propargyl alcohol (OHP) was dried over anhydrous Na_2SO_4 and distilled under reduced pressure before use. The other reagents were commercial analytical or

chemical grade products and were used without further purification.

The complex $[\text{Pd}(\text{C}\equiv\text{C}-\text{CH}_2\text{OH})_2(\text{PPh}_3)_2]$ was prepared as previously reported⁴. The complex $[\text{Rh}(\text{cod})\text{Cl}]_2$ is a Fluka product.

Polymerization reactions

Polymerization in the presence of Pd-C. A mixture of 60 mg of Pd-C (0.082 mmol) and 6 ml of freshly distilled OHP (103 mmol) (catalyst/monomer ratio = 1/1274) were introduced into a 50 ml reaction flask, and the mixture maintained, with stirring, at a constant temperature (60°C) for 24 h. The viscous product was then dried under vacuum, to eliminate the unreacted OHP. A brown powder was obtained by grinding the resulting glassy mass. The powder was washed with warm tetrahydrofuran (THF) (at about 60°C) and dried under vacuum. Yield 90%. The polymer is soluble in DMSO, DMF and OHP.

Polymerization in the presence of Rh-C. (1) Polymerization reaction in the presence of NaOH. Into a 50 ml reaction flask 40 mg of Rh-C, 3.5 ml of freshly distilled OHP (catalyst/monomer ratio = 1/745) and 1 ml of a 0.2 M solution of NaOH in MeOH were introduced, with stirring. The exothermic reaction started immediately. The reaction temperature was maintained at about 65°C for 24 h. At the end of the reaction the brown viscous mixture was worked up as reported above for Pd-C. Washing of the brown powder was carried out with a warm methanol (20%)/THF mixture. The yield

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of the dried product indicated a 30% conversion of the monomer to the polymer.

(2) Polymerization reaction in the presence of NH_4Et_2 . To the same amounts of monomer and catalyst as in (1), 0.1 ml of a solution 2 M of NH_4Et_2 in EtOH were added. The reaction started immediately. The temperature was controlled at 65°C by an external oil bath for 24 h. The product was worked up as reported above and dried under vacuum to give 45% yield.

Doping of polymers

Doping with I_2 . Powdered POHP (500 mg) was suspended in 30 ml of a saturated solution of I_2 in *n*-hexane. To these mixtures further amounts of I_2 (250, 400, 600 mg) were added to increase the amount of I_2 adsorbed by the polymer. The mixtures were stirred at room temperature for 20 h. The resulting black solid was filtered off and washed with *n*-hexane to remove the unreacted I_2 . The uptake of I_2 was determined by weight increase and by elemental analysis of the doped polymers.

Doping with FeCl_3 . A suspension of 350 mg of POHP in 20 ml of MeOH, in which 350 mg of FeCl_3 was previously dissolved, was stirred at room temperature for 18 h. The polymer was not completely soluble in the mixture. The solvent was removed under vacuum and a powder obtained by grinding the black residue.

Preparation of POHP films

The procedure was as follows:

- (1) 60 mg of Pd-C were used as catalyst to polymerize 4 ml of OHP (catalyst/monomer ratio $\approx 1/850$) at 60°C for 2 h. After this period the oily mixture was poured on a Teflon disk and the reaction continued in an oven at 60°C for about 6 h. The Teflon plate was then introduced into a vacuum chamber and, after pumping, a dry film was obtained;
- (2) 120 mg of Rh-C, 3 ml of a saturated solution of NaOH in MeOH and 3.5 ml of OHP (catalyst/monomer ratio = 1/106) were maintained at 65°C for 2 h. Then the procedure described above was followed;
- (3) 350 mg of POHP were dissolved in 0.7 ml of the monomer OHP and a solution of 350 mg of FeCl_3 in 1 ml of OHP added. The mixture was stirred for about 10 min and then spun to obtain a POHP-doped film.

Apparatus

The spectra were recorded with the following instruments: Perkin Elmer model 1700 FTIR interferometer; Perkin Elmer Lambda 5 UV/VIS Spectrophotometer; Varian XL-300 NMR Spectrometer.

The determination of molecular weights was carried out with a HPLC/GPC Perkin Elmer system, by using polystyrene standards, in DMF at 35°C.

Viscosity measurements were carried out with a Ubbelohde Viscosimeter.

Micrographic measurements of the films were carried out with a SEM Cambridge 100 instrument by using an accelerating potential of 20 keV. Electric measurements have been made by a Keithley 616 apparatus on pellets (1 cm diameter, 0.1 cm thick) obtained with a Specac P/N 150 press at 8 tons or on films of POHP spun on substrates on which four gold electrodes were photolithographically defined. Potential applied was 1 V. The spinner was an Electron MEC.PRS 5V apparatus.

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

RESULTS AND DISCUSSION

Polymerization reactions

Polymerization reactions of OHP in the presence of Pd-C were carried out under different reaction conditions to discover the influence of solvents on the yield of products. Some selected results are reported in *Table 1*. It can be seen that better yields were obtained when using chlorinated solvents, but the apparent high yield (80%) of the reaction carried out in the $\text{CH}_3\text{OH}/\text{CCl}_4$ mixture is due to the presence (about 17%) of chlorine in the resulting polymer, as determined by the elemental analyses. This chlorinated polymer appears black and insoluble in most organic solvents.

When the Pd-C is used as catalyst in bulk reactions (*Table 2*), the almost complete conversion of the monomer is obtained with a very low catalyst/monomer ratio. If the reaction temperature is maintained at about 60°C, crosslinking reactions with elimination of water between the alcoholic pending groups are avoided, and an elemental analysis in fairly good agreement with the theoretical one is obtained: calculated C% = 64.43; H% = 7.14; found C% = 63.44; H% = 7.33.

The resulting polymer (Pd-POHP) is soluble in DMSO, DMF and OHP. Homogeneous films are obtained by spinning solutions of POHP in these solvents.

Table 1 Polymerization reactions of OHP in the presence of Pd-C in different solvents

Catalyst (mg)	Solvent	Volume (ml)	Monomer (ml)	Reaction temperature (°C)	Reaction time (h)	Catalyst monomer ratio	Yield (%)
120	CHCl_3	4	1.3	25	48	1/135	40
60	MeOH	4	1.3	25	24	1/270	25
60	THF	5	1.3	25	24	1/270	17
60	$(\text{CH}_3)_2\text{CO}$	4	1.3	30	48	1/270	15
60	MeOH + CCl_4	1.3 + 1.3	1.6	60	24	1/340	80
60	CCl_4	4	1.3	65	24	1/270	62

Catalyst: 120 mg = 0.16 mmol; 60 mg = 0.08 mmol
 Monomer: 1.3 ml = 22 mmol; 1.6 ml = 27.6 mmol

Table 2 Polymerization reactions of OHP in bulk

Catalyst (mg)	Cocatalyst	Monomer (ml)	Reaction temperature (°C)	Yield (%)	Catalyst monomer ratio	Elemental analysis	
						C%	H%
Pd-C: (60)	–	6	60	90	1/1274	63.44	7.33
Rh-C: (40)	NaOH	3.5	65–70	35	1/745	61.37	7.10
Rh-C: (40)	NHEt ₂	3.5	65–70	45	1/745	60.97	6.95

Catalyst Pd-C: 60 mg = 0.08 mmol; Rh-C: 40 mg = 0.08 mmol

Monomer: 6 ml = 103 mmol; 3.5 ml = 60.4 mmol

Elemental analysis: calculated: C% 64.43; H% 7.14

Cocatalyst. NaOH: 1 ml of NaOH 0.2 M in MeOH; NHEt₂ = 0.1 ml of NHEt₂ 2 M in MeOH

Reactions were carried out in bulk also in the presence of Rh-C as the catalyst. This complex has been found to be active in reactions with other monosubstituted acetylenes^{5,6} and very effective in reactions with phenylacetylene, giving a polymer with high stereoregularity⁷. The yield in (Rh-POHP) polymer is of about 45% of the monomer when NHEt₂ in MeOH is used as cocatalyst. Lower yields are obtained with NaOH as cocatalyst.

The elemental analyses of Rh-POHP agree less with the theoretical values, probably as a consequence of the hygroscopicity of these polymers.

Interaction with environmental moisture occurs; however, by vacuum pumping the samples under heating at ≈100°C, some loss of weight (≈2%) owing to water vapour desorption is observed: the original weight is readily restored in about 1 h of exposure to ambient conditions.

The influence of various factors on the OHP polymerizations were investigated. The final yields were found to depend on the catalyst/monomer ratio, the reaction temperature, and the rate of stirring. Comparable yields have been obtained in air or in a dry atmosphere in the absence of oxygen, showing a good stability of POHP prepared under the reported reaction conditions.

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

The i.r. spectra of Pd-POHP and Rh-POHP are shown in *Figure 1*. The Pd-POHP exhibits a broad band at about 3330 cm⁻¹, a band at 1019 cm⁻¹ due to OH groups, and a band centred at about 1650 cm⁻¹ due to the conjugated double bonds. This last band shows a shoulder at about 1715 cm⁻¹, which can be assigned to some C=O groups, formed in a side oxidation reaction of the double bonds of the chain, which occurs to a minor extent.

The i.r. spectra of Rh-POHP are similar, but a shift of the double bonds band at about 1600 cm⁻¹ is observed.

An attempt to characterize Pd-POHP and Rh-POHP by ¹H and ¹³C n.m.r. was carried out with difficulty because the relatively low solubility of the polymers does not allow us to obtain a concentration suitable for good-quality n.m.r. spectra. Rh-POHP spectra are roughly similar to those for Pd-POHP discussed here.

The Pd-POHP proton n.m.r. spectrum is reported in *Figure 2* (solvent DMSO-d₆). The spectrum of *cis*-transoid polyphenylacetylene (PPA)⁸ shows a clear single resonance of the hydrogens bonded to the main chain C=C at 5.84 ppm; this does not appear in the spectrum of Pd-POHP because it is probably masked under the broad features observed. The broad series of resonances between 5 and 3.8 ppm can be attributed to

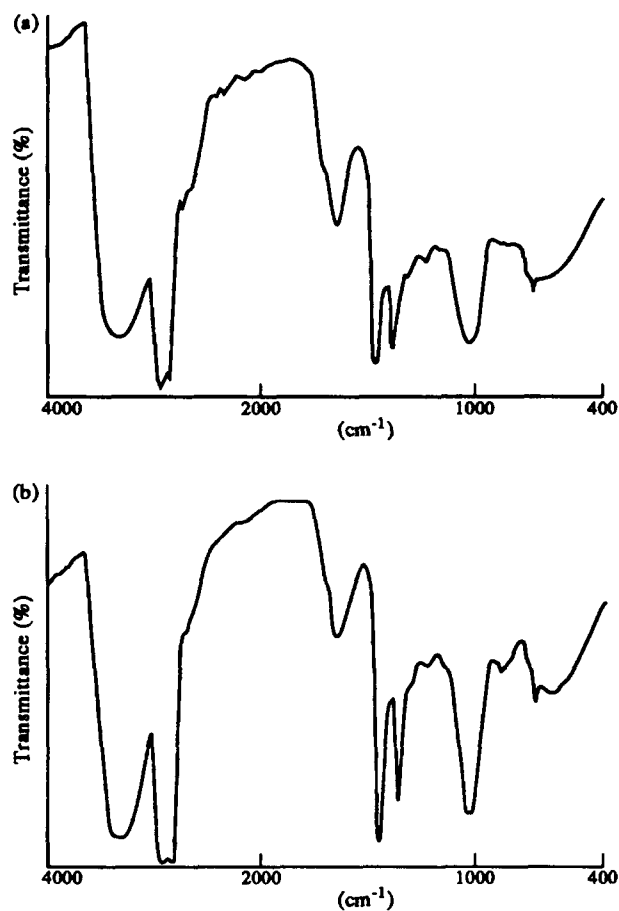


Figure 1 I.r. spectra (nujol mulls): (a) Pd-POHP; (b) Rh-POHP

hydroxyl (OH) and methylenic (CH₂) protons (in the spectrum of the monomer the respective resonances are found at 4.0 ppm and 4.28 ppm). The broadness of the signals and the lack of resolution are due to the random configuration of the polymer, which may be a characteristic of the as-grown material or a consequence of chain folding during the long accumulation time required for the acquisition of the spectra. A similar broadening effect was observed in ¹H n.m.r. spectra of stereoregular PPA, when maintained in solution or treated with solvents⁸. The resonances at 3.58 and 1.74 ppm are due to THF (the reaction solvent) trapped in the polymer matrix, which cannot be removed by vacuum pumping of the sample. However, the resonances of nonequivalent pendant OH groups can also contribute to the intensity of the peak at $\delta = 3.58$ ppm. DMSO gives a sharp signal at 2.49 ppm

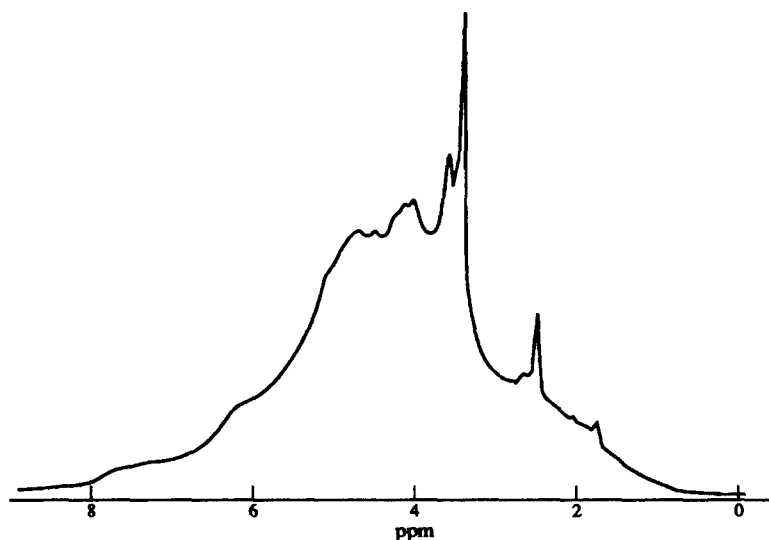


Figure 2 ^1H n.m.r. spectrum of Pd-POHP (solvent $\text{DMSO}-d_6$) after 8 h accumulation

and the signal at 3.42 ppm results from water contamination of the solvent.

The ^{13}C n.m.r. spectrum of Pd-POHP shows very broad and unresolved resonances centered at 140 and 125 ppm attributed to the carbons of the chain $\text{C}=\text{C}$ double bonds, and at about 65 ppm, carbons of the $\text{CH}_2\text{-OH}$ pendant groups.

Determination of the molecular weights

Molecular weights (m.w.) of soluble conducting polymers are currently determined by g.p.c. and are related to polystyrene calibration curves. This method gives a reasonable estimate of m.w., but more accurate and reliable m.w. can be determined taking into account the hydrodynamic volumes of the polystyrene standard and of the polymer under investigation⁹.

The hydrodynamic volume V_{idr} of a polymer is correlated to the m.w. $[M]$ by the relation

$$V_{\text{idr}} = [\eta]M$$

where $[\eta]$ is the intrinsic viscosity of the polymer in a given solvent. V_{idr} is used as a parameter for the calibration of the g.p.c. columns because, at any given elution volume

$$[\eta_1]M_1 = [\eta_2]M_2$$

The intrinsic viscosity is related to the m.w. $[M]$ of a polymer molecule by the Mark-Houwink relation

$$[\eta] = KM^a$$

The values of K and a for polystyrene in DMF at 35°C , that is, in our experimental conditions, are known. A calibration curve was performed using $l_n V_{\text{idr}} = l_n(KM^{1+a})$, where M = m.w. of polystyrene. Therefore, on the basis of a calibration curve obtained with polystyrene standards of m.w. 156 000, 22 000, 3250 and 580, the hydrodynamic volumes, corresponding to the various elution times were determined.

The intrinsic viscosity of Pd-POHP and Rh-POHP were previously measured using an Ubbelohde apparatus. If the intrinsic viscosity is known the equation $V_{\text{idr}} = [\eta]\bar{M}_{\text{g.p.c.}}$ gives the correct m.w. of the polymer,

Table 3 Hydrodynamic volumes and molecular weights of POHP polymers

Polymer	Elution time	Intrinsic viscosity (l g^{-1})	Hydrodynamic volume (l mol^{-1})	$\bar{M}_{\text{g.p.c.}}$
Pd-POHP	10.14	$3.1 \pm 0.4 \times 10^{-3}$	17.16	$5.5 \pm 0.6 \times 10^3$
Rh-POHP	9.87	$6.9 \pm 0.2 \times 10^{-3}$	38.16	$5.5 \pm 0.2 \times 10^3$

Mol. wt of the monomer = 56.03 amu

considering the efflux time (that is the maximum of the g.p.c. curve) independent of the m.w. of the reference standard. By correlation of the elution times with the hydrodynamic volumes, the $\bar{M}_{\text{g.p.c.}}$ were determined. The chromatograms of the polymers Pd-POHP and Rh-POHP are narrow, showing molecular weight distribution in the range 1.2–1.5; several samples have been investigated, giving the same reproducible $\bar{M}_{\text{g.p.c.}}$ values for each type of polymer.

From these measurements we found that the two polymers have almost the same molecular weight but different hydrodynamic volumes and intrinsic viscosities (Table 3).

SEM measurements

The free-standing Pd-POHP and Rh-POHP films were examined by the electron microscope and two different morphologies have been observed. The Pd-POHP film exhibits a vitreous surface Figure 3a. The Rh-POHP film exhibits a lamellar structure in which the polymer chains are folded and are perpendicular to the surface of the film as can be seen in Figure 3b, c, d (section borders).

Doping and electrical measurements

Iodine can be dissolved in *n*-hexane without formation of polyiodide ions due to apolarity of the solvent. When Pd-POHP or Rh-POHP are added as powders to the I_2 solution a charge transfer between the polymer molecules and the doping agent occurs. The polymer colour becomes black. The amount of adsorbed I_2 can be increased, as reported in the Experimental section, by adding I_2 to the suspension of POHP in the I_2 -saturated

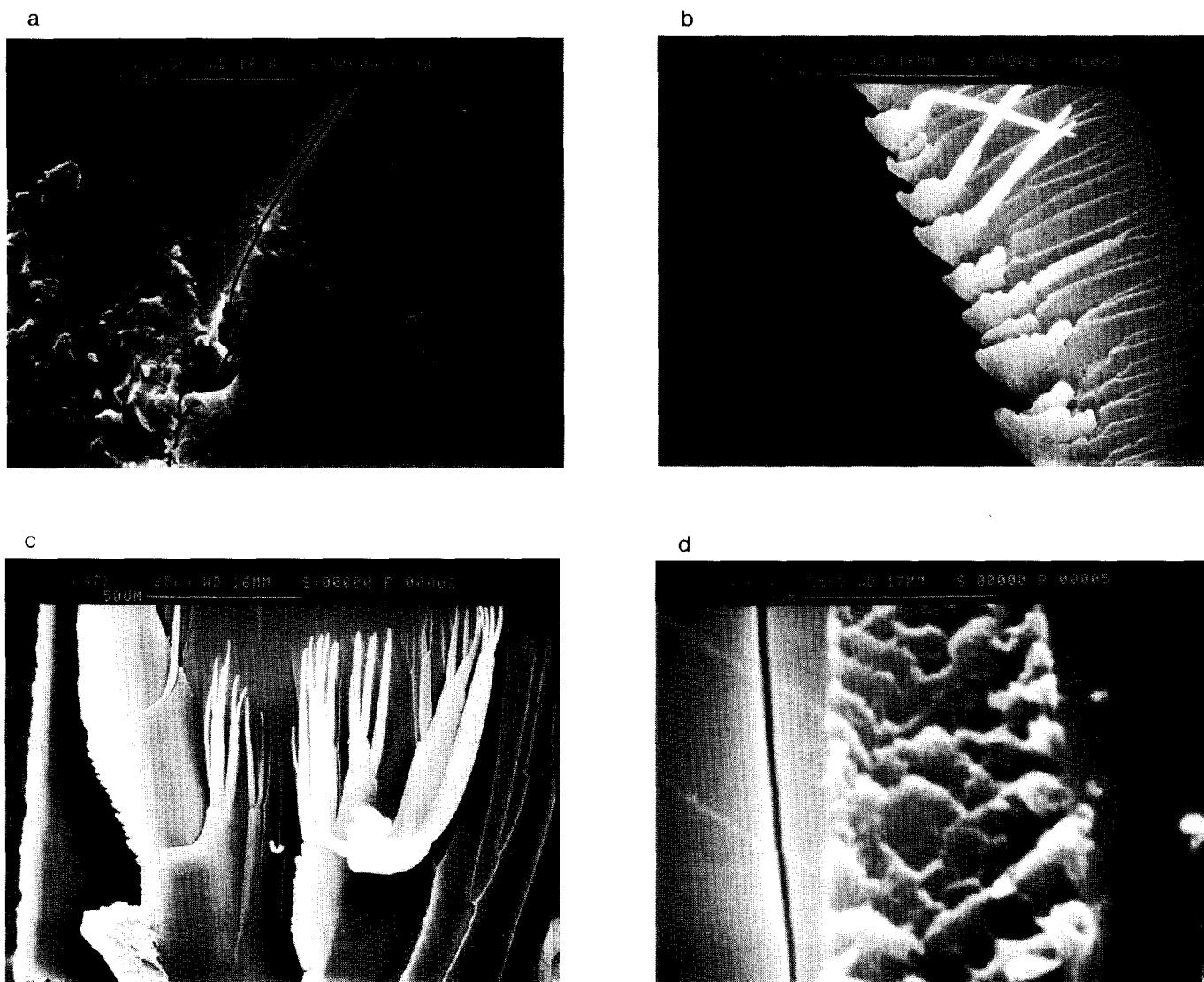


Figure 3 SEM of (a) film of Pd-POHP, (b–d) film of Rh-POHP; (b) and (c) are section borders; (d) lamellar structure seen throughout a surface scratch

n-hexane solution. The uptake of I₂ reaches a limiting value at about 69% (w/w) of the dopant/polymer system. The i.r. spectra of the doped POHP with increasing amounts of I₂ were obtained and the 1700–1550 cm⁻¹ region analysed in detail. For Pd-POHP a continuous variation towards lower frequencies of the band at about 1650 cm⁻¹, caused by C=C stretching vibrations, was observed (Figure 4). Table 4 gives the

amount of adsorbed I₂ and the resistance of pellets of Pd-POHP at increasing I₂ content. A limiting resistance value is reached at about 69% of adsorbed I₂. The frequency of the i.r. maximum is shifted from 1650 to 1600 cm⁻¹.

Rh-POHP exhibits a different behaviour: after addition of about 40% in weight of I₂ the resistance of the pellet slightly decreases, but at about 60% of adsorbed I₂

Table 4 Doping of Pd-POHP with I₂

Sample	Saturated ^a I ₂ solution (ml)	Amount of Pd-POHP (mg)	Excess of I ₂ (mg)	Reaction time (h)	Adsorbed I ₂ (weight %)	Resistance ^b (ohm)
a	–	–	–	–	–	8.1 × 10 ⁹
b	30	500	0	20	36.1	1.0 × 10 ⁸
c	30	500	250	20	55.6	3.7 × 10 ⁶
d	30	500	400	20	61.4	6.0 × 10 ⁵
e	30	500	600	20	63.6	3.2 × 10 ⁵
f	30	500	1000	20	69.6	1.2 × 10 ⁵

^a Solvent: *n*-hexane

^b Pellet: internal diameter = 1 cm; *h* = 0.1 cm

the resistance of the Rh-POHP/I₂ pellet decreases three orders of magnitude and the observed value is comparable with that of the analogous Pd-POHP/I₂ system (Table 5). Figure 5 shows the i.r. spectra of the Rh-POHP/I₂ systems. The i.r. band at 1660 cm⁻¹ of the pristine polymer does not change its position, but at 30–40% of adsorbed I₂, a new band appears at lower frequencies. At about 60% of adsorbed I₂ this new band is more intense than that at 1660 cm⁻¹ and the maximum is observed at 1607 cm⁻¹, that is in the same position of the band of Pd-POHP with ≈60% in weight of I₂.

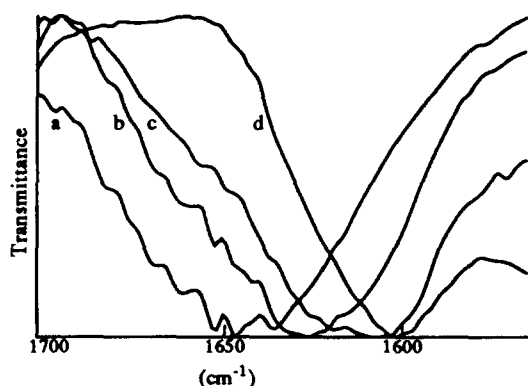


Figure 4 The i.r. spectra of the Pd-POHP/I₂-shift of the maximum of the band from 1646 to 1603 cm⁻¹ due to increase of I₂ absorption (I₂%: a = 0; b = 55.6; c = 61.4; d = 69.6)

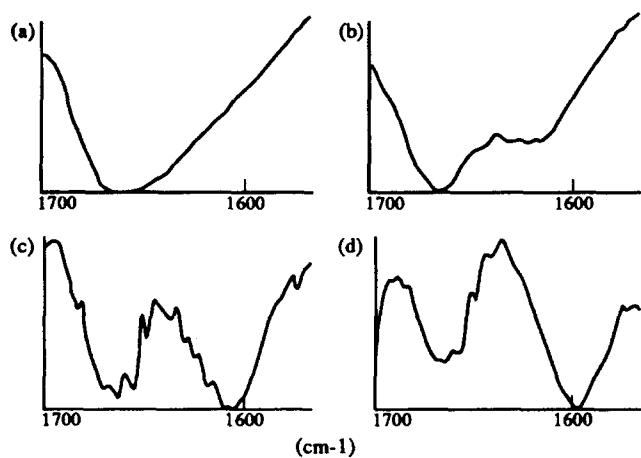


Figure 5 The i.r. spectra of Rh-POHP/I₂. Modification of the band at about 1600 cm⁻¹ due to I₂ absorption (I₂%: a = 0; b = 35; c = 61; d = 65)

Table 5 Doping of Rh-POHP with I₂

Sample	Saturated ^a I ₂ solution (ml)	Amount of Rh-POHP (mg)	Excess of I ₂ (mg)	Reaction time (h)	Adsorbed I ₂ (weight %)	Resistance ^b (ohm)
a	—	—	—	—	—	7.5 × 10 ⁹
b	30	500	0	20	35	4.0 × 10 ⁹
c	30	500	250	20	43	1.0 × 10 ⁹
d	30	500	600	20	61	1.0 × 10 ⁶
e	30	500	800	20	69	2.5 × 10 ⁵

^a Solvent = *n*-hexane

^b Pellet: internal diameter = 1 cm; *h* = 0.1 cm

The Pd-POHP/I₂ and Rh-POHP/I₂ are black powders that are insoluble in the common organic solvents. If treated with polar solvents, iodine is released as I₃⁻ species. The presence of I₃⁻ in the solutions is confirmed by u.v. spectra showing the characteristic bands of I₃⁻ at 360 and 290 nm¹⁰.

Doping of Pd-POHP with FeCl₃ (ca. 50% weight) can be carried out heterogeneously in MeOH or homogeneously by dissolving both the polymer and FeCl₃ in OHP. With this procedure good films of the Pd-POHP/FeCl₃-doped polymer can be obtained.

The i.r. spectrum of the Pd-POHP/FeCl₃ system exhibits a modification of the broad band at about 3400 cm⁻¹, which may indicate a modification of the hydrogen bonds between the OH pendant groups of the polymer and furthermore an interaction of the OH group with the Fe atoms. The C=C stretching band is shifted at 1601 cm⁻¹, similar to the I₂-doped POHP. The electrical resistance of a Pd-POHP/FeCl₃ pellet (ca. 50% w/w) was found to be ca. 10⁶ Ω, similar to the resistance of Pd-POHP/I₂ system at the same doping level. The Pd-POHP/FeCl₃ system, if washed with a polar solvent (MeOH, DMF etc.), loses the dopant and the resistance increases to the values of the undoped Pd-POHP.

The Pd-POHP/FeCl₃ films were used as sensitive membranes to investigate the influence of humidity on the resistance of these systems. The films were spun on a SiO₂ substrate on which four gold electrodes had previously been photolithographically defined. A voltage (1 V) was applied and the current intensity was measured at different relative humidity (r.h.) values. A rapid increase of the current intensity (10⁻⁹–10⁻⁵ A) was observed in the range of 0–40% of r.h. variation. However the system appears to be sensitive in a r.h. range in which several humidity sensors exhibit low sensitivity. Further investigations are now in progress.

DISCUSSION

The experimental results concerning Pd-POHP and Rh-POHP suggest that Pd-C and Rh-C produce POHP polymers with different structures. The difference cannot be easily proven because the ¹H n.m.r. spectra are not resolved and give only little information; moreover the i.r. spectra of the undoped polymers are very similar: the C=C bond stretching mode appears at 1646 cm⁻¹ for the Pd-C polymer and 1661 cm⁻¹ for the Rh-C polymer (Figure 1). However, the different structure of the polymers becomes apparent by accurate analysis of the variation of this band by increasing the I₂ dopant

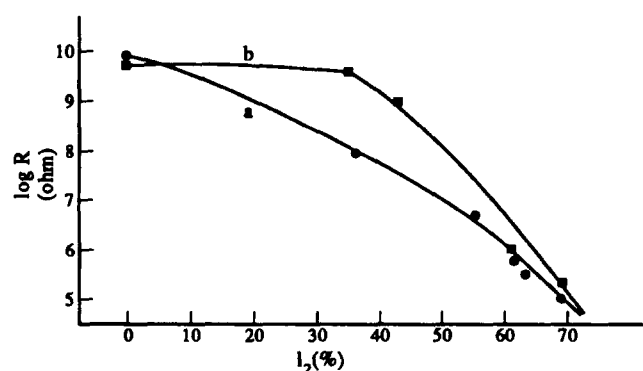


Figure 6 Resistance (R) decrease versus I_2 doping increase (% w/w) for Pd-POHP (a, ●), and Rh-POHP (b, ■) (the curves provide a visual guide)

concentration. For the Pd-POHP polymer only a lowering of the frequency of this band is observed (Figure 4). For the Rh-POHP a new band at lower frequency increases by increasing the amount of dopant (Figure 5). Studies on polyphenylacetylene^{7,8} showed the formation of a stereoregular *cis-transoidal* structure induced by reactions carried out in the presence of Rh(I) complexes. A *cis-transoidal* structure, analogous to that proposed for polyphenylacetylene, cannot be assigned unambiguously to the Rh-POHP. However, it is known that *cis/trans* isomerization is induced by doping of polyphenylacetylene^{11,12} and of π -conjugated substituted polyacetylenes, where the formation of polarons or bipolarons leads to a charge delocalization over chain segments comprising several C=C bonds¹³.

Defects are likewise formed upon doping of the Rh-POHP system; the force constant of the C=C stretching mode is reduced and a lowering of the C=C frequency, by increasing the I_2 concentration is observed. The band at 1660 cm^{-1} , which is present also at high I_2 uptake (ca. 60%), is probably due to the segments of the chain that still maintain a *cis-transoidal* structure. The increase of the band at about $1600\text{--}1620\text{ cm}^{-1}$ of the doped Rh-POHP results from the chain fragments in which a *trans-transoidal* structure is induced.

In the Pd-POHP, by increasing the I_2 content, the charge transfer reaction induces an increase of delocalization on the polymer chain with variation of the C=C stretching frequency towards lower values and an increase of the conductivity of the polymer is observed.

The conductivity of the Rh-POHP increases only after formation of chain-isomerized segments of sufficient length to increase the charge delocalization. The different electrical behaviour correlated to the different polymeric structures interacting with I_2 , is represented in Figure 6.

Information on the polymer structure may be inferred also by the viscosity and g.p.c. measurements. Rh-POHP shows an hydrodynamic volume higher than that of Pd-POHP. If a regular *trans-transoidal* structure of the polymer chain is considered, the R groups are very close

to each other. The CH_2OH groups of POHP may be involved in intramolecular hydrogen bonds, avoiding interactions with the solvent molecules. If we assume for the Rh-POHP a *cis-transoidal* structure, the CH_2OH groups are far apart, so interactions with the molecules of a polar solvent are possible and the measured hydrodynamic volume is larger.

Pd-POHP and Rh-POHP can be dissolved in the monomer and good films can also be obtained in the presence of doping agents. Preliminary results on the increase in conductivity of these films by increasing the relative humidity appear to indicate a possible application of these polymers in the preparation of humidity sensors. These investigations are currently in progress.

CONCLUSIONS

The influence of Pd(II) and Rh(I) catalysts on the polymerization of propargyl alcohol has been investigated. Analysis of the i.r. spectra of the pristine and I_2 doped polymers (POHP) indicate that POHP obtained with Rh(I) catalyst probably has a *cis-transoidal* configuration. G.p.c. measurements also offer support for this conclusion. ^1H and ^{13}C n.m.r. spectra show an average of contributions from random structures in solution.

Good electrical response in the low range of relative humidity variations was detected for FeCl_3 -doped POHP films: these could be used for resistive-type sensors.

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