A spectroscopic study of polyacetylene prepared by using Rh(I) catalysts

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The polymerization of acetylene, using [Rh(1,5-Cod)Cl]$_2$, where 1,5-Cod is *cis,cis*-cycloocta-1,5-diene or [Rh(NBD)Cl]$_2$, where NBD is bicyclo⟨2,2,1⟩hepta-2,5-diene, has been followed by u.v.–vis. spectroscopy in solution. The growing polyacetylene was identified by three fine structure maxima in the spectrum, at 500, 544 and 590 nm, which were obtained by subtracting the catalyst spectrum from that of the reaction mixture. In addition, by using the first-order derivative of the absorption spectrum of the growing polyacetylene it is possible to detect vibrational maxima at 480, 515, 550 and 600 nm for the *cis* isomer and at 640, 670 and 710 for the *trans* isomer. U.v.–vis., as well as Fourier transform infra-red (*FT*i.r.) spectroscopy, was used to study the structure of the thin free-standing films of *cis*-rich and *trans*-isomerized polyacetylene obtained by using Rh(I) complexes. The absorption spectrum of thin films of polyacetylene produced in this way reveals the absence of the vibrational structure which has been detected in ethanolic solutions during acetylene polymerization. The microstructure of the polyacetylene is very similar to that formed when using a Luttinger catalyst, in terms of defects, which are present as sp^3 hybridized carbon atoms in the polymer, and which can be detected by *FT*i.r. spectroscopy.

(Keywords: polyacetylene; rhodium (I) complexes; *cis/trans* content)

INTRODUCTION

Recently, we reported for the first time that univalent rhodium complexes are able to promote acetylene polymerization, and thin free-standing films of polyacetylene (Rh-PA) with good mechanical properties can be easily obtained[1].

We hypothesized that the general mechanism of action of these rhodium catalysts is very similar to that of the Luttinger catalysts[2,3], which are obtained by reducing Co (II) or Ni (II) salts with NaBH$_4$. Here, a low valent state of the transition metal is involved as the active polymerizing species, while in the case of the Rh complex this low valent state is ligand-stabilized. Taking into account the fact that the polyacetylene (L-PA) produced by using the Luttinger catalyst is richer in chemical defects than the more widely used Shirakawa polyacetylene (S-PA) or Naarman polyacetylene (N-PA), obtained by Ziegler–Natta catalysis[3–5], in this present work we have tried to determine if Rh-PA is more similar in its microstructure to L-PA or to S-PA and N-PA, and hence confirm indirectly if the mechanism of action of a Rh catalyst is similar or not to that of a Luttinger catalyst.

In addition, we have also studied the mechanism of interaction between the catalyst, monomer and co-catalyst, and the optical properties of Rh-PA.

EXPERIMENTAL

Acetylene was purified as described in earlier work[1]. [Rh(1,5-Cod)Cl]$_2$, RhCl$_3$ (aq.), *cis,cis*-cycloocta-1,5-diene-(1,5-Cod), bicyclo⟨2,2,1⟩hepta-2,5-diene (NBD) and all solvents used were obtained from Fluka. The u.v.–vis. spectra of the reaction mixtures were recorded at room temperature under non-flowing conditions on a Shimadzu UV-160A spectrophotometer; from the absorption curves obtained we subtracted the catalyst absorption curve and/or we calculated the first-order derivative of the absorption curve in order to obtain evidence for the presence of particular chemical species.

The u.v.–vis. spectra of free-standing thin polyacetylene films were recorded directly with the above mentioned spectrophotometer. The *FT*i.r. spectra were obtained by using a Perkin–Elmer 1710 spectrometer, and were recorded directly for the free-standing polyacetylene films.

Synthesis of [Rh(NBD)Cl]$_2$

0.12 g of RhCl$_3$, containing 12 wt% H$_2$O, were dissolved in 5 ml of absolute ethanol and 4 ml of NBD were then added. The reaction mixture was left to react at room temperature without stirring, and after 7 days the first yellow crystals of the rhodium complex appeared in the bottom of the flask. After a further 20 h the mixture consisted of crystals of the complex mixed with the mother solution.

Synthesis of polyacetylene

In a solvent mixture. 1.10 g of [Rh(NBD)Cl]$_2$ ($\sim 3.6 \times 10^{-5}$ mol) in its mother solution were mixed with 2.52 g of benzene, which homogenized the mixture. Then 0.3 ml of a sodium ethoxide solution in methanol (0.323 M) (9.7×10^{-5} mol) were added and after rapid mixing the system was cooled down to -78°C, the flask evacuated and acetylene was admitted. The flask was then left to warm up to room temperature (under a slight acetylene overpressure). At 5°C, the mixture is completely red. The system was then kept overnight at room temperature

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without stirring. A thin free-standing acetylene film, with a metallic lustre, was recovered from the flask the following day by rapid filtration of the gelatinous viscous mixture. The polyacetylene film deposited on the surface of the filter paper was washed with acetone and then dried *in vacuo*. The *cis* content of the polymer, measured by i.r. analysis[6], was 78.4%.

In ethanol. 2.33 g of the mother solution of ethanol and NBD, saturated with $[Rh(NBD)Cl]_2$, was filtered, diluted with 5 ml of ethanol and then treated with 0.2 ml of methanolic sodium ethoxide solution (0.323 M). The reaction flask was evacuated, cooled to $-78°C$, and acetylene was then admitted into the flask and the solvent saturated with gas by stirring. The mixture was allowed to warm up normally to room temperature and then left to react overnight under a slight acetylene overpressure. The polyacetylene film recovered from the surface of the solution had a *cis* content (from i.r. analysis) of 70%.

RESULTS AND DISCUSSION

Study of the catalyst interaction with co-catalyst and acetylene

In *Figure 1* we report the spectrum (A) of $[Rh(1,5\text{-}Cod)Cl]_2$ in dichloromethane (8.1×10^{-5} M). This spectrum is characterized by two maxima at 237 ($\varepsilon = 23\,150$) and 350 nm ($\varepsilon = 3200$), followed by a shoulder at 390 nm.

The effect of the addition of sodium ethoxide in ethanol (0.235 M) to achieve a molar ratio of sodium ethoxide/Rh complex of 14.5/1 is shown by spectrum B: there is a reduction in the intensity of the maximum at 237 nm, while the other peaks at 350 and 390 nm remain practically unchanged, with a new shoulder appearing at 265 nm. On the other hand, if acetylene (in the absence of sodium ethoxide) is added to the system spectrum C is obtained; here there is a slight increase in the intensity of the band at 237 nm, with a new band appearing at 280 nm. The maximum at 347 nm is no longer detectable, although the maximum at 390 nm is retained.

If acetylene is bubbled into the solution of $[Rh(1,5\text{-}Cod)Cl]_2$ in dichloromethane in the presence of sodium ethoxide (molar ratio of EtONa/Rh complex = 2/1) there is a rapid increase in the intensity of the maximum recorded at 237 nm, and an increasing intensity in the tailing absorption at longer wavelengths, with shoulders at 550 and 600 nm (see *Figure 2*).

The action of the co-catalyst, which must be a base such as EtONa, EtOK, KOH in alcohol, etc., can be interpreted in terms of cleavage of the chlorine bridges connecting the two rhodium atoms of the complex, with formation of monomeric species from the dimer, which is linked with a molecule of the base. The spectrum (B) in *Figure 1* is compatible with this interpretation, since the new band (shoulder) at 265 nm could be due to this monomeric species.

Regarding the action of acetylene on the Rh(I) dimer (in the absence of any base), the new band at 280 nm in spectrum C of *Figure 1* could be interpreted in terms of a partial ligand substitution reaction, e.g. the partial displacement of the 1,5-Cod by acetylene; however, complexes of 'simple' acetylene and a transition metal are known to be very unstable[7], but this transient species could, nevertheless, start the polymerization process. In fact, rhodium complexed with NBD is able to promote the acetylene polymerization even in the absence of a base (co-catalyst) and this can happen only if the acetylene is coordinated by rhodium, with the NBD being displaced by the acetylene. On the other hand, rhodium complexed with 1,5-Cod always requires the addition of a base as co-catalyst in order to start the polymerization; this ligand forms very stable complexes with transition metals[8], and is only partially displaced by acetylene.

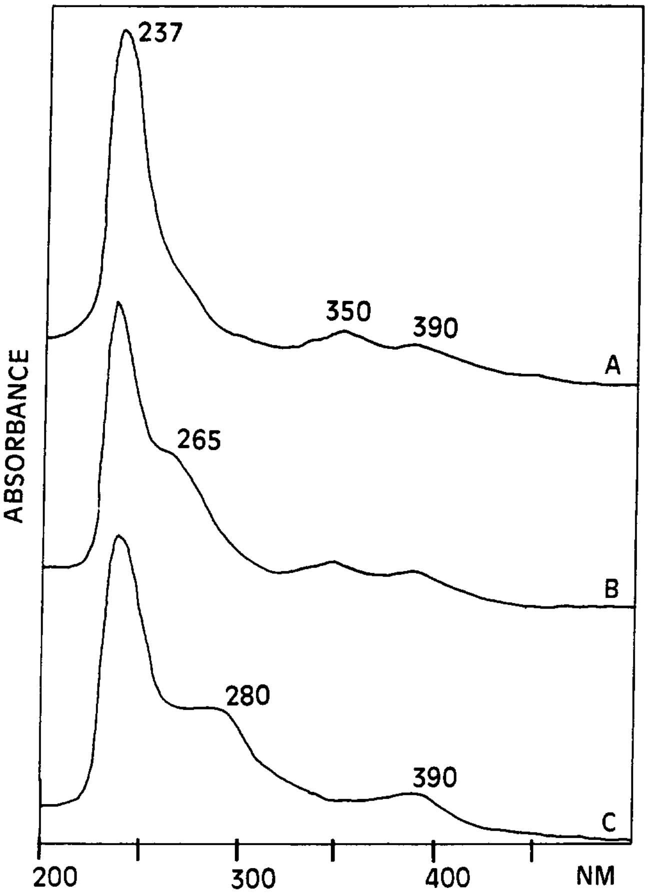

Figure 1 U.v.–vis. spectra of: (A) $[Rh(1,5\text{-}Cod)Cl]_2$ in dichloromethane (8.12×10^{-5} M); (B) the same solution as in (A), in the presence of sodium ethoxide (EtONa/Rh complex = 14.5/1); the same solution as in (A), saturated with acetylene (no sodium ethoxide added)

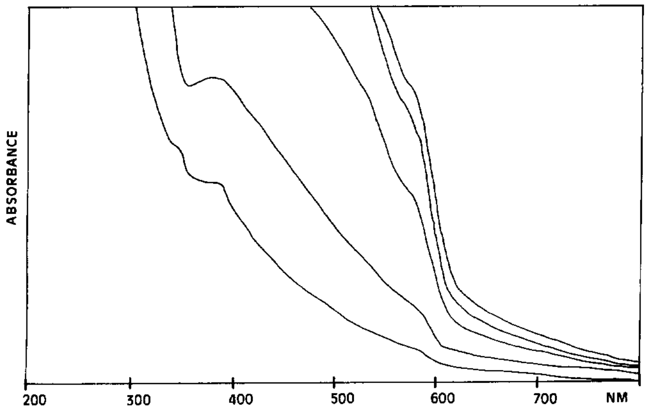

Figure 2 Spectra of a solution of growing polyacetylene, using $[Rh(1,5\text{-}Cod)Cl]_2$ in dichloromethane (4.1×10^{-3} M), saturated with acetylene and treated with EtONa (0.23 M) so that EtONa/Rh complex = 1/1

Base is often used at a concentration which gives a molar ratio of base/Rh complex of 2/1, or higher, for starting the acetylene polymerization. We can also show

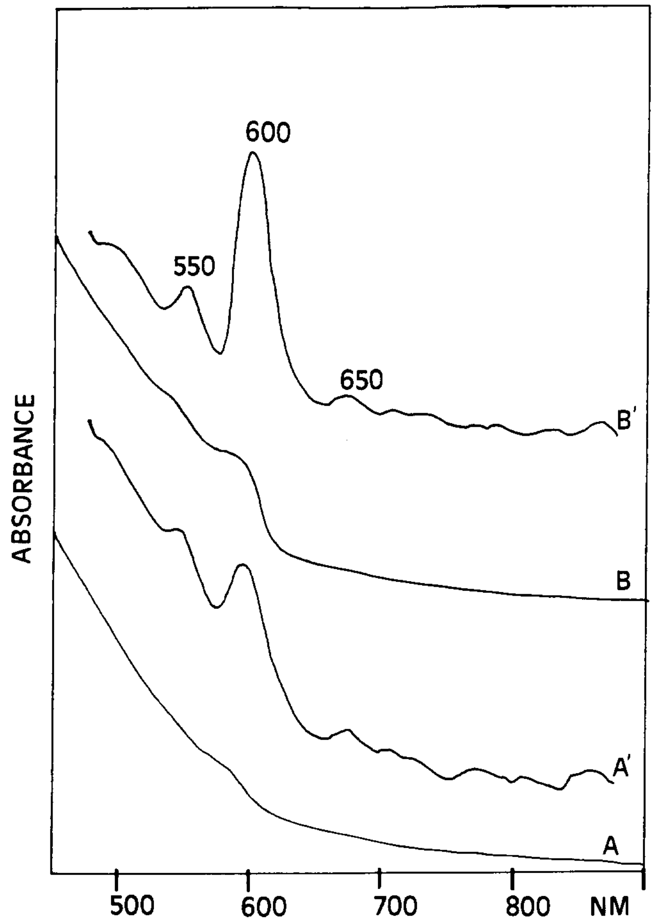

Figure 3 Absorption curves (A, B) and relative first-order derivative spectra (A', B') of growing polyacetylene on $[Rh(1,5\text{-}Cod)Cl]_2$ in dichloromethane (8.5×10^{-5} M), in the presence of triethylamine; Et_3N/Rh complex = 423/1. Spectra A and A' were recorded after 5 min polymerization time, while spectra B and B' were recorded after 15 min polymerization time

(see *Figure 3*) that even basic solvents such as triethylamine can act as co-catalysts in acetylene polymerization, in combination with rhodium dimer complexes, in which the halogen bridges are again cleaved to form two molecules of the Rh(I) complex in its monomeric form, which then coordinates with a molecule of triethylamine[7].

Detection of fine structure maxima of growing polyacetylene

Recently, the polymerization of acetylene with a Luttinger catalyst has been followed by u.v.–vis. spectroscopy[9,10]. This author used ethanol, or ethanol containing at least 1.5% of polyvinylbutyral (PVB), as the reaction medium, in the presence of cobalt (II) nitrate and sodium borohydride. It has been found that in ethanolic solution (in the absence of PVB) polyacetylene with a fibrillar morphology is formed, while the presence of PVB at a concentration higher than 1.5% leads to the formation of a polyacetylene with a globular morphology[9]. It has been shown[10] that the optical spectra of such polymerizing mixtures in the presence of PVB are characterized by narrow absorption bands of *cis*-polyacetylene with fine structure, as well as by a shoulder of *trans*-polyacetylene, also with fine structure. On the other hand, the absence of any globular morphology for the polyacetylene formed in neat ethanol leads to less well defined spectra with only broad bands.

In *Figure 2* we have recorded the spectra of a growing polyacetylene at room temperature in ethanol using a $[Rh(1,5\text{-}Cod)Cl]_2$ catalyst. Under these conditions, we are able to detect only two shoulders at 550 and 590 nm in the final stages of polymerization.

In order to obtain more well defined spectra for the acetylene polymerization process over Rh(I) complexes we have followed two distinct strategies. Initially, we have recorded the spectrum of $[Rh(NBD)Cl]_2$ in an ethanol/NBD solution and then we have recorded the spectrum of the growing polyacetylene in the same solution, and have subtracted from the latter the original absorption curve of the catalyst. We have at this point a spectrum of polyacetylene which shows three distinct fine structure maxima at 500, 544 and 590 nm (*Figure 4*) due to the *cis*-polyacetylene, while bands for the *trans* portion of the polymer and their fine structure at longer wavelengths are not detected at all. The second strategy followed has been to calculate the first-order derivative spectrum of the absorption curve of the growing polyacetylene and as shown in *Figures 3* and *5* these derivative spectra show two distinct maxima at 550 and 600 nm, with additional absorptions appearing at 480, 515, 640, 670 and 710 nm, which are the fine structure maxima of the *cis* and *trans* portions of the polyacetylene (see *Figure 5*). Other investigators[10] have recorded, at −50°C, fine structure maxima for *cis*-polyacetylene at 484, 515 and 550 nm, while at −20°C fine structure peaks at 613, 651, 698 (shoulder) and 752 nm have been found.

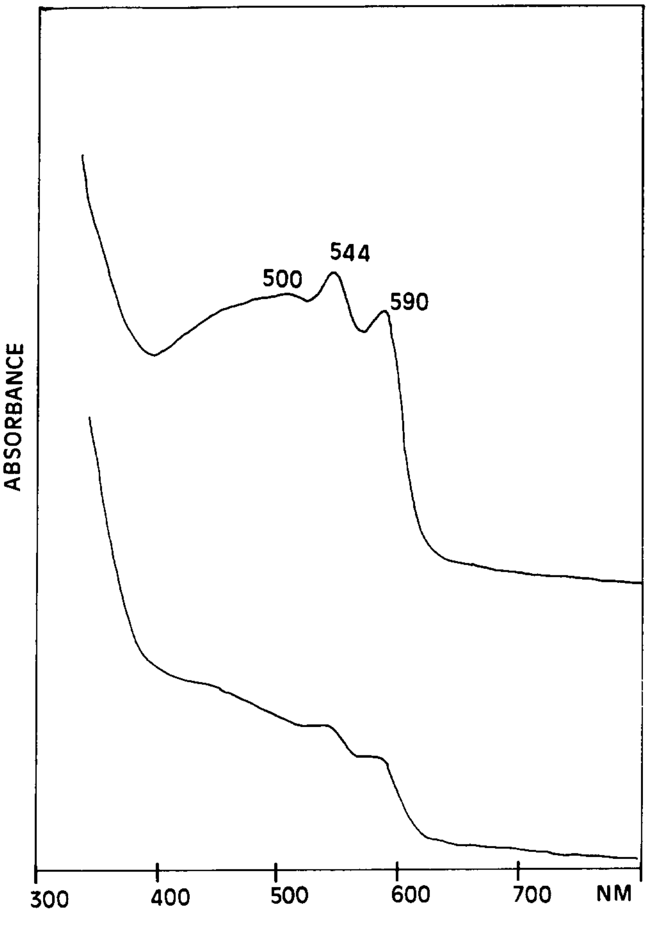

Figure 4 Spectra of growing polyacetylene in a saturated solution of $[Rh(NBD)Cl]_2$ in ethanol, with traces of unreacted NBD present, and co-catalyst absent. From the original absorption curve (bottom) the spectrum of the catalyst recorded before acetylene saturation has been subtracted to give the better defined spectrum (top) showing the fine structure maxima (see text for details)

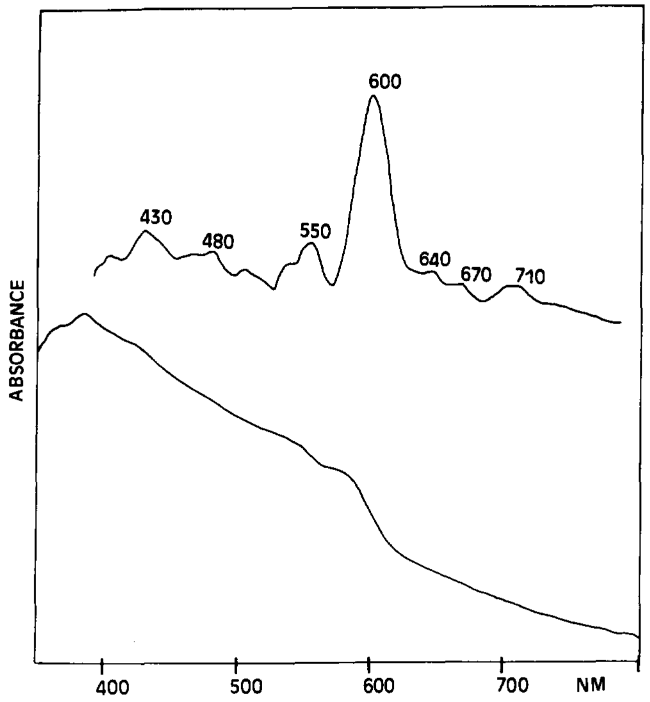

Figure 5 The absorption curve (bottom) and first-order derivative spectrum (top) of growing polyacetylene in a saturated solution of $[Rh(NBD)Cl]_2$ with traces of unreacted NBD, using EtONa as co-catalyst (EtONa/Rh complex = 2/1)

Moreover, it has been shown[10] that the positions of the absorption maxima of *cis*-polyacetylene are practically independent from degree of polymerization, time and temperature; in particular, the positions of the fine vibrational maxima due to the presence of *cis*-polyacetylene do not undergo any significant shift in position or change in intensity by heating the reaction mixture from −50°C up to room temperature. Concerning the bands assigned to *trans*-polyacetylene, it has been noticed that the maximum at 752 nm recorded at −20°C (band possibly due to the presence of a neutral soliton), completely disappears at room temperature, while the other three maxima at 613, 651 and 700 nm are reduced in intensity at room temperature, but do not change their positions[10]. These facts explain why in *Figure 4* we are able to detect only the fine vibrational maxima due to *cis*-polyacetylene, but not those due to the *trans*-polyacetylene, i.e. because of the low intensity of the latter and the absence of PVB in our system so that we are measuring the absorption spectra of fibrous polyacetylene dispersed in the solvent, and not the globular one studied by others, which does give better defined spectra.

With the first-order derivative spectra (*Figures 3* and *5*) we are able to highlight again all of the fine vibrational bands of *cis*-polyacetylene, and in addition we are able to detect a series of bands which we can assign to the fine structure maxima of *trans*-polyacetylene, but which, however, do not coincide exactly with the positions of the already mentioned bands recorded in the presence of PVB by other workers[9,10]. It is likely that the use of a different solvent medium, as well as different polymerization conditions and catalysts could affect the position of these bands. Moreover, first-order derivative calculations could introduce some distortions/shifts into these bands. However, Rh-PA with a probable fibrillar morphology gives a spectrum in ethanol which is very similar to that shown by L-PA, particularly with regard to its *cis*-portion, as confirmed by our difference and derivative spectra.

*Optical properties of thin films of Rh-PA (*cis*- and* trans*-rich)*

The optical properties of S-PA films (*cis* and *trans*) have been studied in both transmission and reflection spectroscopy[11]. It has been found that the reflection and absorption spectra of *cis*-polyacetylene are very similar and are characterized by two maxima of vibronic origin at 600 and 555 nm. After careful isomerization to *trans*-polyacetylene, the reflectance spectrum still shows two distinct maxima (of vibronic origin) at 833 and 770 nm, while the absorption spectrum is characterized only by a broad absorption at 657 nm and a shoulder at 813 nm. The lowest energy maximum (at the longer wavelength) has been assigned to a polaron absorption[11].

We have only examined our Rh-PA samples by absorption spectroscopy, and as shown in *Figure 6* the spectrum (A) is practically free from any detectable fine vibrational structure, and is characterized by broad absorption bands at 600 and 720 nm, due, respectively, to the *cis* and *trans* portions of the polymer. The lack of

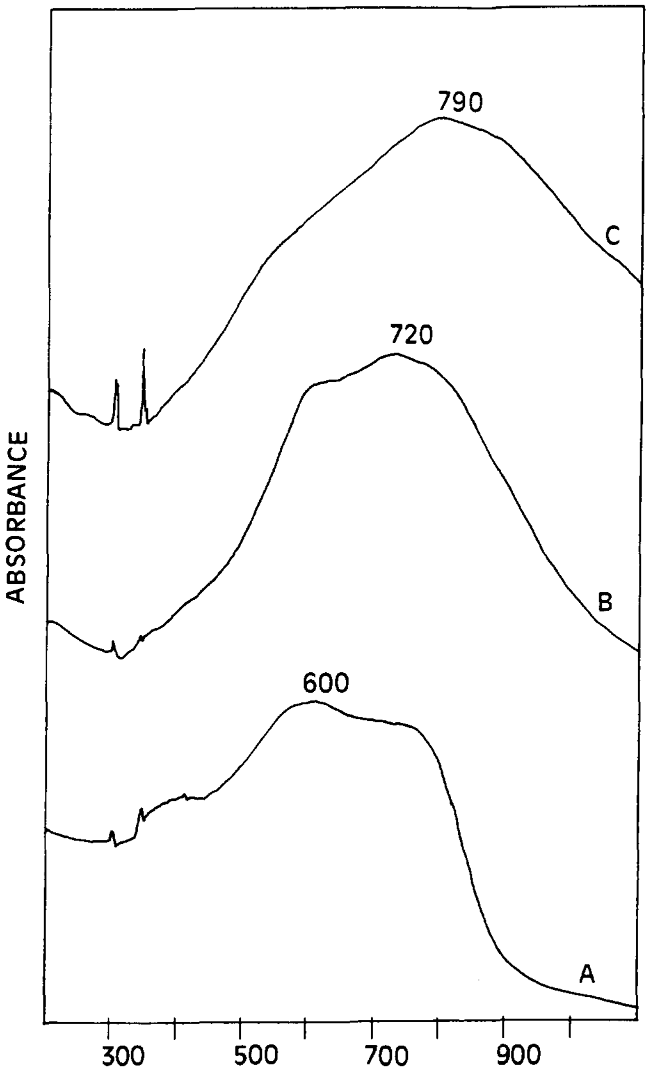

Figure 6 Absorption spectra of thin films of Rh-PA: (A) *cis*-rich; (B) *trans*-rich; (C) all-*trans*

fine structure could be due to the fact that the film used was too thick, and also to the equal presence of a large amount of both *cis* and *trans* isomers, with the fine structure only being seen in samples with either a high *cis* or a high *trans* content.

Figure 6 also shows the spectrum (B) of a partially *cis–trans* isomerized sample: here, the maximum at 720 nm has a higher intensity than that at 600 nm, and this indicates that now the *trans* content is higher than the *cis* content. The spectrum (C) of a fully *trans* isomerized sample is also shown in *Figure 6*, where we can observe a broad maximum centred at 790 nm; here, also, no fine structure is detectable.

Similar to *cis* S-PA, *cis* Rh-PA also has a maximum at 600 nm, but does not show the second maximum at 555 nm (detected, however, in an ethanol dispersion, as described above). On the other hand, *trans* S-PA has a broad maximum at 657 nm, followed by a shoulder at 813 nm, while *trans* Rh-PA has a broad maximum at 790 nm; it may well be that in this last case we detect an unique absorption which approximately represents the average of the two absorptions at 813 and 657 nm present in the *trans* S-PA, but lack of resolution prevents us from detecting two separate peaks.

FT*i.r. spectroscopy of Rh-PA thin films*

Figures 7 and *8* show, respectively, the *FT*i.r. spectra of a *cis*-rich Rh-PA film and that of the *trans* isomer which is obtained by thermal isomerization of the *cis*-rich material by heating *in vacuo* for 1 h at 180°C.

The spectrum of the *cis*-rich Rh-PA (*Figure 7*) is characterized by typical bands of *cis*-polyacetylene, and generally speaking is analogous to the spectrum of S-PA[12,13]. In particular, we can detect the *cis* bands at 3056 and 3047 cm^{-1} (=C—H stretching), the combination band at 1800 cm^{-1}, the *cis* C=C stretching at 1645 cm^{-1} and bands at 1375, 1329, and 1253 cm^{-1} (the last two are due to in-plane =C—H bending). Other bands appear at 740 and 446 cm^{-1}, and are respectively due to out-of-plane =C—H bending and carbon-chain bending. After *trans* isomerization has taken place (*Figure 8*) the most intense and typical *trans* bands are found at 3012 (=C—H stretching), at 1584 (*trans* C=C stretching), with a band at 1450 and absorptions at 1012 (=C—H out-of-plane bending) and 896 cm^{-1} (=C—H in-plane bending). Absorptions at 1720 and 1667 cm^{-1} are detectable in the spectrum of the *trans* isomer and are due, respectively, to a ketonic group and a ketonic group conjugated with a double bond, which is probably formed during thermal isomerization by the reaction with traces of oxygen or moisture.

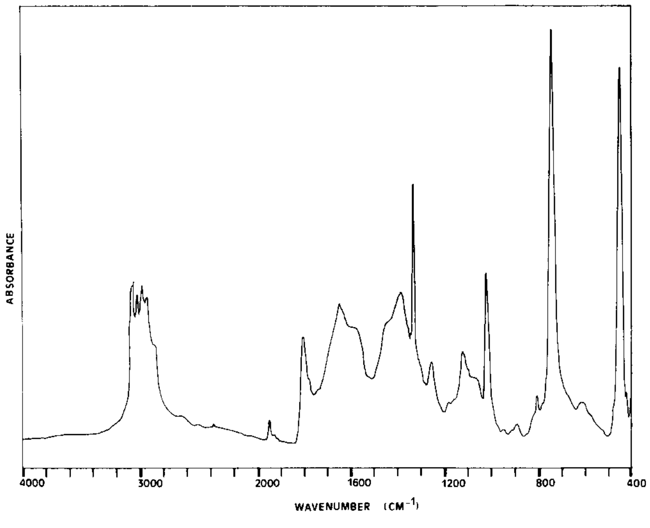

Figure 7 *FT*i.r. spectrum of a *cis*-rich Rh-PA film

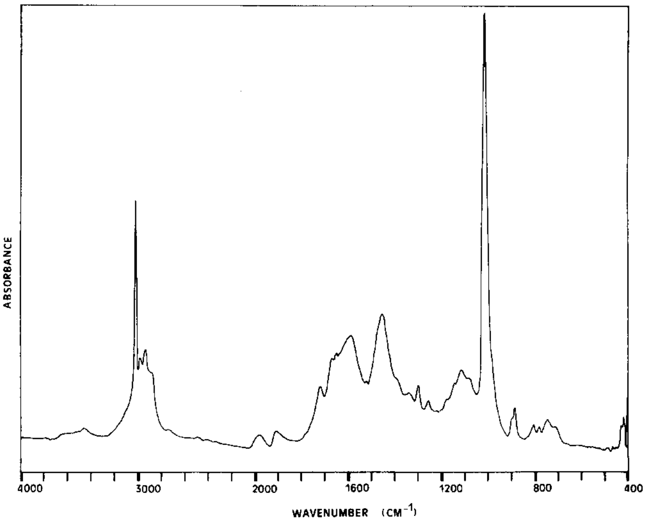

Figure 8 *FT*i.r. spectrum of a *trans*-rich Rh-PA film

One of the main spectral features of the Rh-PA is the relatively intense absorption in the spectral region between 3000 and 2850 cm^{-1}, both in the *cis*-rich and *trans* isomerized samples, while for S-PA other workers have recorded only very weak to negligible absorptions in this spectral region[12,13]. These absorptions lead us to think that Rh-PA could be relatively rich in methyl side and end-groups, as shown by the methyl asymmetric and symmetric stretching at 2972 and 2870 cm^{-1} respectively[14]. The methyl C—H stretching absorptions (see *Figures 7* and *8*) are so strong that they lead us to suggest that there is a relatively high concentration of methyl groups in the polymer chains, and hence these levels cannot be ascribed only to end-groups. The presence of alkyl side and end-groups in the Rh-PA is not so surprising if we consider that both high-density (HDPE) and low-density (LDPE) polyethylenes contain a certain amount of alkyl groups, i.e. 20–30 methyl groups per 1000 carbon atoms in the LDPE chain and 5–7 ethyl groups per 1000 carbon atoms in Ziegler-catalysed HDPE[15]. The presence of —CH$_2$— groups, probably connected to the already mentioned methyl groups to form ethyl side groups, or even inserted into the main polymer chain, is suggested by the absorption at 2930 cm^{-1} (ref. 14). The interchain crosslinking cannot be detected because the tertiary C—H stretching is very weak and is generally hidden by other bands[14]. These defects, which can be detected by infra-red spectroscopy of Rh-PA confirm unequivocally that this material can be classified as a L-PA. In the past, it has been found[4,5] that S-PA, obtained by using a Ziegler–Natta catalyst, can be generally characterized by a high degree of crystallinity (70–80%), and a very low content or a complete absence of defects such as interchain crosslinks, the presence of —CH$_2$— groups on the main chain, and alkyl branches. Generally, all of these defects have been reported as a percentage of the number of sp^3 carbon atoms with respect to the total number of carbon atoms in the polymer chain and have been measured by ^{13}C n.m.r. spectroscopy. The sp^3 carbon atom content in S-PA, determined by n.m.r. spectroscopy, varies from 0 to 3%, while a Luttinger-type polyacetylene with a crystallinity of 70% has a sp^3 content of $\sim 11\%$[4,5]. Hence, a relatively intense absorption in the spectral region of the alkyl C—H stretching is expected for a L-PA, as can be seen for our Rh-PA system; this absorption should be very weak, or even negligible, in the case of S-PA.

CONCLUSIONS

We have proposed and shown that $[Rh(1,5\text{-}Cod)Cl]_2$, as well as $[Rh(NBD)Cl]_2$, can be considered as being members of a special class of Luttinger catalysts[2,3]. These catalysts are usually composed of a transition metal salt, such as $Co(NO_3)_2$ or $Ni(NO_3)_2$, and an equimolar or an excess amount of $NaBH_4$ as a reducing agent. It is believed that the low-valent unstable intermediate which is formed by reducing the transition metal is responsible for the acetylene polymerization. By analogy, the above mentioned Rh complexes can be considered as low-valent ligand-stabilized molecules which are able to promote acetylene polymerization, particularly in the presence of a co-catalyst of an alkaline nature, such as sodium ethoxide, potassium hydroxide or triethylamine. The role of these co-catalysts can be interpreted in terms of a cleavage of the halogen-bridged rhodium complexes, thus generating a low-valent monomeric species which is able to coordinate acetylene and/or the growing polyacetylene chains. It has also been suggested that the acetylene may be able to displace the diene ligand which is linked to the metal and coordinate itself to the latter in a weak fashion so that this intermediate is able to start the polymerization.

The optical properties of Rh-PA with a fibrillar morphology, present in an ethanol suspension, are comparable to that of a L-PA under similar conditions, particularly with regard to the *cis* component of the polymer. The optical properties of thin *cis*-rich or *trans*-rich Rh-PA films are generally similar to that of S-PA films, but no clear fine structure is detectable in these samples.

Rh-PA resembles L-PA in its relatively high content of sp^3 carbon atoms i.e. defect structures such as methyl and alkyl side chains and end-groups, or interactions with —CH_2— groups in the principal conjugated chain, as well as crosslinks, as detected by *FT*i.r. spectroscopy.

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