

POLYAMIDE-BOUND METAL COMPLEX CATALYSTS: SYNTHESIS, CHARACTERIZATION AND CATALYTIC PROPERTIES

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Summary

A series of polyamides having different numbers of methylene groups in their repeating units have been synthesized by interfacial polycondensation of terephthaloyl chloride with piperazine and aliphatic diamines $H_2N(CH_2)_nNH_2$ ($n = 2, 6, 10$). These materials, which have high thermal stability, were used for immobilization of rhodium and platinum complexes. Chloroplatinic acid and the compounds $PtCl_2(CH_3CN)_2$ and $[RhCl(CO)_2]_2$ were used as precursors of the supported catalysts. Low molecular weight analogues of the polyamides were prepared for a study of the coordination mode between the metal ion and the polymer by IR spectroscopy. The results suggest that the carbonyl oxygen of the polyamide is the site of coordination to both rhodium and platinum. The bound catalysts exhibited high activity in hydrosilylation of hexene-1. The activities of the rhodium complexes were found to be dependent on the structure of the polyamide support, decreasing with increasing distance between the amide groups, and closely paralleled the changes in the degree of crystallinity of the polymers. Repeated use of the polymers bearing rhodium complexes showed that the bond between the metal and polyamide is fairly stable.

Introduction

Polymers of styrene and divinylbenzene are the most commonly used supports for the attachment of active transition metal complexes. They can be prepared in several forms with a wide range of crosslinking. A drawback of the crosslinked networks is the nonequivalence of the active sites. This leads to differences in accessibility, microenvironment, stability and activity. In this respect polymer-attached catalysts share similar problems with traditional heterogeneous catalysts. Therefore a study of noncrosslinked polymers was undertaken. Of special interest are polymers with higher thermal and mechanical stabilities than those of styrene and which contain functional groups which can act as chelating ligands, and so the study focused on the use of polyamides.

Synthetic polyamides and natural polypeptides have been used for a long time as supports for immobilization of homogeneous metal complexes. In most cases the supported species have been used for catalytic hydrogenation; for this purpose they have to be reduced to the metallic state before use [1–15], and so the precise nature of the bond between the metal and the support before any reduction has not usually been considered important. Some attempts have been made to establish the coordination structure of polyamide-bound metal complexes, but the results were contradictory [16,17].

The purpose of the present work was to prepare a series of these polyamides which contain aromatic and aliphatic fragments in their repeating units and to evaluate them as supports for the attachment of transition metal complexes. Another objective was to study the influence of the polymer structure on the activity of supported catalysts and to gain more information about the mode of bonding between the metal atom and the functional groups of the polyamide.

Experimental

Reagents

Terephthaloyl chloride ("For Synthesis"; Merck) and hexamethylenediamine (Fluka) were used without further purification. Benzoyl chloride (POCh, Gliwice) was redistilled (77°C/12 torr). 4-Butylamine (Koch-Light Laboratories Ltd) and triethylamine (VEB Jenapharm-Laborchemie Apolda DDR) were dried over solid KOH and distilled at 77–78°C and 88–90°C, respectively. Toluene (POCh, Gliwice) was dried over metallic sodium and distilled at 120–121°C. Methanol (POCh, Gliwice) was dried over magnesium and distilled at 64–65°C. Benzene was freshly distilled from sodium benzophenone ketyl before use. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was the POCh (Gliwice) product. PtCl_2 and $\text{PtCl}_2(\text{PhCN})_2$ were prepared by standard procedures [18,19], as was $[\text{RhCl}(\text{CO})_2]_2$ [20]. Hexene-1 was passed through activated alumina and distilled before use. The silane Me_2PhSiH was prepared as described elsewhere [21].

Preparation of polyamide supports

Synthesis of the polyethyleneterephthalamide (2 T), polyhexamethyleneterephthalamide (6 T) and polydecamethyleneterephthalamide (10 T) [22]. A typical procedure was performed as follows. To a solution of 0.0028 mol of appropriate diamine and 0.0056 mol of potassium hydroxide in 100 ml of water, a solution of 0.0028 mol of terephthaloyl chloride in 100 ml of toluene was added rapidly with high speed stirring. The polycondensation was allowed to proceed for 10 min at room temperature then the solid polymer which had separated out was filtered off and washed several times with acetone then with boiling distilled water. It was then extracted with acetone in a Soxhlett apparatus for 17 h, then dried, initially at 50°C and 15 torr and then under high vacuum.

Synthesis of the polypiperazine terephthalamide (Pip T) [23]. To a vigorously stirred solution of 0.86 g (0.01 mol) of piperazine and 0.02 mol of KOH in 100 ml of distilled water, cooled in an ice-bath, 2.03 g (0.01 mmol) of terephthaloyl chloride in 100 ml of dry benzene was rapidly added. The mixture was stirred for 10 min. at high speed during which the polymer separated out. The flocculent product was repeatedly washed with acetone, water, methanol, and ether, then dried initially under reduced pressure at 50°C and 20 torr and then under high vacuum.

Preparation of the model compounds

Synthesis of N,N'-dibenzoyl-1,6-hexamethylenediamine (I). 5 g (0.036 mol) of benzoyl chloride dissolved in 50 ml of toluene was added at room temperature during 5 min with vigorous stirring to a solution of 2.079 g (0.018 mol) 1,6-hexamethylenediamine and 4 g (0.04 mol) triethylamine in 120 ml of dry toluene. The product immediately separated, and to the suspension 100 ml of dry toluene was added and the stirring was continued for 30 min. The product was washed several times with distilled water then dried under reduced pressure. It was recrystallized from 150/15 v/v toluene/methanol. The product was filtered off, washed with toluene, and dried at 50–60°C under reduced pressure, 1 torr. The melting point was 154–155°C.

Synthesis of the di-n-butylterephthalamide (II). To a stirred solution of 3 g (0.041 mol) of n-butylamine and 4.1 g of triethylamine in 40 ml of dry toluene, a solution of 4 g (0.02 mol) of terephthaloyl chloride in 20 ml of dry toluene was added during 5 min. at room temperature. A precipitate immediately appeared, and to this 75 ml of dry toluene was added. The stirring was continued over 40 min, then the product was filtered off and unchanged reactants and salts were removed by washing with distilled water. The product was then dried, and recrystallized from 105/25 v/v toluene/methanol solution, washed with toluene and dried. The melting point was 228–229°C.

Synthesis of n-propylbenzamide (III). To a vigorously stirred solution of 3 g (0.05 mol) of n-propylamine and 7.6 g (0.075 mol) of triethylamine in 200 ml of dry toluene a solution of 7 g (0.05 mol) of benzoyl chloride in 50 ml of dry toluene was added dropwise at room temperature during 5 min. To this suspension was added 50 ml of toluene, and the stirring was continued for 1 h. The salt was dissolved out with 150 ml of water, and the toluene layer was thoroughly washed with distilled water then dried with magnesium sulphate. Toluene was then distilled off and the product recrystallized from 2/1 v/v benzene/hexane solution. M.p. was 81.5–82°C.

Phosphination of the polyamides

In a typical experiment, 1 g of polyamide was suspended in 50 ml of freshly distilled toluene and a solution of 3.5 g (16 mmol) of PPh_2Cl_2 in 15 ml of toluene was added dropwise with stirring. The mixture was refluxed under nitrogen for 48 h. Gaseous HCl was purged from the system by the nitrogen flow. The phosphinated

TABLE I
PROPERTIES OF POLYAMIDE SUPPORTS

Polyamide	$-(\text{CH}_2)_n-$	S^a ($\text{m}^2 \text{g}^{-1}$)	T_{dec}^b (°C)	Crystal. ^c (%)	P ^d (%)
Pip T	2+2	6.76	350	24.35	
2 T	2	8.36	354	24.75	0.92
6 T	6	11.35	322	40.35	1.27
10 T	10	23.5	295	29.85	0.84

^a By BET method. ^b T_{dec} = decomposition temperatures measured by thermogravimetric analysis.

^c Crystallinity was measured by X-ray analysis relative to an amorphous standard. ^d Phosphorous content of phosphinated polyamides.

polymer was washed several times with benzene, THF, THF/water, water, THF, MeOH, benzene, then dried initially at 14 torr and then under high vacuum. It was pale yellow in colour. (See Table 1 for elemental analysis).

Characterization of the polyamides

The surface areas of the polymers were determined by a flow method using N_2 as the adsorbate on a Sorptomatic 2000 adsorption apparatus (Carlo Erba).

The thermogravimetric analyses were performed using a Hungarian derivatograph with the Paulik, Paulik and Erdley systems.

X-Ray diffraction patterns were obtained with a powder Siemens diffractometer using nickel-filtered $Cu-K_\alpha$ radiation. The crystallinity of the polymers was estimated from the ratio of crystalline to amorphous scattering in wide-angle x-ray diffraction patterns of powdered samples.

Preparation of the rhodium catalyst

A benzene solution of 0.1 mmol rhodium complex was added with stirring at room temperature to 1 g of polymer powder suspended in benzene with nitrogen flowing over the solution. The mixture was refluxed for 4–6 h then allowed to stand at room temperature overnight. The colourless solution was decanted and the yellow polymer was extracted several times with boiling benzene then filtered off and dried in vacuo.

Preparation of the platinum catalyst

To the suspension of 1 g of polyamide powder in water was added 0.12 g of 30% aqueous solution of H_2PtCl_6 (0.1 mmol of Pt). Stirring was continued for 6 h at room temperature then the catalyst was washed several times with hot water and dried under vacuum at 50–70°C.

The platinum catalyst made from $PtCl_2(CH_3CN)_2$ was prepared similarly but with methylene chloride as solvent.

Preparation of metal complexes of the model compounds

Reaction of rhodium complex with compound I. To a solution of 0.324 g (1 mmol) of I in 10/1 v/v benzene/methanol was added a solution of 0.389 g (1 mmol) of $[RhCl(CO)_2]_2$ in benzene (3 ml). The solution was refluxed for 6 h under nitrogen with stirring, then filtered and evaporated to dryness to give brown crystals. The product was recrystallized from benzene by the slow addition of ether.

Reaction of rhodium complex with compound III. Use of a similar procedure with $[RhCl(CO)_2]_2$ (0.389 g, 1 mmol) and n-propylbenzamide (0.3260 g, 2 mmol) in methylene chloride gave the product as brown crystals.

Reaction of $PtCl_2$ with compound III. A molten mixture of 0.133 g (0.5 mmol) of $PtCl_2$ and 0.5 (3 mmol) of n-propylbenzamide was kept at 85–90°C in a water bath and stirred under N_2 for 4 h. After cooling the mixture was dissolved in dry acetone and the solution was filtered then evaporated in vacuo. The solid was repeatedly washed with dry ether (7 × 5 ml) to remove an excess of III then dried under reduced pressure.

Infrared spectra

Infrared spectra were recorded on a Specord IR 75 spectrophotometer in 4000–400

cm^{-1} range. Samples were prepared as KBr discs (800 mg of KBr mixed with 2 mg of substance) or as suspensions in Nujol between KBr plates. IR spectra in the range 450–200 cm^{-1} were recorded on a Perkin–Elmer 325 grating spectrophotometer with Nujol mulls using CsI optics.

Activity measurements

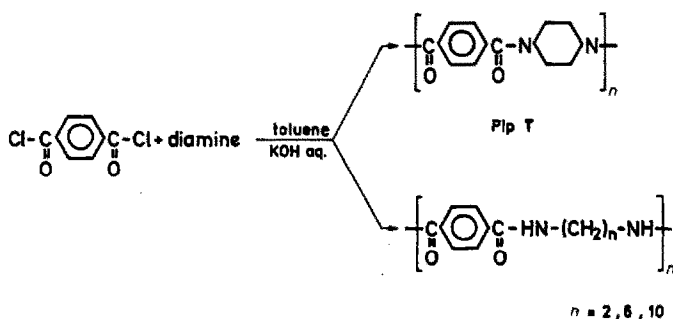
The procedure used for determining the activity of the supported catalysts has been described in detail elsewhere [24].

Results and discussion

Synthesis of polyamide supports

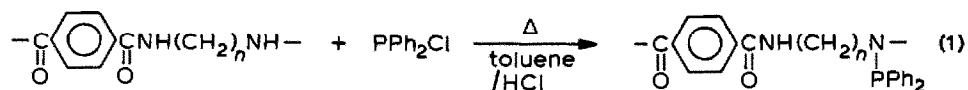
Several types of polyamides have been used previously as supports for the immobilization of transition metal compounds, including aliphatic polymers such as Nylon 3, 6, 64, 66 and 6, 10 [1–15] and aromatic ones such as polyphenylene-terephthalamide [25] and poly-*m*-phenyleneisoterephthalamide [26]. For the present study polyterephthalamides incorporating aliphatic primary diamines were selected for two reasons, namely their higher thermal stability (over 300°C) compared with aliphatic polyamides and their greater flexibility compared with aromatic polyamides. To our knowledge such materials have not been examined as catalyst supports.

The polyamides were prepared by interfacial polycondensation of terephthaloyl chloride with diamines using a toluene water system with potassium hydroxide as HCl acceptor, Scheme 1.



SCHEME 1. Interfacial polycondensation.

The polyamides were partially phosphinated using diphenylphosphine chloride:



This procedure enabled us to compare the stability of the bond between the metal and polyamide support with that of the phosphinated polyamide in respect to leaching out.

Properties of the polymers

The outstanding property of the prepared polymers was their high thermal

TABLE 2

SELECTED INFRARED BANDS OF THE POLYAMIDES AND THEIR RHODIUM CARBONYL COMPLEXES. (Nujol; cm^{-1}).

Polymer	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C-N})-\delta(\text{N-H})$	$\nu(\text{Rh}(\text{CO})_2)$
Pip T	3467	1623		2075 2000
2 T	3287	1630	1530	2070 2000
6 T	3300	1625	1537	2070 1997
10 T	3310	1623	1533	2075 1998

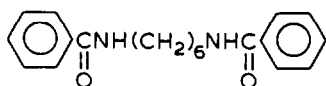
stability. As seen from Table 1 the decomposition temperatures determined by thermal gravimetry were above 300°C .

Table 1 also shows the degree of crystallinity determined by X-ray analysis. It can be seen from the table that the crystallinity increases with the increase of the number of the methylene groups in the aliphatic part of a chain, a feature consistent with earlier findings [27,28]. The X-ray diffraction patterns of the polyamides after immobilization of the rhodium complex did not differ much from those of the parent polymers, suggesting that the complexation does not change the polymer structure. Thus the chelation with the metal ion can compete with the hydrogen bonding between the polymer chains.

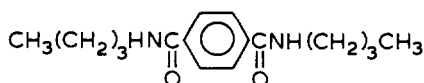
Preparation and characterization of polyamide-bound catalysts. The immobilized rhodium and platinum complexes were prepared by treating the appropriate precursors such as $[\text{RhCl}(\text{CO})_2]_2$, $\text{PtCl}_2(\text{CH}_3\text{CN})_2$ and H_2PtCl_6 with the polyamides and/or phosphinated polyamides. When the rhodium precursor was complexed only a small amount of CO was evolved (0.25 mol CO/Rh atom). Although various concentrations of the rhodium complex were used, the amount of metal attached to the polyamide support remained the same, up to 1.5%. It is evident that the polymers were saturated with the metal and still retained a relatively large number of nonaccessible coordination sites.

Infrared studies

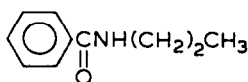
As shown in Table 2 the rhodium complexes, derived from $[\text{RhCl}(\text{CO})_2]_2$ by reaction with the polyamides, exhibit two strong carbonyl bands in the region $2100\text{--}1950\text{ cm}^{-1}$, indicating the presence of rhodium *cis* dicarbonyl species. However, this kind of interaction between polyamide functional groups and the metal could not be detected because of the low concentration of the metal complex on the surface of polyamides (Fig. 1). Therefore three model compound, I, II and III were synthesized as close models of the polyamides in order to try to establish the site of coordination:



(I)



(II)



(III)

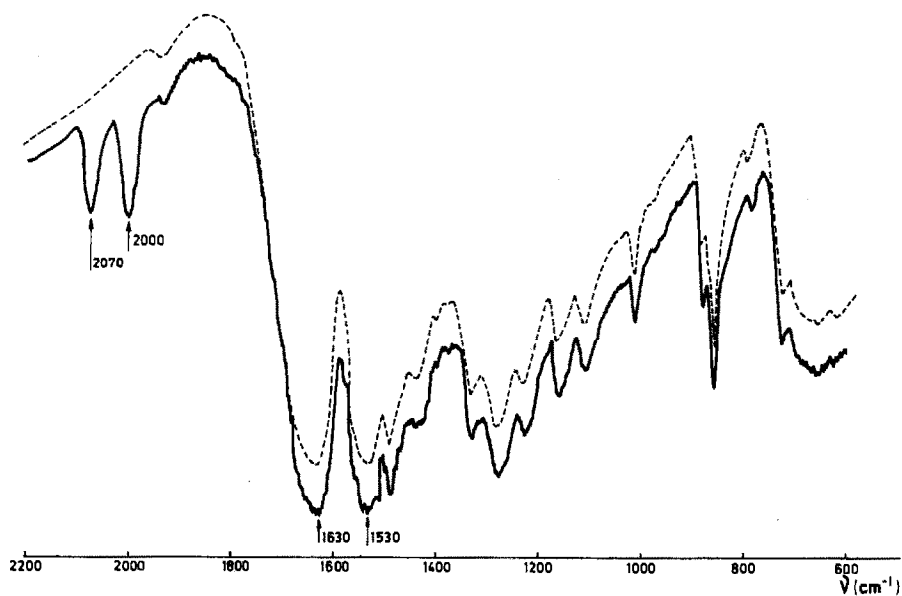


Fig. 1. Infrared spectra of $[\text{RhCl}(\text{CO})_2]_2$ supported on polyamide 2 T-; spectrum of the polyamide 2 T -----.

The polyamide unit has two possible coordination centers, O or N, to which a metal ion can be bound. Reports on the coordination structures of polyamide-metal complexes are rather inconsistent; some reports based on infrared evidence conclude

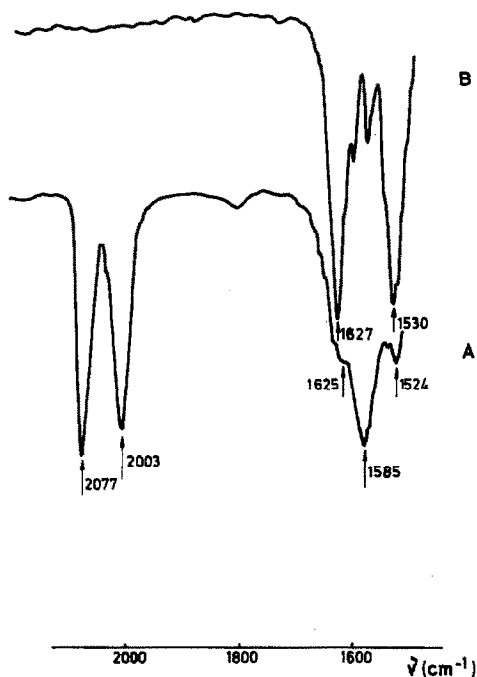


Fig. 2. (A) Infrared spectra of $[\text{RhCl}(\text{CO})_2]_2$ complexed with the model compound I; (B) spectrum of I.

TABLE 3

SELECTED INFRARED BANDS OF THE MODEL AMIDES AND THEIR METAL COMPLEXES (KBr, CH₂Cl₂; 4000–750 cm⁻¹)

Compound	$\nu(\text{N-H})$	$\nu(\text{N-H})_{as}$	$\nu(\text{C=O})$	$\nu(\text{C-N}) + \delta(\text{N-H})$	$\nu(\text{Rh}(\text{CO})_2)$
I	3312		1627s	1530	
II	3310		1620s	1533	
III	3313		1630s	1544	
	3295				
I + [RhCl(CO) ₂] ₂	3317	3447, 3573	1625sh, 1585s	1573sh	2077 2003
II + [RhCl(CO) ₂] ₂	3310	3447, 3550	1590s	1575sh	2077 2003
III + [RhCl(CO) ₂] ₂	3300 ^a		1596s ^a	1563 ^a	2083 2030 ^a
III + PtCl ₂	3317		1606s	1567s	

^a In CH₂Cl₂.

that the rhodium and platinum complexes are bonded to the polyamides through the carbonyl oxygen [16], whereas others conclude from ESCA evidence that the rhodium is bonded to the polyamide via amide nitrogen [17].

Examination of IR spectra of the model compounds I and II coordinated to the rhodium dicarbonyl dimer revealed the disappearance of the I and II amide bands at 1627 cm⁻¹ ($\nu\text{C=O}$) and 1530 cm⁻¹ ($\nu\text{CN} + \delta\text{NH}$) for the free model ligands and the appearance of a new band at 1585 cm (Fig. 2, Tab. 3). More marked changes in the IR spectra were found after complexation of the model compound III with the rhodium and platinum precursors. As shown in Fig. 3, in both cases the carbonyl absorption frequencies were lowered about 30 cm⁻¹ and the C–N frequency raised by about 20 cm⁻¹. The observed shifts were comparable to those previously reported for other rhodium and platinum complexes with simple amides [16,29]. It was concluded that the carbonyl oxygen of the amide group -CNH- is the site of

coordination to both rhodium and platinum atoms in the polymer attached species.

Observation of the far-infrared region (Tab. 4) of the model compounds I and II revealed the presence of three bands in the region of 274 to 240 cm⁻¹ characteristic of bridging chlorines, and a weak band at 296 cm⁻¹ consistent with the terminal $\nu(\text{Rh-Cl})$. This indicated that the rhodium complex maintained its dimeric structure upon coordination to the ligands I and II, but that a small amount of a mononuclear complex was also formed. The far-infrared spectra of III with [RhCl(CO)₂]₂ complex showed only one strong band at 282 cm⁻¹, suggesting splitting of the bridged structure by a simple amide.

Only one active metal–chlorine absorption band at 317 cm⁻¹ was found when the platinum precursor PtCl₂(CH₃CN)₂ was complexed with compounds I and III. This is in agreement with the expected range for $\nu(\text{Pt-Cl})$, and suggests *trans* coordination of L₂PtCl₂ [16].

Catalytic studies

The activities of the platinum and rhodium catalysts anchored to the polyamides were studied in hydrosilylation of hexene-1. The results summarized in Table 5 show very high turn-over numbers (T.N.) at 10°C for the polyamide/H₂PtCl₆ systems. A large enhancement in activity for this catalyst was noticed after the first run and this

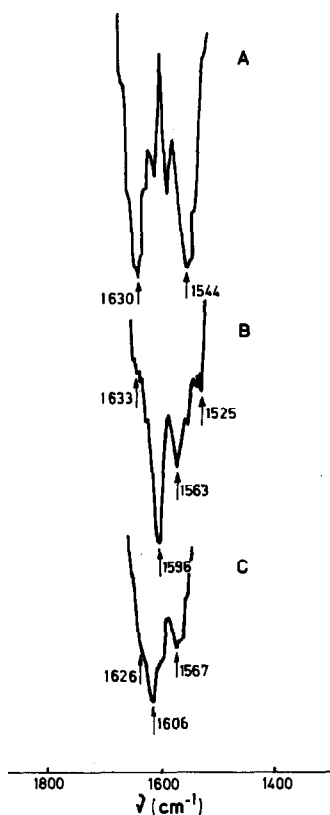


Fig. 3. Changes in the position of the amide bands of *n*-propylbenzamide (model compound III) (A) after complexation with $[\text{RhCl}(\text{CO})_2]_2$ (B) and PtCl_2 (C).

was maintained for the subsequent runs, suggesting that the actual active platinum catalyst was probably generated during the first run. A lower activity however was found for the platinum catalyst derived from $\text{PtCl}_2(\text{CH}_3\text{CN})_2$ as the precursor, T.N. 1.4 s^{-1} .

A high activity was also observed for the rhodium complexes attached to the polyamides, but the activity decreased with increase in the number of methylene groups in the aliphatic linkage between the amide centres. The changes in the activity closely parallel the changes in the degree of crystallinity of the polymer

TABLE 4

ABSORPTION FREQUENCIES IN FAR-INFRARED OF THE METAL COMPLEXES OF THE MODEL COMPOUNDS (Nujol, cm^{-1})

Compound	$\nu(\text{M}-\text{Cl})$	Other bands
I + $[\text{RhCl}(\text{CO})_2]_2$	299w, 285s, 272s, 261s, 249w	312ms, 306ms, 240s, 216s
II + $[\text{RhCl}(\text{CO})_2]_2$	296ms, 286s, 274s, 263s, 240m	338s, 332s, 313w, 217s
III + $[\text{RhCl}(\text{CO})_2]_2$	283vs, 276sh, 263sh	333ms, 325ms, 219m
III + PtCl_2	317ms	285m, 263m, 234m, 221m

TABLE 5

ACTIVITIES OF THE POLYAMIDE (PA)-ATTACHED COMPLEXES IN HYDROSILATION (Conditions, hexene-1/silane/catalyst, molar ratio $1/1/5 \times 10^{-4}$ (Rh) and $1/1/3 \times 10^{-4}$ (Pt)).

PA	T.N. (s^{-1})	
	Rh/PA (20°C)	Pt/PA (10°C)
Pip T	1.50	3.90
2 T	3.67	8.40
2 T-PPh ₂	3.33	4.83 ^a (8.40 ^b)
6 T	1.33 (1.30 ^b ; 1.57 ^c)	6.11
6 T-PPh ₂	1.33	1.66 ^a (6.10 ^b)
10 T	2.67	7.05
10 T-PPh ₂	2.82	

^a After the initial induction period. ^b After 1st use. ^c After 2nd use.

supports; thus, the activity of the rhodium complexes decreased linearly with increase of the crystallinity of the polyamides (Fig. 4). These results suggest that the active sites attached to the polymers having a higher proportion of microdomains of crystallites, where intermolecular hydrogen bonding forces are operative, are less accessible for incoming substrates than those linked to the polymers with a higher proportion of the amorphous phase. This appears to be the first report of such a relationship.

Partial phosphination of the polyamides markedly increased the rate of complexation but, as seen from Table 5, did not greatly affect the activity of the rhodium complexes. It did however, affect the activity of the platinum catalyst, and induction periods were observed for the platinum catalyst bonded to phosphinated polyamides, which is consistent with earlier observations [24]. The inhibition was observed only in the first run, and in the subsequent runs the activity was identical to that of the catalysts on non-phosphinated polyamides.

Repeated use of the rhodium catalyst (Tab. 5) showed a good stability of the polyamide bound complexes. Presumably this is due to the high concentration of the functional groups in the polymer which efficiently prevent the metal leaching even though these are rather weakly coordinating ligands.

Conclusions

The results demonstrated that the polyamides used meet the requirements for organic supports in that they can be readily synthesized in a form suitable for

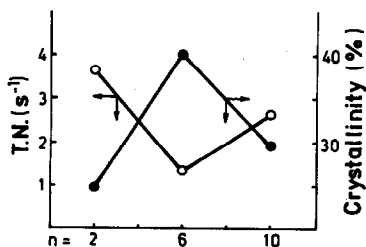


Fig. 4. Influence of diamine chain length on the activity of the polyamide supported complexes, and relative crystallinity of the polyamides.

heterogenization, do not need any further functionalization, and exhibit much higher thermal stability than conventional polystyrene supports. It has been shown that their structures, which are a function of the diamine chain length, greatly influence the catalytic behaviour of the supported complex catalyst. The activity of the catalysts decreases linearly with increasing polymer crystallinity.

Infrared studies on low molecular weight compounds indicated that the carbonyl oxygen of the amide groups provide the coordination site for the rhodium and platinum complexes. The results also indicate that the rhodium carbonyl complexes bonded to polyamides are mainly present as *cis* dicarbonyl chlorides-bridged dimers.

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