Pergamon

0014-3057(94)00100-6

Eur. Polym. J. Vol. 30, No. 11, pp. 1237–1242, 1994

0014-3057/94 \$7.00 + 0.00

POLYMERIZATION OF PHENYLACETYLENE WITH DI-μ-PENTAFLUOROTHIOPHENOLATE BIS (1,5-CYCLOOCTADIENE) RHODIUM (I) AND ITS ANALOGUES

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(Received 9 August 1993; accepted in final form 16 December 1993)

Abstract—Polyphenylacetylene, in good yields and with high molecular weight, has been obtained using three new Rh based catalytic systems, i.e. $[Rh(COD)(SC_6F_5)]_2$, $[Rh(COD)(SC_6H_5)]_2$ and $Rh(SC_6F_5)(P\phi_3)(COD)$ where COD = 1,5-cyclooctadiene. ^{1}H- and ^{13}C-NMR spectra have shown that the polyphenylacetylene obtained is highly stereoregular. The dependence of polyphenylacetylene yield and molecular weight on different experimental factors, namely solvent characteristics and monomer initial concentration, is also discussed in this work. Although the mechanism by which these catalysts polymerize phenylacetylene has not been completely elucidated due to its high complexity, new information was obtained and a catalytic mechanism has been proposed.

INTRODUCTION

The polymerization of phenylacetylene has been studied by many workers in the last few decades. Kern has studied the catalytic and thermal polymerization of phenylacetylene and obtained low molecular weight polymers [1]. Simionescu *et al.* [2] have reported an extensive study of the characterization of the product of the anionic polymerization of phenylacetylene. Tungsten and molybdenum catalyst systems have been studied in detail by Katz and his coworkers [3]. Masuda *et al.* [4] have obtained high molecular weight polymers of various phenylacetylenes using a molybdenum based catalyst and they have proposed a living metathesis polymerization mechanism.

The organometallic compounds of metals of groups 8–10 are also known to catalyze the polymerization of acetylenes. Sen *et al.* [5] have used palladium based catalysts, and Furlani *et al.* have reported the polymerization of phenylacetylene with nickel [6] and platinum [7] catalysts.

Various rhodium compounds have been reported in the literature as effective polymerization catalysts of acetylenes. Kern [1] used tris (triphenylphospine) rhodium chloride for the polymerization of phenylacetylene. Furlani and coworkers [8] have also studied the polymerization of phenylacetylene using catalysts such as $[Rh(COD)Cl]_2$, $[Rh(COD)bipy]PF_6$ and $[Rh(NBD)bipy]PF_6$. Tabata *et al.* [9] have obtained polyphenylacetylene with very high molecular weights using a $[Rh(NBD)Cl]_2$ triethylamine catalytic system and they suggested that a living polymerization is taking place. Thus, rhodium metal compounds appear to be very effective for the polymerization of phenylacetylene. Samples of polyphenylacetylene (PPA) obtained have high molecular weights and a stereoregularity. However, the mechanism has not been totally clarified, although it has been discussed in the above literatures.

Torrens *et al.* [10] of our university have recently found that some thiolato-bridged dinuclear rhodium compounds are good catalysts for the hydroformylation of olefins. The catalytic activities of these compounds for the polymerization of phenylacetylene are reported in this work.

EXPERIMENTAL PROCEDURES

Materials

The following rhodium catalysts were used for the polymerization of phenylacetylene. They were prepared by the methods reported previously:

$[Rh(COD)(SC_6F_5)]_2$ = di-μ-pentafluorothiophenolatobis (1,5-cyclooctadiene) dirhodium(I)[11] **(1)**
$[Rh(COD)(SC_6H_5)]_2$ = di-μ-thiophenolatobis (1,5-cyclooctadiene) dirhodium(I) [12] **(2)**
$Rh(COD)(SC_6F_5)(P\phi_3)$ = tri-phenylphosphine pentafluorothiophenolato (1,5-cyclooctadiene) rhodium(I) [13] **(3)**

where COD = 1,5-cyclooctadiene.

Phenylacetylene supplied by Aldrich Chemical Co. was used after distilling over calcium hydride under a reduced pressure. The solvents employed were purified by distillation before use.

Polymerization

In a typical experiment, the Rh catalyst **1** (0.018 mmol) was dissolved in 20 ml of different distilled solvents namely: tetrahydrofuran (THF), dioxane, N,N dimethylformamide

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(DMF) and chloroform. Distilled phenylacetylene (7 ml) was added and the mixture was stirred at room temperature for several hours. After the reaction was finished, the polymer was precipitated in methanol, filtered and washed with methanol and n-hexane.

Characterization

Average molecular weights were determined by GPC using a Waters Associates ALC/GPC-501, 502 chromatograph at room temperature with THF and with polystyrene standards for calibration. i.r. spectra were obtained using a Nicolet 510P FT-i.r. spectrometer, and NMR spectra of the polymers were obtained using a Gemini 200 (for ^{1}H) and 50 (for ^{13}C). A Varian NMR spectrometer VXR-300s (300 MHz) was used for the study of the polymerization system.

RESULTS AND DISCUSSION

[Rh(COD)(SC$_6$F$_5$)]$_2$ system

The polymerizations carried out in different solvents showed that there is an important solvent dependence of PPA molecular weight. In DMF the molecular weights were low, being only around 7000 and the reaction was very slow. In dioxane the molecular weights were around 10,000 and around 35,000 in THF. This dependence of the molecular weight on the solvent indicates that the activity of the catalyst is reduced under certain conditions. In the case of DMF (a bidentated ligand) it is probable that the solvent is coordinating to some metallic centers reducing the catalytic activity. On the other hand the difference between the molecular weight of the PPA obtained in dioxane and THF may be explained in terms of basicity, THF being more effective in solvating the terminal acetylenic proton than dioxane.

Both ^{13}C- and ^{1}H-NMR spectra (see Tables 1 and 2) of the PPA formed in the different solvents, seem to be in good agreement with those previously reported by Simionescu *et al.* [2] and by Furlani *et al.* [8]. The spectra of PPA obtained in different solvents were all identical and they may correspond to the cis-transoidal structure previously proposed by Furlani *et al.* [8]. i.r. spectra of the PPA obtained in the different solvents did not present differences between them and were the same as those results previously reported by Simionescu *et al.* [2].

Table 1. ^{13}C-NMR spectra data for PPA obtained in different solvents

Reaction solvent	a	b, c	d	e	f
DMF	126.7	127–128	131.9	139.2	142.9
Dioxane	126.9	127–128	132.0	139.3	143.0
THF	126.7	127–128	131.8	139.3	142.9
Chloroform	126.5	127–128	131.7	139.3	142.8

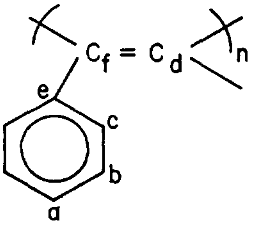
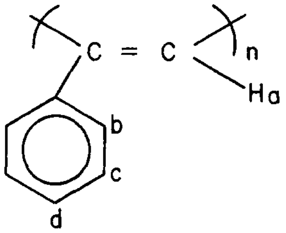


Table 2. ^{1}H-NMR spectra data for PPA obtained in different solvents

Reaction solvent	a	b	c, d
DMF	5.8	6.6	6.9
Dioxane	5.8	6.6	6.9
THF	5.9	6.6	6.9
Chloroform	5.8	6.6	6.9



In order to see the relationship between the molecular weight of PPA and the initial monomer concentration, the polymerization was carried out using catalyst **1** with different initial monomer concentrations. The results (see Fig. 1) show that the molecular weight increased with an increase in the monomer concentration. This is more prominent at low monomer concentrations and the molecular weight became more or less independent with a further increase in the monomer concentration. These results indicate that a termination reaction exists.

Some mechanisms have been proposed [14, 15] to explain the catalytic activity of bimetallic Rh compounds towards different substrates, some of which are shown in Fig. 2. For the polymerization of phenylacetylene with rhodium catalysts, Furlani proposed [8] a mechanism for bimetallic rhodium compounds with bidentated ligands, in which one of the metal–ligand linkages is broken leaving an active site for the polymerization (see Fig. 2, mechanism 2). On the other hand, Tabata suggests a mechanism which

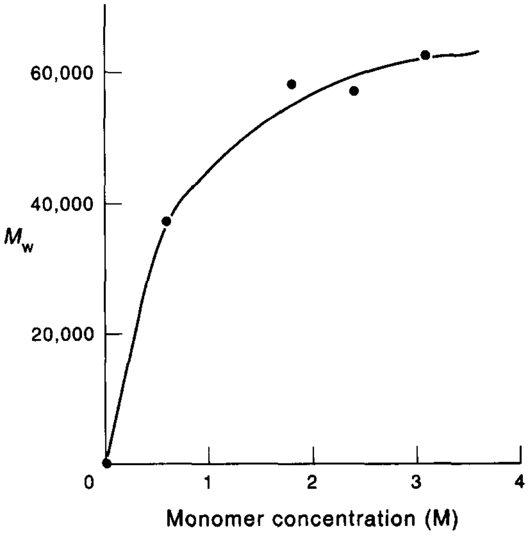


Fig. 1. Relationship between the initial monomer concentration (M) and the average molecular weight (M_w).

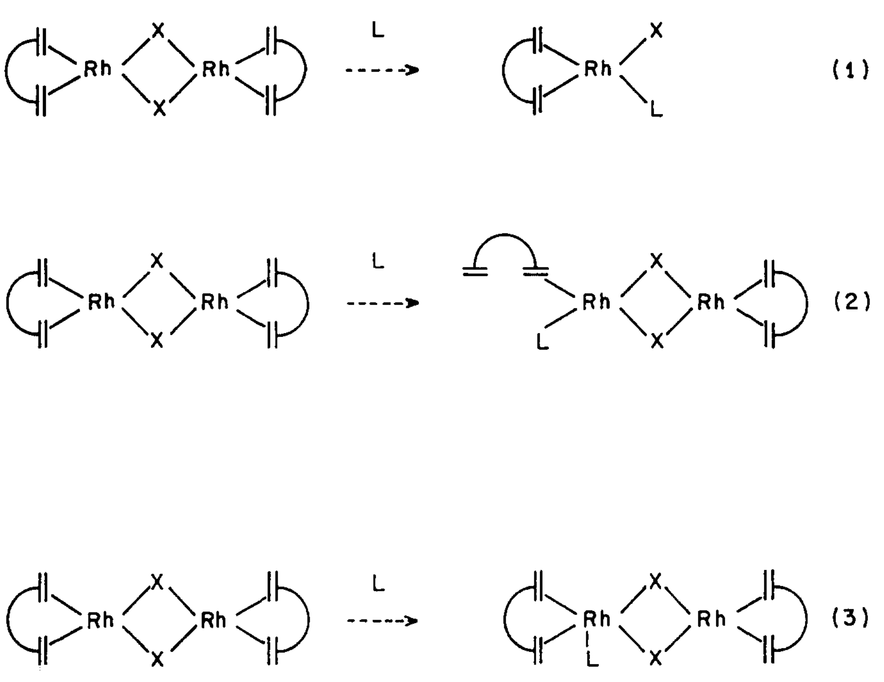


Fig. 2. Some of the catalytic mechanisms proposed in the literature [14, 15] for bimetallic rhodium compounds.

involves a slow dissociation of the bimetallic rhodium catalyst ($[Rh(NBD)Cl]_2$) into a monomeric form, similarly to the mechanism 1 shown in Fig. 2.

In order to elucidate the mechanism of polymerization of phenylacetylene with catalyst **1**, the reaction was studied by NMR to observe differences in the spectra of catalyst **1** during the polymerization. The results may indicate if the mechanism involves a rupture of a bimetallic bridge, a cooperative reaction between the two metallic centers or a substitution of one COD double bond by the acetylene.

For this study, the polymerization was carried out inside the NMR spectrometer at different temperatures. After taking separately the NMR spectra of catalyst **1** and phenylacetylene, equimolar amounts of phenylacetylene and catalyst **1** were mixed at −45°C and several NMR spectra were recorded with time intervals at different temperatures. No reaction was observed below 5°C, but from 10 to 45°C the reaction took place and it was followed by the ^{1}H-NMR spectra. The reaction proceeded without any change in the spectrum of the Rh bimetallic compound. In Fig. 3(A) the spectrum of the Rh compound is shown for comparison with Fig. 3(B) which shows the spectrum of the reaction mixture (catalyst and phenylacetylene) at −5°C. It can be seen that at this temperature there was no polymerization. In Fig. 3(C) the spectrum of the reaction mixture at 20°C after some minutes of reaction is shown. It can be seen that the acetylenic proton signal disappeared and the characteristic PPA proton signals appeared, but the signals of the bimetallic Rh compound did not change during the reaction. This suggests that there is no rupture of the Rh–sulfur–Rh bridges during the polymerization. If this bridge were broken, a spread and displacement of the compound proton signals should be observed.

The above results indicate that two main possible mechanisms stand: (a) as Rh is a 16 electron metal, it can receive another ligand without violating the 18 electron rule. For this reason, the catalytic mechanism can proceed with no changes in the metallic compound. (b) As has been proposed before by Furlani *et al.* [8], the mechanism may involve a rupture of one COD double bond allowing phenylacetylene to bond the metal, grow the chain and finally be removed from the metallic center. At this stage the COD double bond is able to return to its initial position. If this mechanism were correct, changes in the double bond protons signals should be observed. However, this was not observed in the spectra and therefore the latter mechanism appears to be unlikely for the catalyst **1**, although this is not yet conclusive.

Under the same experimental conditions used for the polymerization of phenylacetylene, aliphatic alkynes did not polymerize, and this probably indicates that for the polymerization with the catalyst **1** it is very important that an aromatic system is attached to the triple bond of the monomer. In order to understand the way in which catalysts **1** and **2** act, it is also interesting to observe the fact that $CH_3{-}C{\equiv}C{-}Ph$ did not polymerize at all under the same experimental conditions as those for phenylacetylene, indicating that the acetylene terminal proton is very important.

$[Rh(COD)(SC_6H_5)]_2$ *and* $[Rh(COD)(SC_6F_5)(P\phi_3)]$ *systems*

In order to observe the effect of electronic density on the Rh on its catalytic activity, the polymerization was carried out using a catalyst with the same structure as **1** but with non-fluorinated groups (catalyst **2**). A monometallic compound (catalyst **3**)

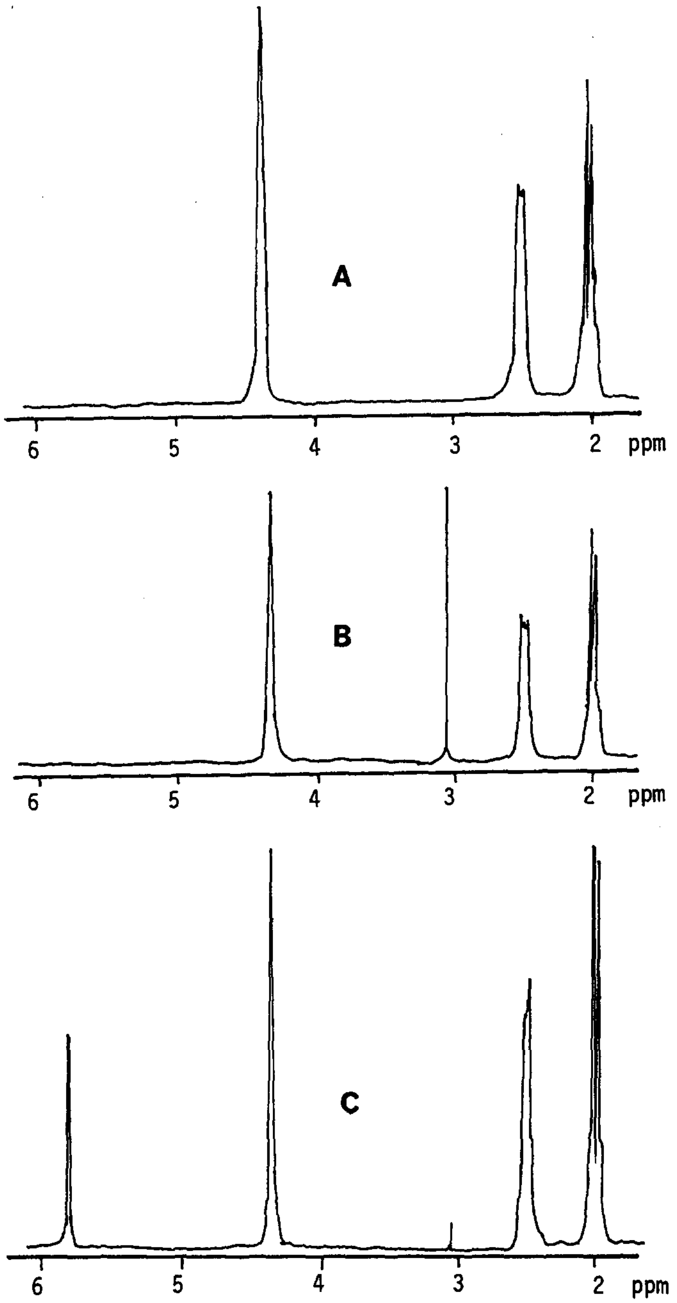


Fig. 3. ^{1}H-NMR spectra of: (A) catalyst **1** at 25°C in $CDCl_3$; (B) reaction mixture (catalyst **1** and phenylacetylene) at 5°C before the polymerization reaction has started and (C) reaction mixture at 25°C after the reaction has finished.

was also employed in order to observe the sterical and electronic effects on the Rh catalytic activity.

In Table 3 polymerization results are shown using catalysts **1**, **2** and **3**. It can be seen that the polymerization is faster with bimetallic catalyst **2** than with **1**. This difference in reactivity is probably due to the lower electronegativity of group —SC_6H_5 of catalyst **2** as is discussed later.

Table 3. PPA yield when **1**, **2** or **3** were used as catalysts. The reaction was performed at room temperature, under stirring and using THF as solvent. The phenylacetylene concentration was 2.8 M and the ratio of catalyst/monomer was 1/2500

Time (hr)	Catalyst (**1**) [yield (%)]	Catalyst (**2**) [yield (%)]	Catalyst (**3**) [yield (%)]
0.17	8.9	21.6	1.4
0.67	22.8	33.1	6.5
0.83	32.5	34.1	11.2
4.58	50.2	62.5	41.4

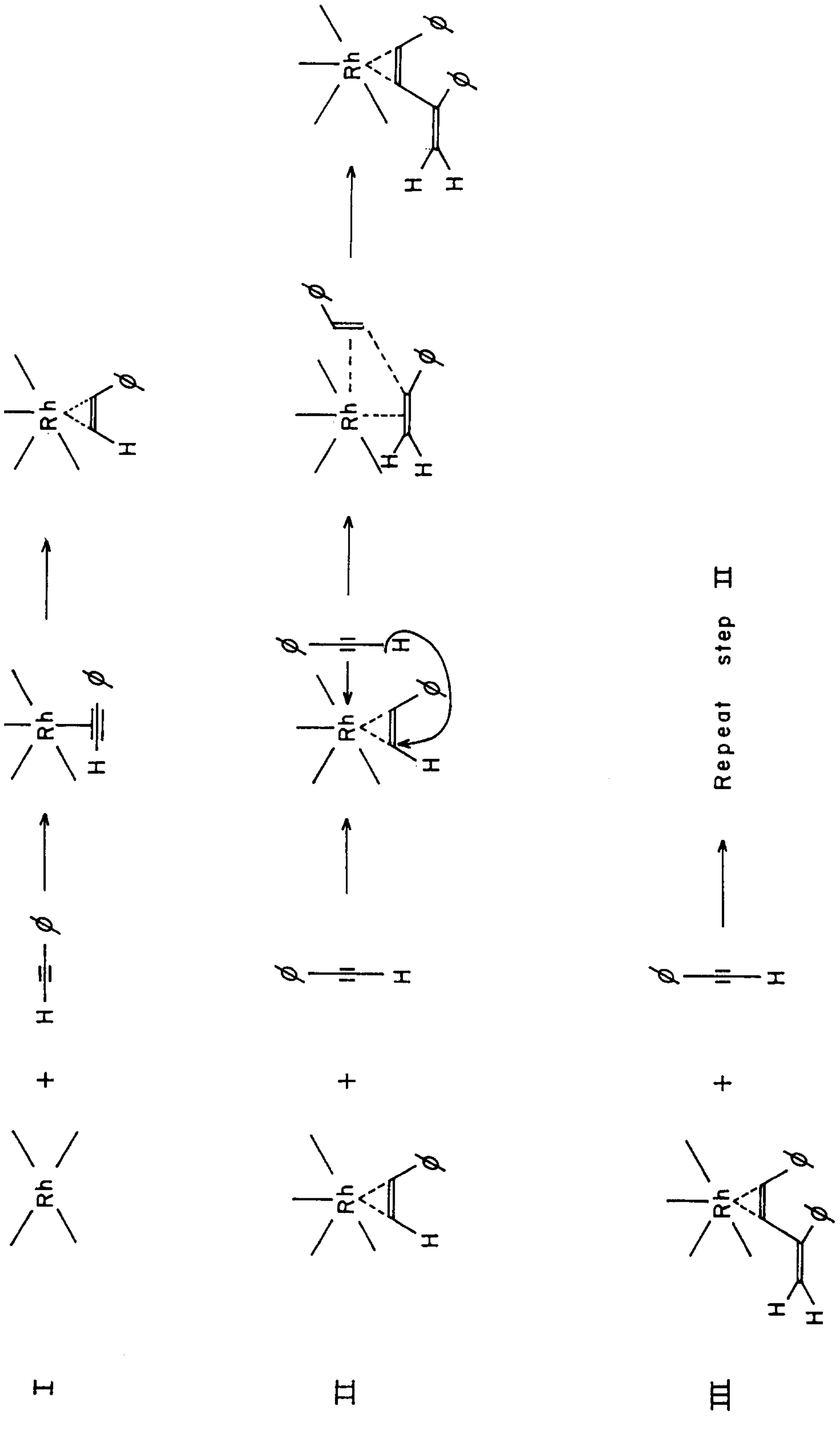


Fig. 4. Catalytic mechanism proposed in this work for the polymerization reaction of phenylacetylene in the presence of catalysts **1** or **2**.

From the above results and previously reported mechanisms [16] for oligomerization of acetylenes it is possible to propose a mechanism by which compounds **1** and **2** catalyze the polymerization of phenylacetylene (see Fig. 4). Considering that the basic solvents such as THF and dioxane favor polymerization in this work, and that very high molecular weight polyphenylacetylene is obtained by a Rh catalyst in the presence of triethylamine [9], the acetylenic terminal proton is of vital importance for the polymerization. The fact that 1-hexyne does not yield a polymer under the same conditions as those for phenylacetylene, also supports the importance of acidity of the acetylenic proton. Methylphenylacetylene which does not have a terminal proton did not polymerize at all. The steric effect of a methyl group may be responsible for this, but it is thought to be of secondary importance. Another important experimental result that may help to elucidate a mechanism, is the NMR study made for catalyst **1**. As mentioned above, in this study the catalyst did not suffer any structural change during the polymerization. Finally, the fact that the polymerization rate is higher for catalyst **2** than for catalyst **1**, indicates that the electronegativity of the thiol ligand is important. Pentafluorothiophenolate (ligand in catalyst **1**) is more electronegative than thiophenolate (ligand in catalyst **2**), i.e. Rh may have a higher electronic density in catalyst **2** than in catalyst **1**, and therefore the electrophilic migration of the proton of the entering acetylene, may become easy for catalyst **2**.

When the monometallic (**3**) was used as catalyst, the reaction was slower than in the other two cases. This probably means that the bimetallic compounds can use two active centers independently to polymerize the monomer or it is simply due to the steric hindrance of the triphenylphosphine group. However, no conclusion can be obtained.

In Table 4, molecular weights at different reaction times are shown for the three catalytic systems. For the catalyst 3 system, PPA molecular weight dramatically decreases with reaction time indicating that this is not a living polymerization. On the other hand, catalysts **1** and **2** seem to act differently: the decrease in molecular weight as time proceeds is very slow.

CONCLUSIONS

From the above results and discussion it can be stated that Rh compounds **1**, **2** and **3** can be used as catalysts to give a stereoregular PPA (possibly cis-transoidal) in good yields and with high molecular weights. Although the mechanism has not been completely elucidated due to its high complexity, new information was obtained and a catalytic mechanism has been proposed for catalysts **1** and **2** (Fig. 4). The cleavage of the thiol bridge between the metallic centers does not appear to take place during the catalyzed polymerization. The fact that basic solvents such as THF, dioxane and triethylamine favor the polymerization suggests that the behavior of the acetylene proton may be very important in the polymerization. It has also been observed that good electron donor ligands, increase the reactivity of the Rh catalysts. The fact that aliphatic alkynes do not polymerize under the experimental conditions of this work, gives evidence that the acidity of the proton of terminal acetylenes is important and probably that some of the reaction intermediates require some stabilization by a conjugated system.

Table 4. Average molecular weight (MW) at different times for systems with catalysts **1**, **2** and **3**. The reaction was performed at room temperature, under stirring and using THF as solvent. The phenylacetylene concentration was 2.8 M and the ratio of catalyst/monomer was 1/2500

	Catalyst **1**		Catalyst **2**		Catalyst **3**	
Time (hr)	MW	MW/min	MW	MW/min	MW	MW/min
0.17	38,000	2.5	71,000	2.7	—	—
0.67	37,000	3.5	70,000	3.5	90,000	2.6
0.83	34,000	3.5	80,000	2.4	86,000	2.7
4.58	35,000	3.1	69,000	2.6	65,500	2.9
8.40	—	—	—	—	21,500	4.4

Acknowledgements—The authors wish to thank Dr H. Torrens' group for the donation of the three catalysts used in this work. We would specially like to thank Jorge Tiburcio and Dr Erika Martin for their valuable suggestions to this work. We also want to thank DGAPA-UNAM for the financial support under contract No. IN100492 and to J. M. García and R. Suárez for the molecular weight measurements.

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