

# Polymerization of phenylacetylene and of *p*-tolylacetylene catalyzed by $\beta$ -dioxygenato rhodium(I) complexes in homogeneous and heterogeneous phase

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## Abstract

The catalytic polymerization of phenylacetylene and *p*-tolylacetylene under homogeneous and heterogeneous conditions is described. The catalysts used are either (cod)Rh(AAEMA) [cod: 1,5-cyclooctadiene (cod), AAEMA<sup>-</sup>: deprotonated form of 2-(acetoacetoxy)ethylmethacrylate] or the supported metal complex obtained by thermal copolymerization of (cod)Rh(AAEMA) with suitable comonomers and cross-linkers. Complexes of general formula (diene)Rh(acac) [diene: 2,5-norbornadiene (nbd) or 1,5-cyclooctadiene (cod)] have also been used for comparison. High yields in poly(arylacetylene) are achieved in the homogeneous phase for both substrates using THF as solvent at room temperature even in the absence of any co-catalyst. The use of the supported rhodium(I) catalyst facilitates the polymerization of arylacetylenes yielding, in the case of poly(phenylacetylene) (PPA), a polymer having high stereoregularity and higher molecular weight respect to that obtained in homogeneous phase. A new correlation between IR data and the *cis*-percentage of PPA is proposed and discussed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Supported metal complexes; Rhodium; Polymerization; Poly(phenylacetylene); Stereoregularity

## 1. Introduction

The transition metal catalyzed polymerization of arylacetylenes is a highly interesting reaction because of the potentialities of the obtained materials, especially those resulting from stereospecific catalysis. Poly(phenylacetylene) (PPA) is an intriguing polymer from the synthetic point of view and because of its various physical properties [1]. Photoconductivity [2], photoluminescence [3], non-linear optical properties

[4,5] and membrane properties [6–8] of these material have been investigated. PPA doped with iodine has also been recently studied with an eye to potential technological applications [9].

Widely different methodologies have been used to obtain PPA, including cationic [10,11] and radical [12–14] polymerization. Ziegler–Natta systems [15], as well as WCl<sub>6</sub>, MoCl<sub>5</sub> [16–18] and Co(NO<sub>2</sub>)<sub>2</sub>/NaBH<sub>4</sub> [19] were reported as active catalysts for the synthesis of PPA and, recently, polycondensation of phenylacetaldehyde was shown to be an efficient methodology to yield *trans*-cisoidal PPA [20]. Several studies on the topic stemmed from

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Furlani et al.'s pioneering work that proved how the polymerization of phenylacetylene could be catalyzed by rhodium(I) complexes [21,22]. Precursor complexes of formula  $\text{Rh}(\text{C}\equiv\text{CPh})(\text{nbid})[\text{P}(\text{Ph})_3]_2$  [23],  $[\text{Rh}(\text{diene})\text{Cl}]_2$  and  $\text{Rh}(\text{diene})(\text{tosylate})(\text{H}_2\text{O})$  [24,25], as well as in situ catalytic systems containing  $[\text{RhCl}(\text{nbid})]_2/\text{Ph}_2\text{C}=\text{C}(\text{Ph})\text{Li}/\text{PPh}_3$  [26], or  $[\text{Rh}(\text{cod})\text{Cl}]_2/[2,6-(\text{PPh}_2\text{CH}_2)_2\text{C}_6\text{H}_4]$  [27] proved to be efficient catalysts for the polymerization of phenylacetylene. The effect of the co-catalyst has also been thoroughly studied [28] and recently compressed carbon dioxide has been used as a novel solvent for this reaction [29].

In the framework of heterogeneous catalysis, metal complexes supported on an organic polymer cover an important role, because of the ease of functionalization and chemical inertness of the organic matrices [30]. Moreover, their physical properties can be simply controlled by suitable variations of the cross-linking degree of the support. Transition metal complexes supported onto organic polymers are often referred to as hybrid materials because of their intermediate properties between homogeneous and heterogeneous catalysts.

To the best of our knowledge the only heterogeneous catalytic system reported for phenylacetylene polymerization is that obtained by supporting  $\text{MoCl}_5$  on polyethylene grafted with acrylonitrile, allylic alcohol or propargyl alcohol [31].

No hybrid system has to date specifically been devised for the rhodium-catalyzed polymerization of phenylacetylene, although in principle the constrained geometry of the catalytic center embedded in an insoluble matrix may have a beneficial effect on both catalyst activity and selectivity. For instance, supported Ziegler–Natta catalysts [32,33] resulted much more active than their non-supported analogues in the ethylene polymerization [34] and in the copolymerization of ethylene and 1-hexene [35,36].

We became recently interested in the synthesis of new hybrid catalysts obtained by copolymerization of VIII–X group metal complexes with the anion of 2-(acetoacetoxy)ethylmethacrylate ( $\text{AAEMA}^-$ ) [37–47]. The polymerizable rhodium(I) complex  $(\text{cod})\text{Rh}(\text{AAEMA})$  [48] has been synthesized and copolymerized with *N,N*-dimethylacrylamide and *N,N'*-methylenebisacrylamide to yield an insoluble resin (referred to as Rh-pol) that proved to be an

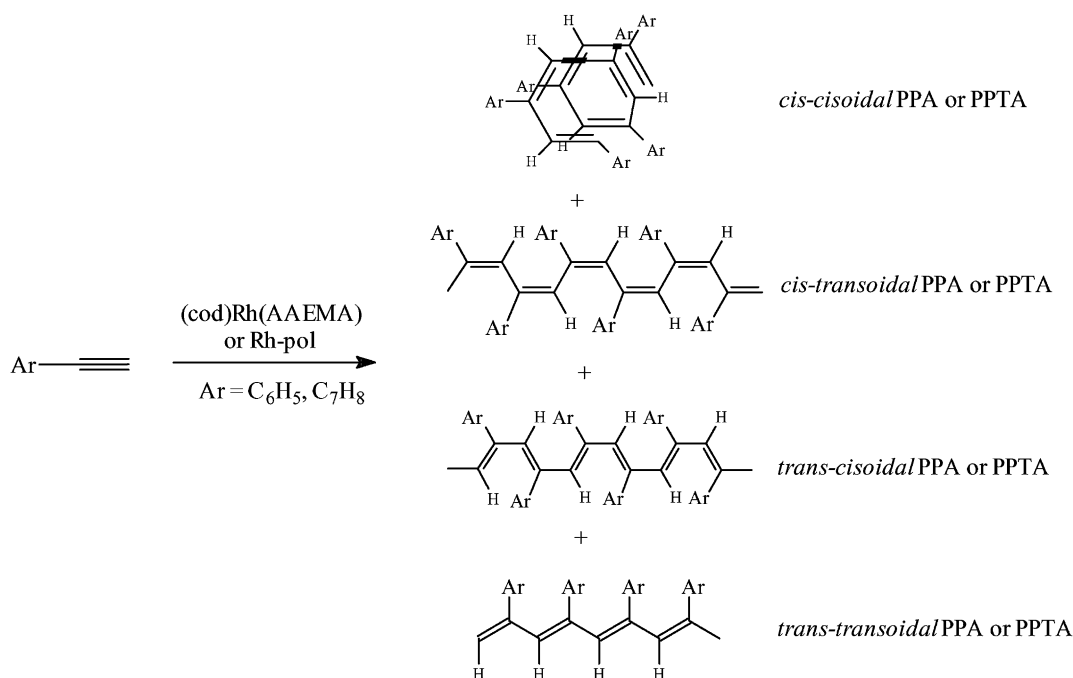


Fig. 1. Scope of the work.

active catalyst for the hydrogenation of several organic substrates under mild conditions [49].

Here we describe the polymerization of phenylacetylene and of *p*-tolylacetylene catalyzed by (cod)Rh(AAEMA) or by its heterogeneous analogue Rh-pol (Fig. 1).

## 2. Experimental

All manipulations were performed under a dry nitrogen atmosphere. Phenylacetylene and *p*-tolylacetylene were purchased from Aldrich and used as received.

(cod)Rh(AAEMA) and its copolymer Rh-pol were prepared as described elsewhere [49]. UV–VIS spectra were recorded on a Uvikon 942 spectrophotometer. IR spectra were recorded on a Perkin Elmer 1710 FT instrument. NMR spectra were recorded on a Bruker AM-500 spectrometer using CDCl<sub>3</sub> as solvent. GPC analyses were carried out on a HP 1050 instrument equipped with a PL-gel 5 μm mixed-D 300 mm × 7.5 mm column. THF solutions for GPC analysis were eluted at 25 °C at a flow rate of 1 ml/min and analyzed using a multiple wave detector set at 254 nm. Molecular weights and molecular weight distributions are reported relative to polystyrene standards. Polymer yields were determined by weighing.

### 2.1. Catalytic runs

In a typical procedure, a Schlenk tube containing (cod)Rh(AAEMA) (13 mg, 0.0306 mmol) or Rh-pol

(33 mg, Rh: 6.02 wt.%) in 5 ml of the relevant solvent was added of phenylacetylene (627.5 mg, 6.144 mmol) or *p*-tolylacetylene (713.7 mg, 6.144 mmol) and the solution kept under vigorous stirring. After due reaction time (1–6 h) the stirring was stopped and the catalyst deactivated with 100 ml glacial acetic acid. In the case of homogeneous catalyses, the solvent was evaporated under high vacuum. The polymer, precipitated as film or flakes, was washed with 4 × 15 ml methanol, dried under vacuum, then dissolved in CHCl<sub>3</sub> and precipitated with methanol as a bright yellow (PPA) or orange-red (PPTA) powder, washed again with methanol, dried under high vacuum and weighed to assess the yield.

In the case of heterogeneous catalyses, after evaporation of the solvent and treatment with CHCl<sub>3</sub> the solution containing the poly(arylacetylene)s and the unreacted substrate was separated from the heterogeneous catalyst by filtration. After drying in vacuo, the procedure described for homogeneous catalysis was followed.

## 3. Results and discussion

The results obtained using (cod)Rh(AAEMA) as homogeneous catalyst for the polymerization of phenylacetylene are collected in Table 1 and show that 82% yield in PPA was achieved within 1 h when THF was used as solvent (entry 1). The corresponding reaction carried out in benzene gave 96% yield (entry 2). The molecular weight and polydispersity index

Table 1  
Homogeneous catalytic polymerization of phenylacetylene<sup>a</sup>

Entry	Catalyst	Solvent	Isolated yield (%)	$M_w$	$M_w/M_n$	Cis-% <sup>b</sup>
1	(cod)Rh(AAEMA)	THF	82	11200	3.0	77
2	(cod)Rh(AAEMA)	C <sub>6</sub> H <sub>6</sub>	96	16200	4.4	74
3 <sup>c</sup>	(cod)Rh(AAEMA)	DCE	84	10300	2.3	70
4	(nbd)Rh(acac)	THF <sup>d</sup>	92	110000	2.2	84
5 <sup>e</sup>	(nbd)Rh(acac)	THF <sup>d</sup>	88	265000	1.9	79
6	(nbd)Rh(acac)	THF	97	173000	1.8	84
7	(cod)Rh(acac)	THF	87	19700	2.1	86

<sup>a</sup> Conditions:  $t = 22$  °C; substrate/catalyst = 200 mol/mol; solvent, 5 ml; reaction time, 1 h.

<sup>b</sup> From the correlation described in Fig. 3.

<sup>c</sup> Reaction time 4 h.

<sup>d</sup> In 13 ml THF (this solvent volume was chosen as the minimum amount of solvent to reproduce the results obtained in THF by other authors in compressed CO<sub>2</sub> [29]).

<sup>e</sup> Triethylamine/co-catalyst = 10:1.

were slightly higher in benzene ( $M_w = 16,200$  Da,  $M_w/M_n = 4.4$  in  $C_6H_6$  respect to  $M_w = 11,200$  Da,  $M_w/M_n = 3$  in THF). In 1,2-dichloroethane (DCE) the reaction was slower (4 h to reach 84% yield of PPA) although the polymer weight and polydispersity index (entry 3) were comparable with those obtained in THF.

In order to evaluate the need for a co-catalyst for the polymerization of phenylacetylene [29], we have carried out comparative experiments using (nbd)Rh(acac) or (cod)Rh(acac) in the presence or in the absence of triethylamine: the result was a pronounced catalytic activity of (nbd)Rh(acac) in THF also in the absence of triethylamine as co-catalyst. After 1 h reaction, (nbd)Rh(acac) yielded 92% of PPA in the absence of triethylamine and 88% in the presence of a  $NEt_3/Rh$  10/1 ratio (entries 4 and 5). The presence of triethylamine seemed to affect only the molecular weight of the obtained polymer.

The effect of the less strongly coordinating 1,5-cyclooctadiene [25] is held responsible for the slightly lower activity and for the much lowered molecular weight obtained in the (cod)Rh(acac) catalyzed reaction, respect to those catalyzed by (nbd)Rh(acac). In the first case 87% yield and a  $M_w$  of 19,700 Da were achieved, whereas in the latter case 97% yield and a  $M_w$  of 173,000 Da were obtained (entries 7 and 6). Polydispersity indexes in the range 1.8–2.2 were obtained in all cases when (diene)Rh(acac) complexes were used.

The role of the base as co-catalyst in the phenylacetylene polymerization has been a very recent object of controversy: it has been reported that using [(nbd)RhCl]<sub>2</sub> in triethylamine as solvent leads to enhanced catalyst activity and selectivity [50]. The role of the base has been ascribed to the formation of an active monomeric species of formula (nbd)RhCl( $NEt_3$ ). Other studies [10,11] reported high stereoregularity also in the polymers obtained in THF without triethylamine as co-catalyst. In the mechanism proposed by Escudero et al. the role of the base was to favour the proton-transfer step that is allegedly the key of chain growth [51].

Our observations in the homogeneous phase (Table 1, entries 4 and 5) show that, apart from not playing a role in the activation of the (diene)Rh(acac) complexes towards polymerization of phenylacetylene, the effect of triethylamine might only be limited

to favour proton transfer, with the advantage of a quicker chain growth step resulting in higher molecular weights in the case of the co-catalyzed reaction.

As to stereoregularity, intended as the percentage of segments of analogous configuration in the polymer chain, this is a crucial point in the study of PPA, and notwithstanding the many studies devoted to it, is still to be considered open. Several methods have been proposed to determine stereoregularity in PPA: one of the most accepted is based on <sup>1</sup>H NMR analysis through the equation:  $cis\text{-}\% = [A_{5.82}/(A_{total}/6)] \times 100$  ( $A_{5.82}$  is the area of the vinyl proton in the *cis*-isomer and  $A_{total}$  the total area of the polymer spectrum). An alternative method relies on IR, and uses the interpolation of the intensity ratio of the signals at 760 and 740  $cm^{-1}$  ( $I_{760}/I_{740}$ ) with the *cis*-percentage in the polymer determined with <sup>1</sup>H NMR [52]. Other methods rely on the ratio of the bands at 910 and 870  $cm^{-1}$  [53]. To this purpose, two general considerations must be drawn: (i) it has recently been ascertained that solvent treatment of PPA results in a polymer rearrangement or polymer degradation [54]; (ii) the solubility of PPA is also dependent upon the polymer conformation and molecular weight, *cis*-*cisoidal* PPA exhibiting a lower solubility with respect to other conformations [55]. Solution NMR determination may, therefore, return a somehow distorted estimate of PPA *cis*-content, that should only be taken as a qualitative measure of stereoregularity.

On the other hand, the use of the intensity ratio of the signals at 760 and 740  $cm^{-1}$  ( $I_{760}/I_{740}$ ), that should overcome the problem of the polymer solubility, is again correlated with an NMR determination. While further insight into the PPA full stereochemical assignment is clearly needed, in the framework of our catalytic tests, we have correlated IR features of mixtures of highly stereoregular PPA and annealed (*trans*) PPA with the *cis*-percentage in the polymer.

The following correlation was obtained using a PPA sample obtained as described in [25] that displayed a  $M_w$  of 66,000 Da, a  $M_w/M_n$  of 1.55 and a 100% *cis*-content (determined by <sup>1</sup>H NMR, reported in Fig. 2, top trace, time: 0 h). This polymer showed the expected degradation in solution, its stereoregularity dropping from 100% to 88% after 24 h, to 73% after 48 h, to 57% after 96 h (Fig. 2).

An aliquot of this sample was treated with  $CCl_4$  for 48 h under reflux as described in [22].

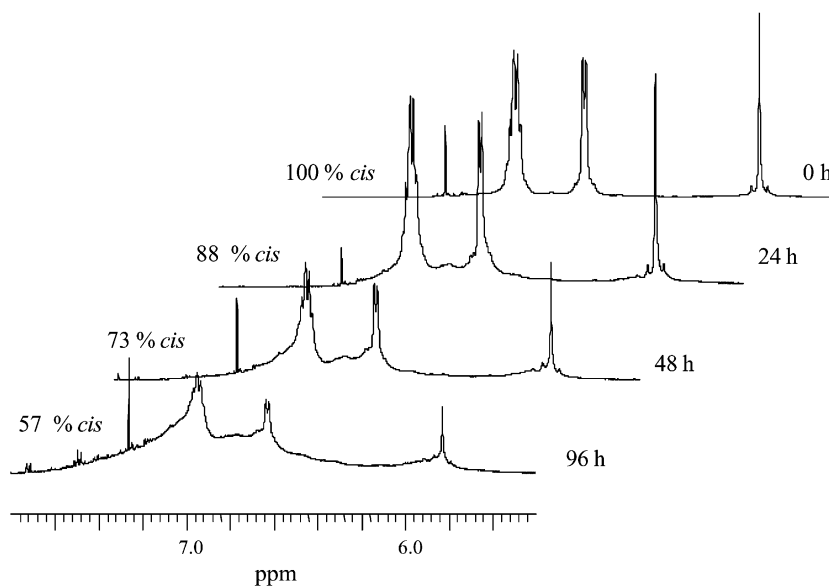


Fig. 2.  $^1\text{H}$  NMR spectra showing PPA degradation in  $\text{CDCl}_3$ .

The obtained polymer (the annealing causes a change in configuration from 100% *cis* to 100% *trans*) displayed only a very broad signal at 7.1 ppm in the  $^1\text{H}$  NMR spectrum that was not subject to evolution with time. In the IR spectrum, no band at  $740\text{ cm}^{-1}$  (the typical absorption of *cis*-structure) and a band at  $1265\text{ cm}^{-1}$  (typical for *trans*-structure) was observable. A  $M_w$  of 10,100 and a  $M_w/M_n$  of 1.62 was determined. Suitable amounts of the two polymers have been thoroughly mixed and analyzed by IR. For each mixture, six replicates were measured. In order to obtain the desired absorption intensities, the considered baseline was that between the first “valley” of the  $760\text{ cm}^{-1}$  peak and the second “valley” of the  $740\text{ cm}^{-1}$  peak. The ratio  $I_{760}/I_{740}$  has been correlated with the mass percentage of *cis*-cisoidal PPA. Data reported in Fig. 3 point out that our data are best fitted with a weighted cubic function in which the weight of each experimental point is proportional to  $1/\sigma^2$ .

*Cis*-percentages lower than 50% were not analyzable due to the deep superimposition of the  $740$  and  $760\text{ cm}^{-1}$  bands. As expected, *cis*-stereoregularity as determined by Percec’s correlation, converges to that determined with ours (Fig. 3) for low values of  $I_{760}/I_{740}$ .

With this tool we were able to evaluate more precisely the stereoregularities in our polymer samples, only by an IR measurement, thus, overcoming the polymer solubility problem. A rough analysis of the proposed correlation points out that the higher the ratio  $I_{760}/I_{740}$  is, the more our evaluation diverges from that reported in the literature. Moreover, over a wide range of *cis*-percentage, the aforementioned ratio is not expected to be linear, being both the bands at  $760$  and  $740\text{ cm}^{-1}$  relative to different vibrational modes of the 100% *cis*-polymer, and being only the band at  $760\text{ cm}^{-1}$  present in the 100% *trans*-structure. (cod)Rh(AAEMA) yielded 77% *cis*-PPA in THF, 74% *cis*-PPA in benzene and 70% *cis*-PPA in DCE (Table 1, entries 1–3). In the case of non-co-catalyzed and co-catalyzed reactions with (nbd)Rh(acac) the IR evaluation seems to point out comparable results (84 and 79% *cis*, respectively, Table 1, entries 4 and 5). Moreover *cis*-percentage seems to be independent of catalyst concentration (solvent volume in entry 4 is 13 ml and in entry 6 is 5 ml and the *cis*-percentage is 84% in both cases) and of olefinic ligand on rhodium (84 and 86% *cis* with (nbd)Rh(acac) or (cod)Rh(acac), respectively; Table 1, entries 6 and 7).

The  $\beta$ -ketoesterato complex (cod)Rh(AAEMA) also proved to be active towards the polymerization

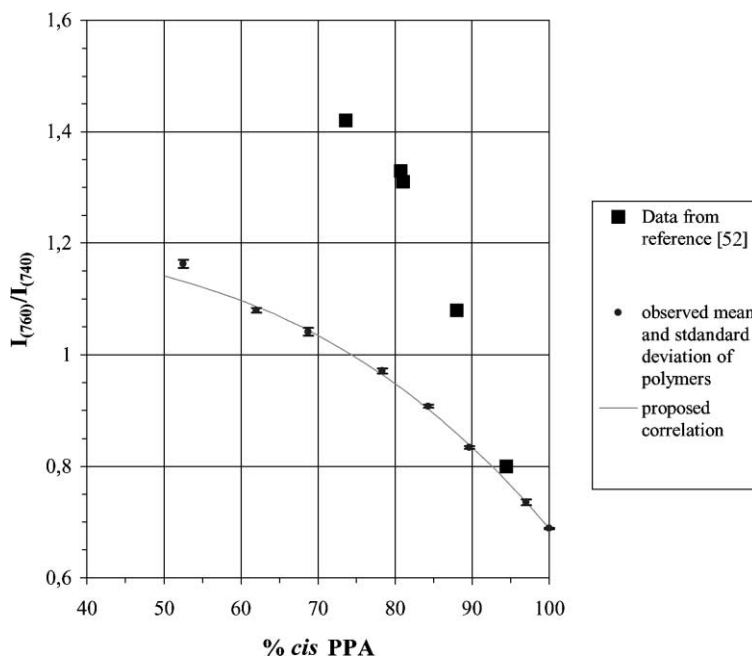


Fig. 3. Correlation between *cis*-percentage and  $I_{760}/I_{740}$  ratio. Best fit:  $I_{760}/I_{740} = a + b(\text{cis-}\%) + c(\text{cis-}\%)^2 + d(\text{cis-}\%)^3$ ;  $a = 1.2150$ ,  $b = -0.001155$ ,  $c = 0.000028077$ ,  $d = -6.92 \times 10^{-7}$ .

of *p*-tolylacetylene. Reactions carried out in THF and DCE gave comparable results in terms of yield and polydispersity (Table 2, entries 1 and 2). In the first case a higher molecular weight was obtained. In benzene the reaction yielded a polymer having lower molecular weight and high polydispersity (Table 2, entry 3). Notably, the catalyst activity in the case of *p*-tolylacetylene was slightly lower, in accordance with the minor acidity of its acetylenic proton [51]. We were unable to deter-

mine *cis*-content in poly(*p*-tolylacetylene) (PPTA) due to its scarce solubility or broad molecular weight distribution.

### 3.1. Polymerization of phenylacetylene and *p*-tolylacetylene in heterogeneous phase

Starting from the preliminary results obtained with the rhodium(I)  $\beta$ -ketoesterate (cod)Rh(AAEMA) in homogeneous phase, we investigated the activity of its heterogeneous analogue Rh-pol as catalyst for phenylacetylene and *p*-tolylacetylene polymerization. The main results obtained in hybrid catalysis are collected in Table 3.

Phenylacetylene was almost completely converted to PPA by Rh-pol in THF (98% after 1 h reaction, entry 1). In DCE the yield was lower (83% after 1 h reaction) but the PPA was found to be more stereoregular (98% *cis*, entry 2). In benzene the reaction proceeded sluggishly, yielding only 23% conversion after 1 h (entry 3). The supported rhodium complex was also moderately active in bulk (69% yield after 1 h reaction, entry 4).

Table 2

Homogeneous catalytic polymerization of *p*-tolylacetylene<sup>a</sup>

Entry	Solvent	Time (h)	Isolated yield (%)	$M_w^b$	$M_w/M_n^b$
1	THF	3	75	11500	1.9
2	DCE	3	76	7200	1.5
3	C <sub>6</sub> H <sub>6</sub>	5	82	3400	6.3

<sup>a</sup> Conditions:  $t = 22^\circ\text{C}$ ; substrate/(cod)Rh(AAEMA) = 200 mol/mol; solvent, 5 ml.

<sup>b</sup> Molecular weights and molecular polydispersity indices are referred to the CHCl<sub>3</sub>-soluble fraction.

Table 3  
Heterogeneous catalytic polymerization of phenylacetylene<sup>a</sup>

Entry	Solvent	Isolated yield (%)	$M_w$	$M_w/M_n$	<i>Cis</i> -% <sup>b</sup>
1	THF	98	39000	2.5	82
2	DCE	83	61000	2.1	98
3	C <sub>6</sub> H <sub>6</sub>	23	43000	2.1	100
4	Bulk	69	47000	2.4	93

<sup>a</sup> Conditions: catalyst, Rh-pol;  $t = 22^\circ\text{C}$ ; substrate/catalyst = 200 mol/mol; solvent, 5 ml; reaction time, 1 h.

<sup>b</sup> From correlation described in Fig. 3.

Table 4  
Heterogeneous catalytic polymerization of *p*-tolylacetylene<sup>a</sup>

Entry	Solvent	Isolated yield (%)	$M_w$	$M_w/M_n$
1	THF	85	2470	3.0
2	DCE	29	4780	4.8
3	C <sub>6</sub> H <sub>6</sub>	44	5820	7.1

<sup>a</sup> Conditions: catalyst, Rh-pol;  $t = 22^\circ\text{C}$ ; substrate/catalyst = 200 mol/mol; solvent, 5 ml; reaction time, 1 h.

Comparing these results with those obtained in the homogeneous phase with the complex (cod)Rh(AAEMA), higher stereoregularities and molecular weights of the polymers in the heterogeneous catalyzed reactions were observed.

Rh-pol was also active in the polymerization of *p*-tolylacetylene (Table 4). Analogously to what observed in the homogeneous phase, a drop in catalytic activity was observed in C<sub>6</sub>H<sub>6</sub> or DCE. While for THF and benzene it was necessary to isolate a chloroform soluble fraction, in DCE the polymer obtained was soluble.

In THF the best features of the polymerization were again obtained in terms of yield and polydispersity (85% yield in PPTA after 1 h with  $M_w/M_n = 3$ ; Table 4, entry 1). In DCE and benzene the reaction yielded a polymer with very broad molecular weight distributions (entries 2 and 3).

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