

# Rhodium(I) catalyzed polymerization of phenylacetylene in ionic liquids

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## Abstract

The ionic liquids *n*-butylpyridinium tetrafluoroborate [bupy]BF<sub>4</sub> and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF<sub>4</sub> have been used as solvents for the Rh(I) catalyzed phenylacetylene polymerization in the presence of triethylamine as co-catalyst, obtaining high yields of poly(phenylacetylene). The complexes used are (diene)Rh(acac) and [(diene)RhCl]<sub>2</sub> [diene: 1,5-cyclooctadiene or norbornadiene]. The (nbd)Rh(acac) complex in both ionic liquids can be recycled without significant loss in activity. Molecular weights in the range between 55,000 and 200,000 Da have been obtained by GPC. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The transition metal catalyzed polymerization of phenylacetylene has been the object of different studies because the obtained material, poly(phenylacetylene) (in the following PPA) is an interesting polymer [1] from many viewpoints among which photoconductivity [2], photoluminescence [3], non-linear optical properties [4] and membrane properties [5]. Iodine doped PPA has also been studied with an eye to potential technological applications [6]. Several PPAs embodying chiral functionalities have been synthesized [7] and tested for chirality assignment of amines by circular dichroism [8]. A recent study dealt

with carbon nanotubes wrapped in PPA that exhibit a strong photostabilization effect and optical limiting properties [9].

Although PPA can be obtained by cationic [10] and radical [11] polymerization as well as by Ziegler–Natta systems [12], or typical metathesis catalysts like WCl<sub>6</sub> or MoCl<sub>5</sub> [13], the most widely studied catalysts for its obtainment are suitable rhodium(I) complexes [14]. Among the most recently used catalysts are precursor complexes of formula Rh(C≡CPh)(nbd)(PPh<sub>3</sub>)<sub>2</sub> [15], [Rh(diene)Cl]<sub>2</sub> and Rh(diene)(tosylate)(H<sub>2</sub>O) [16], in situ catalytic systems [RhCl(nbd)]<sub>2</sub>/Ph<sub>2</sub>C=C(Ph)Li/PPh<sub>3</sub> [17], or [Rh(cod)Cl]<sub>2</sub>/[2,6-(PPh<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>] [18]. The effect of the co-catalyst has also been thoroughly studied [19]. It has recently been shown that the polymerization could be carried out in liquid or supercritical CO<sub>2</sub> [20] and in a biphasic system water/methylene chloride [16a].

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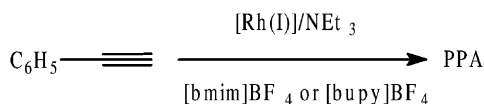


Fig. 1. Scope of the work.

We recently became interested in the use of ionic liquids (in the following ILs) as novel solvents for this reaction. ILs are now ubiquitously used in a wide range of organic reactions and, given the increasing work and interest on them, several reviews have appeared on the topic [21]. Very recent research on low-melting non-chloroaluminate ILs accounts their use as solvents for allylation reactions with tetraallylstannane [22], for the palladium catalyzed Suzuki coupling [23] and for the Sc(III) triflate catalyzed Friedel–Crafts alkylation [24]. Among the investigated reactions are obviously also polymerization reactions, because oxygen and water stable ionic liquids that are tolerant to several functional groups [25] permit a wide choice of monomers. Recent examples are the Cu(I) mediated living polymerization of methylmethacrylate in [bmim]PF<sub>6</sub> [26], or the benzene polymerization to yield poly(*p*-phenylene) obtained either by CuCl<sub>2</sub> promoted oxidative dehydropolycondensation [27] or by electrochemical polymerization [28].

As a following up of our researches, focussed on transition metal catalyzed C–C bond formation [29,30], here we describe the use of ionic liquids as novel solvents for the polymerization of phenylacetylene (Fig. 1).

## 2. Results and discussion

$\beta$ -Dioxygenato complexes of rhodium(I) bearing a suitable diene as co-ligand have successfully been used as catalyst precursors for the phenylacetylene polymerization [20,30], therefore, we have decided to test (nbd)Rh(acac) and (cod)Rh(acac) as first. Our results carried out in THF (in which a remarkable catalytic activity was observed with both of the aforementioned complexes also in the absence of triethylamine [30]) prompted us to perform preliminary tests avoiding the use of a basic co-catalyst, but several

reactions carried out with the (diene)Rh(acac) complexes in the absence of NEt<sub>3</sub>, in either [bmim]BF<sub>4</sub> or [bupy]BF<sub>4</sub> resulted in no reaction. Moreover, no activity of both ionic liquids could be observed in the absence of Rh(I), even in the presence of triethylamine in a 1:20 ratio with respect to the substrate.

Complex (nbd)Rh(acac) in [bmim]BF<sub>4</sub> and in the presence of triethylamine [NEt<sub>3</sub>/Rh(I) = 10 mol/mol] very efficiently catalyzed phenylacetylene polymerization. In order to evaluate the catalytic activity, the polymer formed was isolated after a known reaction time that was fixed to 5 min. The optimal molal catalyst concentration range was determined as  $7 \times 10^{-3} \text{ mol/kg} < m < 9 \times 10^{-3} \text{ mol/kg}$ ; concentrations below  $7 \times 10^{-3} \text{ mol/kg}$  caused an undesired prolonging of the reaction time, while concentrations higher than  $9 \times 10^{-3} \text{ mol/kg}$  caused an uncontrollable polymer formation because of the higher amount of substrate required to satisfy the constant phenylacetylene/Rh(I) ratio that was fixed at 200 mol/mol. To avoid a diffusion control of the reaction, the polymerizations were carried out at a molal concentration of  $8 \times 10^{-3} \text{ mol/kg}$ . Polymer isolation could be carried out by extraction with a suitable solvent for PPA which was at the same time immiscible with the ionic liquid. Several solubility tests revealed that toluene had the best features of PPA solubility and IL immiscibility for the earlier cited extraction. Other very good solvents for PPA such as methylene chloride or chloroform could not be used because they were completely miscible with the ILs, or because, as in the case of THF, they exhibited a partial miscibility in both ILs tested, thus preventing a clean separation of PPA from the ionic liquid used. The extraction procedure brings a disadvantage due to a minor fraction of PPA which is insoluble in toluene and remains suspended in the ionic liquid, thus, lowering the polymer isolated yield. Having ruled out any direct filtration of the solid from the ionic liquid because of its high density, an alternative isolation procedure was performed by adding methanol to the reaction mixture, by which a suspension of PPA in the solvent mixture methanol/IL was formed. Thereby, a much easier filtration of the solid product could be carried out. The earlier described filtration procedure by-passed the disadvantage of the toluene extraction permitting the recovering of a higher polymer quantity. Table 1 lists the results obtained in the polymerization of phenylacetylene catalyzed by

Table 1  
Phenylacetylene polymerization catalyzed by (diene)Rh(acac) in ionic liquids<sup>a</sup>

Entry	Ionic liquid	Catalyst	Isolated yield (%)	$M_w$ (Da)	$M_w/M_n$	% <i>cis</i> (IR)
1	[bmim]BF <sub>4</sub>	(nbd)Rh(acac)	92 <sup>b</sup>	196000	4.5	98
2	[bmim]BF <sub>4</sub>	(nbd)Rh(acac)	80 <sup>c</sup>	175000	10.5	98
3 <sup>d</sup>	[bmim]BF <sub>4</sub>	(nbd)Rh(acac)	86 <sup>b</sup>	160000	4.8	100
4	[bupy]BF <sub>4</sub>	(nbd)Rh(acac)	91 <sup>b</sup>	100000	5.6	100
5	[bupy]BF <sub>4</sub>	(nbd)Rh(acac)	79 <sup>c</sup>	120000	5.7	99
6 <sup>d</sup>	[bupy]BF <sub>4</sub>	(nbd)Rh(acac)	85 <sup>b</sup>	181000	3.7	95
7	[bmim]BF <sub>4</sub>	(cod)Rh(acac)	64 <sup>b</sup>	55000	8.2	99
8	[bupy]BF <sub>4</sub>	(cod)Rh(acac)	71 <sup>b</sup>	58900	10.0	95

<sup>a</sup> Conditions:  $T = 25^\circ\text{C}$ ; molal catalyst concentration,  $8 \times 10^{-3}$  mol/kg; substrate/Rh = 200 mol/mol; co-catalyst, triethylamine; co-catalyst/Rh = 10 mol/mol; solvent, 5 g; reaction time, 5 min.

<sup>b</sup> Polymer isolation carried out by filtration.

<sup>c</sup> Polymer isolation carried out by toluene extraction.

<sup>d</sup> Recycle of the previous run.

(cod)Rh(acac) or (nbd)Rh(acac) with triethylamine as co-catalyst [NET<sub>3</sub>/Rh(I) = 10 mol/mol] and carried out in [bupy]BF<sub>4</sub> or [bmim]BF<sub>4</sub>.

When (nbd)Rh(acac) was used as catalyst in the ionic liquids [bmim]BF<sub>4</sub> and [bupy]BF<sub>4</sub>, the substrate conversion, observed after 5 min reaction was quantitative, as monitored by GC. Entries 1 and 2 as well as entries 4 and 5 (Table 1) differ in the polymer isolation method: in entries 1 and 4, the polymer was isolated by filtration, whereas in entries 2 and 5, the isolation was carried out by toluene extraction. It is apparent that (nbd)Rh(acac) exhibits a comparable catalytic activity in both ILs. The reported yield, as previously pointed out, depends on the isolation method and gives comparable results: filtration allowed the obtainment of an isolated yield of PPA higher than 90% in both ILs (entries 1 and 4) while extraction lowered PPA isolated yield to about 80% (entries 2 and 5). It can, thus, be concluded that among the two PPA isolation procedures, namely extraction and filtration (*vide supra*), the latter permits the recovering of the maximum quantity of product and is to be used whenever a safe comparison of catalytic activity is needed. In order to check out the potential catalyst recyclability, we first used the ionic liquid obtained by recovering the IL from its solution after filtration. The Rh(I) complex solution in the IL obtained after complete methanol evaporation in vacuo showed no residual catalytic activity. On the other hand, a good catalyst recyclability was obtained when PPA was extracted with toluene: a recycle of the

Rh(I) complex solution obtained after (nbd)Rh(acac) catalysis in [bmim]BF<sub>4</sub> and in [bupy]BF<sub>4</sub> (Table 1, entries 3 and 6) yielded 86% and 85% PPA, respectively.

In order to evaluate the difference in reactivity between different chelating dienes, we have tested the catalytic activity of (cod)Rh(acac) in both [bmim]BF<sub>4</sub> and [bupy]BF<sub>4</sub>. The polymer yields (64% in [bmim]BF<sub>4</sub>, entry 7 and 71% in [bupy]BF<sub>4</sub>, entry 8) obtained with (cod)Rh(acac) with respect to 92% (entry 1) and 91% (entry 4) obtained with (nbd)Rh(acac) indicate that also in the ionic liquid media norbornadiene, as a stronger chelating ligand, forms more active catalytic species, as also proved by other studies [31]. Attempts to recycle the (cod)Rh(acac) catalyst were unsuccessful, probably because of catalyst decomposition, caused by the higher lability of cyclooctadiene complexes with respect to norbornadiene ones.

In order to evaluate the activity of the [(diene)RhCl]<sub>2</sub> complexes in both ionic liquids under triethylamine co-catalysis, we have used [(nbd)RhCl]<sub>2</sub> and [(cod)RhCl]<sub>2</sub>. The results are collected in Table 2. Being the two dimeric chloro complexes less active than the acetylacetonato complexes previously discussed, it was decided to check reactions after 15 min. [(nbd)RhCl]<sub>2</sub> yielded 75% PPA in [bmim]BF<sub>4</sub> (Table 2, entry 1) and 63% PPA in [bupy]BF<sub>4</sub> (Table 2, entry 2) whereas [(cod)RhCl]<sub>2</sub> catalytic activity was slightly lower, yielding 52% PPA in [bmim]BF<sub>4</sub> (Table 2, entry 3) and 57% PPA in [bupy]BF<sub>4</sub> (Table 2, entry 4).

Table 2  
Phenylacetylene polymerization catalyzed by [(diene)RhCl]<sub>2</sub> in ionic liquids<sup>a</sup>

Entry	Ionic liquid	Catalyst	Isolated yield (%)	M <sub>w</sub> (Da)	M <sub>w</sub> /M <sub>n</sub>	% <i>cis</i> (IR)
1	[bmim]BF <sub>4</sub>	[(nbd)RhCl] <sub>2</sub>	75	199000	3.9	96
2	[bupy]BF <sub>4</sub>	[(nbd)RhCl] <sub>2</sub>	63	120000	8.5	99
3	[bmim]BF <sub>4</sub>	[(cod)RhCl] <sub>2</sub>	52	57400	5.4	98
4	[bupy]BF <sub>4</sub>	[(cod)RhCl] <sub>2</sub>	57	63400	3.5	96

<sup>a</sup> Conditions: *T* = 25 °C; molal catalyst concentration, 4 × 10<sup>-3</sup> mol/kg; substrate/Rh = 200 mol/mol; co-catalyst, triethylamine; co-catalyst/Rh = 10 mol/mol; solvent, 5 g; reaction time, 15 min; polymer isolation was carried out by filtration.

### 2.1. Characterization of the obtained polymers

Polymer characterization was undertaken by GPC and IR techniques. The molecular weights, showed several interesting aspects: PPAs obtained by (nbd)Rh(acac) catalysis and isolated by filtration exhibited molecular weights of 196,000 Da when the reaction was carried out in [bmim]BF<sub>4</sub> (Table 1, entry 1) and of 100,000 Da when the reaction was carried out in [bupy]BF<sub>4</sub> (Table 1, entry 4). An analogous dependence of the molecular weight upon the ionic liquid used was observed when the polymer isolation was carried out by extraction with toluene (175,000 Da in [bmim]BF<sub>4</sub>, entry 2, and 120,000 Da in [bupy]BF<sub>4</sub>, entry 5 of Table 1). Using [(nbd)RhCl]<sub>2</sub> led to analogous results in terms of molecular weight. The reaction yielded PPA with M<sub>w</sub> = 199,000 Da in [bmim]BF<sub>4</sub> (Table 2, entry 1) and with M<sub>w</sub> = 120,000 Da in [bupy]BF<sub>4</sub> (Table 2, entry 2). It seems, therefore, that when norbornadiene is the chelating diene, the molecular weight depends on the ionic liquid used. When cyclooctadiene was used as diene ligand, the molecular weight was considerably lower and independent of the ionic liquid used. In the case of (cod)Rh(acac), the polymer, isolated by filtration, reached a molecular weight of 55,000 Da in [bmim]BF<sub>4</sub> (Table 1, entry 7) and of 58,900 Da in [bupy]BF<sub>4</sub> (Table 1, entry 8). In the case of [(cod)RhCl]<sub>2</sub>, the polymer, isolated by filtration, reached a molecular weight of 57,400 Da in [bmim]BF<sub>4</sub> (Table 2, entry 3) and of 63,400 Da in [bupy]BF<sub>4</sub> (Table 2, entry 4). GPC revealed polydispersities of the obtained polymers ranging from 3.5 to 10.5.

As to the percentage of segments with *cis* configuration in the polymer chain, which is considered a crucial point in the study of PPA [31], we have used the correlation found between IR features of mixtures

of highly *cis* stereoregular PPA and annealed (*trans*) PPA.<sup>1</sup> IR analyses displayed intensities ratio of the signals at 760 and 740 cm<sup>-1</sup> (*I*<sub>760</sub>/*I*<sub>740</sub>) in the range between 0.843 and 0.688. The correspondent %*cis* range is 95% ≤ %*cis* ≤ 100%.

### 3. Conclusions

The use of ionic liquids as reaction media for the polymerization of phenylacetylene catalyzed by (diene)Rh(acac) and [(diene)RhCl]<sub>2</sub> complexes under basic co-catalysis was investigated. Quantitative yields of poly(phenylacetylene) with high *cis* percentage (95–100%) were obtained within 5 min with (nbd)Rh(acac) in both [bmim]BF<sub>4</sub> and [bupy]BF<sub>4</sub>. A considerably higher molecular weight was obtained with the same catalyst in [bmim]BF<sub>4</sub> with respect to [bupy]BF<sub>4</sub> and the catalyst solution in ionic liquid could be recycled without significant loss in activity provided that PPA separation was performed by toluene extraction.

### 4. Experimental

#### 4.1. General procedures

All manipulations were performed under a dry nitrogen atmosphere with common Schlenk techniques. Phenylacetylene and NaBF<sub>4</sub> were purchased from Aldrich, *N*-methylimidazolium was purchased from

<sup>1</sup> Correlation between *cis* percentage and *I*<sub>760</sub>/*I*<sub>740</sub> ratio. Data: *I*<sub>760</sub>/*I*<sub>740</sub> = *a* + *b*(%*cis*) + *c*(%*cis*)<sup>2</sup> + *d*(%*cis*)<sup>3</sup>; data: *a* = 1.2150, *b* = -0.001155, *c* = 0.000028077, and *d* = -6.92 · 10<sup>-7</sup>, as described in [30].

Fluka, *n*-butyl bromide was purchased from Carlo Erba. Reagents were used as received.

IR spectra were recorded on a Bruker Vector 22 instrument. Chromatographic analyses were carried out on Hewlett Packard 6890 instruments using a HP-5 phenyl–methyl siloxane 30.0 m × 320 μm × 0.25 μm capillary column. GPC analyses were carried out on a HP 1050 instrument equipped with a Pl-gel 5μ Mixed-D 300 mm × 7.5 mm column. THF solutions for GPC analysis were eluted at 25 °C at a flow rate of 1.0 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. The ionic liquids [bupy]BF<sub>4</sub> and [bmim]BF<sub>4</sub> [32], as well as the complexes [(cod)RhCl]<sub>2</sub>, [(nbd)RhCl]<sub>2</sub> [33], (cod)Rh(acac) and (nbd)Rh(acac) [34] were prepared according to literature procedures.

#### 4.2. Catalytic runs and polymer isolation

In order to solubilize (diene)Rh(acac) and [(diene)RhCl]<sub>2</sub> complexes, methylene chloride was added to the suspension of the relevant complex in ionic liquid under vigorous stirring. CH<sub>2</sub>Cl<sub>2</sub> was then removed in vacuo giving a clear solution.

Polymerizations were carried out in 50 ml Schlenk flasks. In a typical run, to the solution of the complex in ionic liquid (0.04 mmol of rhodium in 5 g of ionic liquid), obtained as described earlier and kept under vigorous stirring, were added first a known amount of phenylacetylene and then triethylamine (co-catalyst/rhodium = 10/1 mol/mol) which triggered the polymerization. PPA is insoluble in the reaction medium and precipitates as a yellow flocculent solid. After due reaction time, the stirring was stopped and the polymer was obtained by extraction with toluene (6 × 5 ml, in which a red solution of PPA was obtained<sup>2</sup>) and addition of MeOH which caused the precipitation of PPA as a yellowish-orange powder. PPA was filtered-off, washed with MeOH

(3 × 10 ml) and dried. Alternatively, 10 ml MeOH was added to the reaction mixture obtaining a suspension of PPA that was easily filtered, washed with MeOH and dried in vacuo yielding a yellowish-orange powder. Polymer yields were determined by weighing.

Recycling tests were performed only when the phenylacetylene conversion was quantitative. The solution of the complex in ionic liquid, obtained after toluene extraction of PPA, was added again of a known amount of phenylacetylene and then of triethylamine (co-catalyst/rhodium = 10 mol/mol). The filtration procedure was then followed for polymer isolation, in order to recover the maximum amount of product. For correctly evaluating, the yield obtained in the recycle, the amount of polymer formed was calculated as shown in the following equation:

$$\frac{\{ \text{isolated polymer mass (recycle)} - [\text{substrate mass (first cycle)} - \text{isolated polymer mass (first cycle)}] \}}{\text{substrate mass (recycle)}} \times 100 = \text{corrected yield (recycle)} \quad (1)$$

This was necessary in order to take in due account the polymer mass formed in the first cycle and not separated from the ionic liquid.

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<sup>2</sup> The red color of the toluene solution might be due to conformational modifications in toluene which do not influence the molecular weight or do not induce isomerization, but only the hydrodynamic radius of the polymer, and on a time-scale much higher than the time required for the extraction (about 20 min). This solvent effect has been described in [35].

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