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Catalytic polymerization of phenylacetylene with dimeric $[Rh(OMe)(cod)]_2$ complex in ionic liquids

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Dimeric rhodium(I) complex $[Rh(OMe)(cod)]_2$ was found to be an active catalyst of phenylacetylene polymerization to poly(phenylacetylene) (PPA) in ionic liquids containing imidazolium or pyridinium cations. The highest yield of PPA (92%) was obtained in 1-butyl-4-methylpyridinium tetrafluoroborate as reaction medium. The yield of PPA in imidazolium ionic liquids containing BF_4^- or PF_6^- anions increased to 83–99% when Et_3N or cycloocta-1,5-diene were added as co-catalysts. In 1-methyl-3-octylimidazolium chloride (MOI · Cl) polymerization rate was much lower than in other ionic liquids, although the highest M_w (72 400) was obtained. Spectroscopic studies confirmed that $[Rh(OMe)(cod)]_2$ reacted with MOI · Cl forming new carbene Rh(I) complex, which can participate in the polymerization process. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: rhodium complexes; catalysis; polymerization reaction; ionic liquids; carbene complex

INTRODUCTION

Rhodium complexes with coordinated dienes, such as cycloocta-1,5-diene (COD) or norbornadiene (NBD), as ligands are known to be active catalysts of phenylacetylene polymerization under homogeneous and heterogeneous reaction conditions.[1–13] Application of ionic liquids as reaction media offers easier separation of catalyst from the polymer, similarly to in heterogenized systems. In addition, some ionic liquids can react with rhodium catalyst precursor, forming new species of different catalytic activity. Therefore understanding these processes is very important in the design of new catalytic systems for polymerization of phenylacetylenes in which ionic liquid can be used as both reaction medium and co-catalyst. Surprisingly, polymerization of phenylacetylenes in ionic liquids has been described until now in only a few papers. The rhodium(I) complexes [Rh(acac)(nbd)] and [Rh(acac)(cod)] in ionic liquids 1-butyl-3-methylimidazolium (BMI) or 1-butyl-4-methylpyridinium (BMP) fluoroborates were found to be active in phenylacetylene polymerization only when Et_3N as cocatalyst was added to the system.[14]

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The rhodium(I) tris-pyrazolylborate and bis-pyrazolylborate complexes[15] in such ionic liquids as BMI · Cl, BMI · BF_4, MOI · BF_4, BMP · BF_4 or CH_2Cl_2 in the presence of tetraalkylammonium halides ($R_4N \cdot X$, R = Bu, Et; X = Cl, Br) were found to be active catalysts for phenylacetylene polymerization at 20 °C (56% of PPA after 24 h).[15] The yield of PPA increased to 100% when alcohols [CH_3OH, $(CH_3)_2CHOH$ or $(CH_3)_3COH$] were added.[15] Combination of ionic liquids and/or ammonium salts with alcohols as reaction medium allowed higher-molecular-weight polymers to be obtained.[15]

In this paper we describe another example of application of ionic liquids as reaction media for polymerization of phenylacetylene catalyzed by dimeric rhodium(I) complex $[Rh(OMe)(cod)]_2$. This catalyst precursor has been used by other authors for polymerization of phenylacetylene in organic solvents but not in ionic liquids.[16] The aims of the studies presented in this paper were:

- elucidation of the influence of ionic liquids on the yield and structure (M_w and M_w/M_n) of PPA formed;
- recognition of the interactions of ionic liquids with catalyst precursor and description of catalytically active forms generated *in situ*;

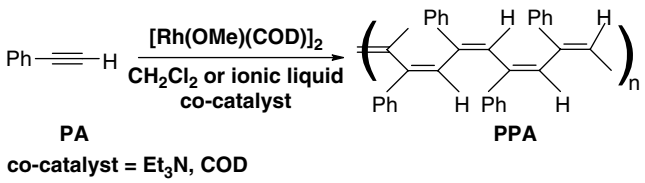
The following ionic liquids have been used as the solvents: MOI · BF_4, MOI · Cl, BMI · PF_6, BMI · BF_4, BMI · I and BMP · BF_4 (where MOI and BMI are imidazolium cations, and BMP pyridinium cation).

RESULTS AND DISCUSSION

The polymerization of phenylacetylene was carried out in the catalytic system presented in Scheme 1, in CH_2Cl_2 or in ionic liquids. The influence of co-catalysts Et_3N and COD was also studied.

The results of polymerization [yields (%), molecular weight (M_w) and polydispersity (M_w/M_n) of PPA] are presented in Table 1. Polymerization in CH_2Cl_2 in the absence of ionic liquids and without co-catalysts leads to the yield of the polymer of *ca* 75% (after 4 h). All ionic liquids containing imidazolium cations (BMI or MOI) demonstrate similar properties as reaction media for catalytic polymerization (*ca* 75% PPA). An exceptionally high polymer yield was obtained for ionic liquid with pyridinium cation, BMP · BF_4 (92% PPA after 4 h). In all cases the polymers obtained contain *ca* 100% *cis* isomer as determined from the ratio of intensities of two bands at 760 and 740 cm^{-1} in IR spectra.[9] ^1H NMR spectra of isolated PPA and those measured *in situ* during polymerization presented three signals at 5.8, 6.6 and 6.9 ppm, which are characteristic for the *cis* isomer.[6]

Further experiments were performed in the presence of co-catalysts Et_3N or COD. Addition of co-catalysts increased polymer yields in most of the imidazolium ionic liquids used, but not in a case of MOI · Cl (the yield of PPA decreased from 75% to 51 or 42% after addition of Et_3N or COD respectively; Table 1). In reaction performed in BMP · BF_4, the addition of COD caused a decrease of PPA yield from 92 to 78%. An influence of co-catalysts on polymerization was studied by Tabata *et al*.[10] According to the literature data, Et_3N was proved to promote dissociation of $[RhCl(cod)]_2$[11] and the same role may also be assumed for $[Rh(OMe)(cod)]_2$. Interaction of Et_3N with $[Rh(OMe)(cod)]_2$ was confirmed by ^1H NMR spectrum, presenting broadening and splitting of signals of rhodium dimer. In the ^1H NMR spectrum of the solution containing $[Rh(OMe)(cod)]_2$ and Et_3N ([Rh] : [Et_3N] = 1) new signals at 1.76, 3.46 and 3.84 ppm were observed, indicating the lowering of complex symmetry caused probably by splitting of the dimer and coordination of Et_3N to rhodium.



Scheme 1.

Positive influence of COD addition on the yield of polymerization (in most cases, Table 1) could be explained by often postulated supression of COD dissociation from coordination sphere of rhodium. Although ^1H NMR spectra measured during polymerization did not show signals characteristic for free COD (expected at 2.36 and 5.56 ppm), this mechanism cannot be excluded.

Worth noting are the effects of ionic liquids and the co-catalysts on the molecular weight of PPA (Table 1). Generally, imidazolium ionic liquids with BF_4^- and PF_6^- anions caused a significant decrease in PPA M_w from 50 700 (in CH_2Cl_2) to *ca* 25 000 (24 600 in MOI · BF_4, 22 700 in BMI · PF_6 and 25 200 in BMI · BF_4). The same effect was also observed for BMP · BF_4 (23 100). Only when MOI · Cl and BMI · I were used as solvents instead of CH_2Cl_2 was a significant increase in PPA M_w was observed (72 400 and 67 700, respectively), when compared with PPA M_w obtained in CH_2Cl_2 (50 700; Table 1).

In all the tested polymerizations taking place in ionic liquids, addition of triethylamine significantly increased the M_w of the polymer (Table 1), whereas addition of COD generally led to the opposite effect, producing polymer with high yield but low M_w (Table 1). It should be noted that polymerization performed in MOI · Cl in the presence of Et_3N or COD led after 4 h to PPA of M_w 94 400 or 96 100, respectively. These are the highest M_w values found in these studies.

The rate of polymerization was also analyzed and results are presented in Table 2. In some ionic liquids (like BMP · BF_4, BMI · PF_6, MOI · BF_4 and BMI · BF_4), the polymerization is very fast and can be complete within 1 h at relatively low

Table 1. Polymerization yield (%), molecular weight (M_w) and polydispersity (M_w/M_n) of poly(phenylacetylene) in various solvents and the effect of co-catalysts

	No co-catalyst		Et_3N		COD	
Solvent	Yield (%)	M_w (M_w/M_n)	Yield (%)	M_w (M_w/M_n)	Yield (%)	M_w (M_w/M_n)
CH_2Cl_2	75	50 700 (1.98)	78	20 900 (1.96)	81	22 700 (2.53)
MOI · BF_4	78	24 600 (2.00)	97	53 700 (2.26)	99	19 800 (2.33)
BMI · PF_6	77	22 700 (2.24)	93	65 700 (2.24)	83	12 100 (2.79)
MOI · Cl	75	72 400 (1.65)	51	94 400 (1.72)	42	96 100 (1.72)
BMI · I	57	67 700 (1.70)	67	91 000 (1.94)	60	61 100 (1.81)
BMI · BF_4	72	25 200 (1.88)	89	47 600 (2.05)	86	19 600 (2.22)
BMP · BF_4	92	23 100 (1.99)	92	48 100 (2.59)	78	18 400 (2.56)

Reaction conditions: 35 °C, 4 h, 0.5 cm^3 of CH_2Cl_2 or 0.5 g of ionic liquid, 0.3 cm^3 phenylacetylene (PA); Rh : PA = 1 : 200, Rh : Et_3N = 1 : 10; Rh : COD = 1 : 30.

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Table 2. Polymerization yield (%) and molecular weight (M_w) of poly(phenylacetylene) in various ionic liquids

	PPA yield (%) and (M_w)				
Reaction time (min)	BMP · BF_4	BMI · PF_6	BMI · BF_4	MOI · BF_4	MOI · Cl
15	78	65	86	83	
30	88	62	79	85	13
60	79	72	78	97	30 (70 000)
120					44 (70 700)
240	92 (23 100)	77 (22 700)	78 (25 200)	97 (24 600)	75 (72 400)

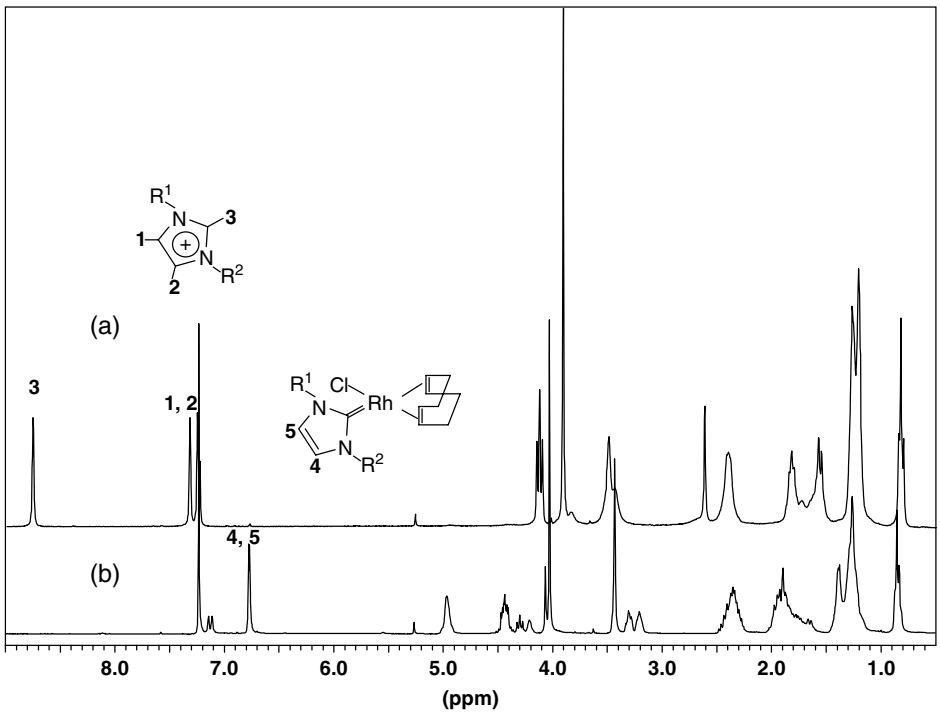

Figure 1. ^{1}H NMR spectra in $CDCl_3$ of: (a) [Rh(OMe)(cod)]$_2$ + MOI · BF_4; (b) [Rh(OMe)(cod)]$_2$ + MOI · Cl. Concentrations of [Rh(OMe)(cod)]$_2$ and MOI · X were 4.13×10^{-2} and 8.26×10^{-2} M, respectively.

temperatures (≤35 °C). However, the M_w of the polymer obtained in fast polymerization were rather low and did not exceed 25 000 (Table 2). In contrast, the polymerization in MOI · Cl was much slower but allowed a high-molecular-weight polymer to be obtained (*ca* 72 400 after 4 h).

The effect of co-catalysts is also different in the case of MOI · Cl compared with that in other ionic liquids and addition of Et_3N or COD led to decrease of PPA yield with simultaneous increase in its M_w. The clearly different polymerization course in MOI · Cl (Fig. 1) may suggest the existence of processes in which dimeric [Rh(OMe)(cod)]$_2$ complex is transformed into a new rhodium species of different catalytic activity. In order to confirm formation of the new complex, the reaction of [Rh(OMe)(cod)]$_2$ with MOI · Cl was monitored by measuring UV–vis and ^{1}H NMR spectra.

The UV–vis spectrum of the [Rh(OMe)(cod)]$_2$ dimer showing maximum at 350 nm and a shoulder at *ca* 280 nm changed during the reaction with MOI · Cl into the spectrum of only one product (isosbestic points) with two maxima at 394 and 290 nm. When MOI · BF_4 was added to the solution of rhodium dimer, no changes in UV–vis spectrum were observed.

In ^{1}H NMR spectrum of the solution containing [Rh(OMe)(cod)]$_2$ and MOI · BF_4 ([Rh]:[IL] = 1) signals originated from COD ligand were observed at 1.58, 2.40 and 3.50 ppm together with a sharp singlet at 2.62 ppm from methoxy group (Fig. 1). The positions of all these signals were the same as in the starting [Rh(OMe)(cod)]$_2$ complex. The spectrum of the MOI cation was also unchanged when compared with the spectrum of MOI · BF_4. The most characteristic signals of protons of imidazoline ring are represented by two singlets at 7.25 and 7.32 ppm from the NC*H*C protons ring and a singlet at 8.76 ppm from one NC*H*N proton. Significant changes in ^{1}H NMR spectrum of the reaction mixture were observed when MOI · Cl was used instead of

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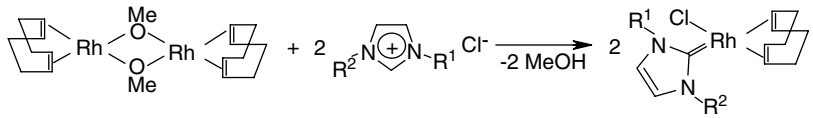

Scheme 2.

MOI · BF_4. The signal of free methanol appeared at 3.43 ppm, confirming the formation of a new rhodium complex. In addition, the signal at 8.76 ppm from NC*H*N proton was missing and only one signal from two NC*H* protons was observed at 6.78 ppm instead of two signals at 7.25 and 7.32 ppm.

Characteristic changes were also observed in the region of signals derived from COD protons, which were split into five groups. Such an effect could be expected when rhodium complex of lower symmetry was formed. Comparison of ^{1}H NMR data with those published for Rh(I) carbene complexes of [Rh(carbene)X(cod)] type[17–19] allowed a similar composition to be proposed for rhodium complex formed *in situ* from $[Rh(OMe)(cod)]_2$ and MOI · Cl. Unfortunately our efforts to isolate this product in solid have so far not been successful.

The effects in UV–vis and ^{1}H NMR spectra, similar to these described above, were observed for the solution containing $[Rh(OMe)(cod)]_2$ and BMI · I, which indicates the possible formation of carbene complex also in this case.

The results obtained do not allow a full explanation of the negative effect of MOI · Cl used as reaction medium to be presented, but a tentative approach could be proposed. Evolution of methanol in reaction of $[Rh(OMe)(cod)]_2$ with MOI · Cl and appearance of only one signal of two NC*H* protons allows the proposition of the reaction pattern shown in Scheme 2.

Although the initial structure of rhodium catalyst precursor is significantly changed as a consequence of its interaction with MOI · Cl, it is not easy to explain the dramatic decrease in activity when $[MOI]^+$ with mobile protons and strongly coordinating Cl^- anions (but not weakly coordinating BF_4^- or PF_6^- anions) are used. It seems reasonable that the PA polymerization reaction rate in MOI · Cl decreases because of replacement of methanolate bridging ligands for less mobile chloride. The obtained carbene complexes, although less reactive, produce longer chain polymers (higher M_w) in a slower reaction.

Our attempts to reuse a catalyst dissolved in ionic liquid after extraction of PPA with toluene (according to procedure described in Kanki *et al.*[13]) gave very poor results. In the second run only up to 15% of PPA was obtained. This could be explained by the partial transfer of catalyst from ionic liquid to toluene extract. Such supposition was concluded from the experiment in which PPA was precipitated from toluene extract and the residual solution was added to the ionic liquid phase forming catalyst for the second polymerization run. The yield of PPA increased in this procedure to *ca* 50%. The best result was obtained when a new portion of phenylacetylene was added to the reaction mixture after the first run without PPA separation. The total yield of 82% PPA was obtained, demonstrating no lost of activity. The observations discussed above allow the assumption that the decrease in activity of the catalyst in repetitive experiments is caused mainly by the non-optimized procedure of catalyst recovery.

CONCLUSIONS

Dimeric rhodium(I) complex $[Rh(OMe)(cod)]_2$ in ionic liquids shows attractive catalytic properties in polymerization of phenylacetylene. It was demonstrated that the reaction yields as well as the M_w of the polymer can be improved by selection of a proper ionic liquid as reaction medium as well as by addition of Et_3N or COD as co-catalysts. In all ionic liquids containing non-halide anions, addition of Et_3N caused an increase in the polymer yield as well as an increase in its M_w. Under these conditions PPA of M_w *ca.* 50 000 can be easily obtained with a yield *ca* 90%. In contrast, the presence of COD caused an increase in the yield (up to *ca* 85%), but not in M_w, which was lower then 20 000.

The rate of polymerization carried out in MOI · Cl was lower than in the other ionic liquids; however, the M_w of the obtained polymer was significantly higher. The effect of co-catalysts was also different when compared with other systems. In the presence of Et_3N and COD, a higher M_w was obtained but the yield of polymer decreased.

Spectroscopic studies confirmed possible formation of a new carbene complex in reactions of $[Rh(OMe)(cod)]_2$ with MOI · Cl, which is probably responsible for the catalytic effects in polymerization performed in these media.

EXPERIMENTAL

Reagents

$[Rh(OMe)(cod)]_2$ was synthesized as described in Uson *et al.*[20]

1-Butyl-3-methylimidazolium iodide BMI · I

BMI · I was synthesized from equimolar amounts of 1-methylimidazol and butyl iodide, stirring for 7 days at 80 °C until the mixture became dark red and thick. The unreacted compounds were removed by repeated extraction with ethyl acetate, which was then vacuum-distilled from the product.

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Analysis: found (calculated for $C_8H_{15}IN_2$), %C 36.11 (35.48), %H 5.68 (6.48), %N 10.53 (10.34).

Performance of catalytic polymerization

Polymerizations in ionic liquids were carried out in a 30 cm^3 thermostated glass reactor under nitrogen using the following procedure. A 0.5 g aliquot of ionic liquid and 3.34 mg of $[Rh(OMe)(cod)]_2$ were introduced to the reactor filled with nitrogen. To dissolve the rhodium complex in the ionic liquid, 1 cm^3 of CH_2Cl_2 was added and stirred for 5 min. Then, CH_2Cl_2 was carefully distilled off under vacuum and the solution was ready for catalytic polymerization. The reactor was filled again with nitrogen and after 24 h 0.3 cm^3 of phenylacetylene was introduced and stirred with a magnetic stirrer for 4 h at 35 °C. In experiments with co-catalysts, COD (0.05 cm^3) and Et_3N (0.02 cm^3) were added to the reactor 2 min before phenylacetylene.

Polymer separation

The polymer was extracted with several portions of toluene, precipitated with methanol, filtered, vacuum-dried and weighed for yield determination. When only CH_2Cl_2 was used as a solvent, the polymer was precipitated with methanol directly from the reaction mixture.

Polymerization experiments in time (Table 2) were performed as independent reactions terminated at various times.

M_w and *cis*-poly(phenylacetylene) content determination

Molecular weight of PPA was determined by the HPLC method using polystyrene standards of known M_w. All measurements were carried out on an HP 1090 II Hewlett-Packard instrument with HP 1047 A detector and a PL-gel 5 μm MIXED-C column.

The content of *cis*-poly(phenylacetylene) in the product was determined from the IR band's intensity ratios at 760 and 740 cm^{-1}.[21] IR spectra were recorded on an FTIR Nicolet Impact 400 spectrometer. UV–vis spectra were measured on Hewlett Packard 8452 Diode Array spectrometer and ^1H NMR spectra were measured on a Bruker 300.

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