Alternative Synthesis of a Dialkylimidazolium Tetrafluoroborate Ionic Liquid Mixture and its Use in Poly(acrylonitrile-butadiene) Hydrogenation

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Abstract: An alternative synthesis of a dialkylimidazolium ionic liquid mixture is developed in order to produce inexpensive solvents for biphasic hydrogenation of poly(acrylonitrile-butadiene) rubbers (NBR) catalyzed by $RuHCl(CO)(PCy_3)_2$.

Keywords: biphasic catalysis; HNBR; hydrogenation; ionic liquids; NBR.

The hydrogenation of polydienes is an important method for their chemical modification resulting in a variety of elastomers and thermoplastic polymers with improved physical-chemical and mechanical properties. The scientific and technological importance of the hydrogenation of materials like poly(acrylonitrile-butadiene) (NBR) has grown dramatically in the last years, basically due to their use as specialty engineering polymers.[1,2]

The production of these hydrogenated poly(acrylonitrile-butadiene) rubbers (HNBR) involves homogeneous catalytic hydrogenation. The catalyst recovery and its separation from the product are major drawbacks of these catalytic, one-phase processes. One of the approaches to solve these basic problems is the use of biphasic catalysis.[3,4] Indeed, some of us have recently showed that NBR can be hydrogenated by $RuHCl(CO)(PCy_3)_2$ (**1**) dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM][BF_4]$) ionic liquid under biphasic conditions. This two-phase system is obtained due to the difference in the partial miscibility of the solution of NBR in toluene and the solution of the catalyst **1** in the ionic liquid $[BMIM][BF_4]$.

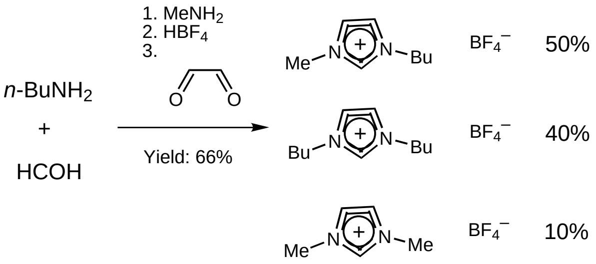
The synthesis of the $[BMIM][BF_4]$ has been described using 1-*n*-butyl-3-methylimidazololium chloride ([BMIM]Cl) and sodium tetrafluoroborate.[5] This route has been largely used[6] and even adopted for the commercial production of these ionic liquids.[7] However, the difficulty to remove residual chlorides from this polar media associated with the use of relatively expensive tetrafluoroborate salts are clearly limitations for the use of this method for the production and the industrial use this ionic liquid. Therefore, the development of an alternative route for the synthesis of $[BMIM][BF_4]$ employing simpler reagents and a lower number of steps is quite desirable.

We report herein that the one-pot reaction of glyoxal, methylamine, *n*-butylamine, formaldehyde, and tetrafluoroboric acid affords a mixture of dialkylimidazolium tetrafluoroborate ($[R^1R^2IM][BF_4]$) ionic liquids that can be used as a mobile phase for the two-phase NBR hydrogenation process.

It is known that dialkylimidazolium salts can be synthesized from inexpensive materials such as amines, glyoxal, and formaldehyde in a one-pot procedure. Indeed, this method is largely employed for the preparation of symmetric dialkylimidazolium salts that are used as intermediates for the synthesis of *N*-heterocyclic imidazolium carbenes.[8] This method tolerates even sterically hindered amines such as (*S*)-1-phenylethylamine or (*R*)-naphthylethylamine in the reaction with glyoxal and formaldehyde, and in the presence of hydrochloric acid. Moreover, different α-dicarbonyls, aldehydes, amines and carboxylic and inorganic acids such as HF, HCl, H_2SO_4, or H_3PO_4, have been successfully used in the preparation of a plethora of symmetric imidazolium salts.[9] However, using different amines such as, for example, methylamine and propylamine, a mixture of 1,3-methylimidazolium chloride (MMIM Cl), 1,3-dipropylimidazolium chloride (PPIM Cl) and 1-methyl-3-propylimidazolium chloride has been obtained in a molar ratio of 1:1:2.

We performed the synthesis of 1,3-disubstituted imidazolium tetrafluoroborate ionic liquids using this one-step procedure. Thus, the reaction of formaldehyde with *n*-butylamine followed by addition methylamine, aqueous HBF_4 solution and aqueous glyoxal solution affords in 66% yield a mixture of $[BMIM][BF_4]$, $[BBIM][BF_4]$ and $[MMIM][BF_4]$ in a molar ratio of 5:4:1 as determined by ^1H NMR (Scheme 1).

This ionic liquid mixture is a light yellow liquid that do not show any detectable contaminants by ^1H NMR or UV spectroscopy. This mixture shows a somehow higher viscosity and Tm (11 °C) than pure $[BMIM][BF_4]$ (−71 °C).



Scheme 1.

This ionic liquid mixture is liquid at room temperature and can be used in the immobilization of the RuHCl(CO)$(PCy_3)_2$ catalyst precursor. The performance of this catalytic ionic liquid solution in the two-phase hydrogenation of NBR was compared to that obtained with RuHCl(CO)$(PCy_3)_2$ dissolved in pure [BMIM][BF_4]. Table 1 shows selected runs of NBR hydrogenation with **1** dissolved in both ionic liquids.

The NBR hydrogenation with **1** exhibits extremely similar behavior when performed in the [R^1R^2IM][BF_4] ionic liquid or in the classic [BMIM][BF_4], as can be seen by comparing entries 4 and 6. This shows that the somehow higher viscosity and Tm do not affect the applicability of these ionic liquids, at least for reactions that have to be performed at temperatures much higher than Tm.

A classic behavior of the ruthenium catalysts is observed for the NBR hydrogenation with RuHCl(CO)$(PCy_3)_2$ (**1**), i.e., (i) enhancement of the conversion with the amount of catalyst (runs 1 to 3) but decrease in the turnover frequency due to the approach to total conversion of the double bonds and (ii) enhancement of the conversion and turnover frequencies with the hydrogen pressure (runs 2 and 4).

Under the same reaction conditions, [BMIM][BF_4] showed a slightly better performance than [R^1R^2IM][BF_4] (compare entries 2 and 6), but the use of the latter overcome reproducibility problems, a technologically relevant problem.

In conclusion, the synthesis of [R^1R^2IM][BF_4] has been performed by the direct reaction of methylamine, butylamine, glyoxal, formaldehyde, and HBF_4 as acid. This is a simple and inexpensive synthesis of an ionic liquid with economic advantages and it also precludes problems with chloride contaminations that are known to deactivate several catalytic systems. The new [R^1R^2IM][BF_4] ionic liquid mixture has been used in the ruthenium-catalyzed hydrogenation of NBR, showing the efficiency of the synthesis.

Experimental Section

Synthesis of the Ionic Liquid Mixture

In a 250-mL, round-bottomed flask 14.8 mL (0.2 mol) of formaldehyde were added dropwise to a solution of 19.8 mL (0.2 mol) of *n*-butylamine in 50 mL of toluene, under stirring. When the addition was complete, the mixture was stirred for further 10 min and methylamine (17.2 mL, 0.2 mol) was then slowly added to the cooled mixture. After 30 min, the cold ice bath was removed and 26.0 mL of 48% aqueous HBF_4 solution (0.2 mol) was slowly added at such a rate that the temperature did not exceed 30 °C. When the acid addition was completed 22.8 mL of 40% aqueous glyoxal solution was added (0.2 mol) and the mixture stirred for 12 h at 25 °C. Diethyl ether (50 mL) and saturated $NaHCO_3$ solution (50 mL) were added and the phases separated. The ionic liquid was extracted from the aqueous layer with CH_2Cl_2 (50 mL). Removal of volatiles under vacuum afforded a mixture of [BMIM][BF_4], [BBIB][BF_4] and [MMIM][BF_4] in a molar ratio of 5:4:1; total yield: 29.8 g (66%).

Hydrogenation Runs

In a typical poly(acrylonitrile-butadiene) hydrogenation run, 150 mL of a 3 wt % solution of NBR in toluene were introduced in a 600 mL 316 stainless steel Parr autoclave with magnetically driven mechanical stirring. A solution of 50 mg (70 μmol) of RuH(CO)$(PCy_3)_2$ in 3 mL of [BMIM][BF_4] was introduced in the reactor, hydrogen was filled at 40 atm and the reactor closed. The reaction temperature was raised to 140 °C using an electrical jacket with a PID control. After the reaction time the mixture was cooled down to room temperature, the residual hydrogen degassed, and the products, separated from the ionic liquid solution by decantation, were analyzed by IR.

Table 1. NBR hydrogenation with ruthenium catalyst under biphasic conditions.[a]

Run	Ionic Liquid	Pressure [atm]	Time [h]	Ruthenium [μmol]	Conversion [%]		TOF cycles/h
					1,4-*trans*	Total	
1	[R^1R^2IM][BF_4]	40	8	30	66	68	158
2	[R^1R^2IM][BF_4]	40	8	70	87	89	124
3	[R^1R^2IM][BF_4]	40	8	130	100	100	70
4	[R^1R^2IM][BF_4]	60	7	70	98	98	156
5	[R^1R^2IM][BF_4]	80	4	70	94	95	265
6	[BMIM][BF_4]	40	6	70	98	98	182

[a] Reaction conditions: catalyst RuHCl(CO)$(PCy_3)_2$; 3 wt % NBR in 150 mL of toluene; reaction temperature: 140 °C.

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