First ring-opening metathesis polymerization in an ionic liquid. Efficient recycling of a catalyst generated from a cationic ruthenium allenylidene complex

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Ring-opening metathesis polymerization (ROMP) of norbornene was carried out in a biphasic medium consisting of the ionic liquid [bdmim][PF_6] and toluene with a cationic ruthenium allenylidene precatalyst. The ionic liquid contained the ruthenium allenylidene complex and toluene dissolved the formed polymer. Both the catalyst and the ionic liquid were reused several times and led to very good polymer yields.

Alkene metathesis has become a powerful tool for the cleavage and formation of C=C bonds to produce fine chemicals, macrocycles or polymers.[1] Indeed, the recent discovery of well-defined metal alkylidene catalysts[2–6] has resulted in the rapid development of various selective metathesis reactions of alkenes and enynes.[7] In particular, ruthenium based precatalysts selectively transform C=C bonds with high tolerance toward most functional groups, thus presenting a high potential for the ROMP of functional cyclic olefins. One major problem for both fine chemistry and ROMP polymerization is the recovery or recycling of the alkene metathesis catalyst to decrease both cost and metal residues. An elegant solution to this problem is the use of ionic liquids (IL), which are known to be nonvolatile, reusable and compatible with many organic and catalytic reactions.[8] Despite the increasing number of catalytic processes performed in ionic liquids after the pioneering work by Chauvin,[9] only a few very recent reports deal with olefin metathesis.[10–13]

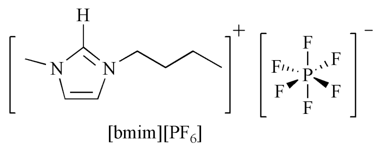
Among metathesis catalysts the cationic ruthenium allenylidene salts[5] [(*p*-cymene)RuCl(PCy_3)(=C=C=CPh_2)]X (X = OTf, PF_6, BF_4), shown in Scheme 1, are valuable candidates for applications in ionic liquids due to their ionic character. Recently these complexes have been used for the ring-closing metathesis (RCM) of various alkenes in [bmim][PF_6].[13] Although it was possible to reuse the catalyst the yield decreased quickly after the second recycling.[13]

We now report for the first time the use of ruthenium allenylidene catalysts for the ring-opening metathesis polymerization of cyclic olefin in the ionic liquid [bdmim][PF_6] (1-butyl-2,3-dimethylimidazolium hexafluorophosphate) and we especially show the remarkable high capacity of the system to be recycled.

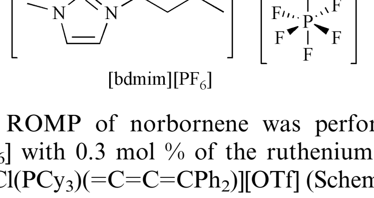
Scheme 1 ROMP of norbornene.

Results and discussion

Several considerations were taken into account for the choice of the anionic as well as the cationic part of the ionic liquid. The [PF_6] anion was chosen since [PF_6] containing ionic liquids are usually hydrophobic and they allow the dissolution of ruthenium based salts. The degradation of [bmim] type (1-butyl-3-methylimidazolium) ionic liquids is supposed to be due to proton abstraction at the 2-position with formation of a carbene species.[14] Another possibility to consider is the oxidative addition of the imidazolium cation to the metal as reported for nickel, platinum, and palladium complexes.[15] To avoid these processes the [bdmim] (1-butyl-2,3-dimethylimidazolium) cation in which the proton at the 2-position is replaced by a methyl group was used. Furthermore, it must be emphasized that the [bdmim][PF_6] synthesis pathway is absolutely identical to that of [bmim][PF_6] without extra cost. The only limitation in using [bdmim][PF_6] is its melting point that is above room temperature, thus requiring a slight heating. Typically, our experiments were performed at 40 °C.



[bmim][PF_6]



[bdmim][PF_6]

First the ROMP of norbornene was performed in neat [bdmim][PF_6] with 0.3 mol % of the ruthenium complex [(*p*-cymene)RuCl(PCy_3)(=C=C=CPh_2)][OTf] (Scheme 1). The dissolution of the complex in the ionic liquid was complete within a few minutes to give a homogeneous dark violet solution. After addition of norbornene the reaction was stirred at 40 °C for 2 h and the polymer extracted from the ionic liquid

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Table 1 Norbornene polymerization: recycling of the catalyst in [bdmim][PF$_6$][a]

Entry	Recycling	Time/h	Polymer yield/%
1	0	2	98
2	1	2	61
3	2	2	10

[a] Reactions were performed at 40 °C, with 4 mmol of norbornene and 0.3 mol % of [(p-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)][OTf] in 2.5 mL of [bdmim][PF$_6$].

with toluene and precipitated from methanol in 98% yield (Table 1). The possibility to reuse the catalyst was tested by addition of a new portion of norbornene. After 2 h at 40 °C the polymer was obtained in a lower 61% yield and the second recycling yielded only 10% of polymer.

It was postulated that the loss of activity could be due to a loss of catalyst during the extraction step, either by removal or decomposition. Indeed, the time necessary to extract the polymer from the ionic liquid phase was exceedingly long. Thus, a biphasic system made of [bdmim][PF$_6$] and toluene was used with the aim to solubilize the polymer in the organic phase during the polymerization reaction. It was found that this biphasic solvent mixture was very appropriate since the polymer could be recovered almost quantitatively by pouring the very viscous toluene upper phase into methanol. One fast subsequent washing with toluene was then enough to complete the polymer extraction. It was also found that 30 min at 40 °C was an appropriate duration for complete polymerization. With these new parameters it has been possible to reuse the catalyst three times with very good polymer yields (Table 2). Even after the 6th recycling a good polymer yield could be obtained provided a longer reaction time was used (Table 2, entry 7). It was established from the GPC results of the first three reaction cycles that the average molecular weight (M_n) increased with the number of cycles, denoting a loss of active catalytic species able to initiate a polymer chain. Interestingly, the polydispersities as well as the *trans*/*cis* ratio remained constant during the recycling. These results clearly show the possibility to reuse the catalyst with good yields. This catalyst recycling is much more efficient than that obtained in fine chemistry,[11,13] probably because of the shorter reaction time and lower temperature required for polymerization.

The ionic liquid used in the previous seven cycles was reloaded with a new portion of [(p-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)][OTf] and a new set of norbornene polymerization started. Here again the polymer was obtained in very good yields until the 5th recycling (Table 3). Consequently, the ionic liquid can be reused without any purification. The polymer properties were also comparable to those obtained in the first set of experiments but without significant influence on the M_n values after each successive run.

Table 2 Norbornene polymerization in [bdmim][PF$_6$]–toluene biphasic system: recycling of the catalyst[a]

Entry	Recycling	Time/h	Polymer yield/%	*trans* %[b]	M_n[c]/g mol^{-1}	PD$_i$[d]
1	0	0.5	96	87	113 800	1.9
2	1	0.5	99	86	168 100	1.9
3	2	0.5	98	86	206 700	1.8
4	3	0.5	97	86	n.d.[e]	n.d.
5	4	0.5	64	86	n.d.	n.d.
6	5	0.5	27	86	303 000	1.5
7	6	2	82	86	260 400	1.6

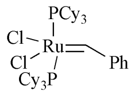
[a] Reactions were performed at 40 °C with 4 mmol of norbornene and 0.3 mol % of [(p-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)][OTf] in 2.5 mL of [bdmim][PF$_6$] and 10 mL of toluene. [b] Determined by ^{1}H NMR. [c] Determined by GPC measurements in THF, calibrated with monodisperse polystyrene standards. [d] PD$_i$ = M_w/M_n. [e] Not determined.

Table 3 Norbornene polymerization: reuse of the ionic liquid with reloaded catalyst[a]

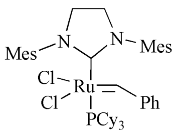
Entry	Recycling	Time/h	Polymer yield/%	*trans* %[b]	M_n[c]/g mol^{-1}	PD$_i$[d]
1	0	0.5	95	87	106 400	1.9
2	1	0.5	98	86	142 300	2.1
3	2	0.5	91	86	145 100	2.1
4	3	0.5	89	85	n.d.[e]	n.d.
5	4	0.5	87	87	n.d.	n.d.
6	5	0.5	57	86	n.d.	n.d.
7	6	0.5	19	86	166 500	2.0
8	7	24	99	86	141 500	2.0

[a] Reactions were performed at 40 °C with 4 mmol of norbornene and additional 0.3 mol % of [(p-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)][OTf] in 2.5 mL of [bdmim][PF$_6$] used in the previous experiments (Table 2) and 10 mL of toluene. [b] Determined by ^{1}H NMR. [c] Determined by GPC measurements in THF, calibrated with monodisperse polystyrene standards. [d] PD$_i$ = M_w/M_n. [e] Not determined.

Two other non-ionic metathesis catalysts, the alkylidene ruthenium Grubbs catalysts **a**[3] and **b**[4] have been tested in the same conditions.



a



b

When (PCy$_3$)$_2$RuCl$_2$(=CHPh) (**a**) was used as a catalyst a rapid loss of activity was observed since no polymer was formed during the second recycling (Table 4, entry 3). In this case the catalyst was completely extracted in the organic solvent or decomposed since it has not been possible to get a polymer even with a longer reaction time (Table 4, entry 4). Better results were obtained with the more robust catalyst **b** as very good yields were reached in the first three experiments (Table 5) but a significant drop of activity was observed in the 3rd recycling.

As observed with the Ru-allenylidene complex a longer reaction time allowed us to recover a very good polymer yield (Table 5, entry 6). It is also noteworthy that the use of the catalyst **b** gave a polymer with a very low *trans*/*cis* ratio. The recycling data are summarized in Fig. 1 and show the better possibilities offered by the cationic ruthenium allenylidene complex.

Table 4 Norbornene polymerization: recycling of catalyst **a**[a]

Entry	Recycling	Time/h	Polymer yield/%	*trans* %[b]	M_n[c]/g mol^{-1}	PD$_i$[d]
1	0	0.5	90	85	79 000	1.2
2	1	0.5	66	86	211 000	1.7
3	2	0.5	0	n.d.[e]	n.d.	n.d.
4	3	2	0	n.d.	n.d.	n.d.

[a] Reactions were performed at 40 °C with 4 mmol of norbornene and 0.3 mol % of catalyst **a** in 2.5 mL of [bdmim][PF$_6$] and 10 mL of toluene. [b] Determined by ^{1}H NMR. [c] Determined by GPC measurements in THF, calibrated with monodisperse polystyrene standards. [d] PD$_i$ = M_w/M_n. [e] Not determined.

Table 5 Norbornene polymerization: recycling of catalyst **b**[a]

Entry	Recycling	Time/h	Polymer yield/%	*trans* %[b]	M_n[c] / g mol^{-1}	PD$_i$[d]
1	0	0.5	99	42	73 700	1.7
2	1	0.5	97	42	99 800	2.0
3	2	0.5	94	41	109 300	1.9
4	3	0.5	31	41	231 700	1.6
5	4	0.5	7	41	n.d.[e]	n.d.
6	5	24	99	42	n.d.	n.d.

[a] Reactions were performed at 40 °C with 4 mmol of norbornene and 0.3 mol % of catalyst **b** in 2.5 mL of [bdmim][PF$_6$] and 10 mL of toluene. [b] Determined by ^{1}H NMR. [c] Determined by GPC measurements in THF, calibrated with monodisperse polystyrene standards. [d] PD$_i$ = M_w/M_n. [e] Not determined.

Conclusion

As a conclusion, we have demonstrated that the cationic ruthenium allenylidene precatalyst [(*p*-cymene)(PCy$_3$)RuCl(=C=C=CPh$_2$)][OTf] leads to a recyclable catalyst for the ring-opening metathesis polymerisation of norbornene in the ionic liquid [bdmim][PF$_6$] (1-butyl-2,3-dimethylimidazolium hexafluorophosphate). The best recycling results were obtained by using a biphasic medium made of [bdmim][PF$_6$] and toluene. The ionic liquid can be reused after the 6th recycling for the same polymerization reaction without any treatment simply by reloading a new portion of the cationic allenylidene complex. Finally we have shown that the allenylidene complex displays better recycling capabilities than the alkylidene catalysts probably because of its ionic character.

Experimental

All the reactions were carried out under an inert atmosphere of argon using Schlenk tube techniques. Toluene was dried by distillation over sodium wires. Other solvents (*p.a.* grade) were used without purification. 1,2-Dimethylimidazole (98%) and norbornene (99%) were obtained from Acros Organics and used as received.

[(*p*-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)][OTf] was prepared as described in the literature.[5] Catalysts **a** and **b** were prepared according to literature procedures.[3,4]

Preparations

1-Butyl-2,3-dimethylimidazolium chloride, [bdmim]Cl. 1,2-Dimethylimidazole (28.3 g, 295 mmol) and 1-chlorobutane (27.6 g, 298 mmol) were stirred at 75 °C for 48 h under argon. The flask was cooled to room temperature and the excess of 1-chlorobutane removed under reduced pressure. The pale-yellow molten product solidified in the flask and was used without further purification. Yield: 50.0 g (265 mmol, 90%).

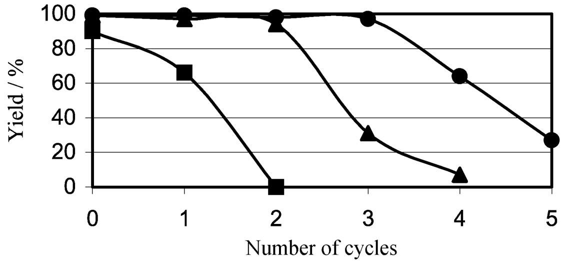


Fig. 1 Recycling comparison using (●) cationic ruthenium alkenylidene complex, (■) catalyst **a** and (▲) catalyst **b**.

1-Butyl-2,3-dimethylimidazolium hexafluorophosphate, [bdmim][PF$_6$]. 1-Butyl-2,3-dimethylimidazolium chloride (50,0 g, 265 mmol) and KPF$_6$ (51.4 g, 268 mmol) were stirred in 75 mL of acetone at room temperature for 4 days. The mixture was filtered on alumina. The acetone was evaporated and the crude product was dissolved in 50 ml of dichloromethane. This solution was extracted 8 times with water to remove the chloride residues. The organic phase was dried over MgSO$_4$, the solvent removed under reduced pressure and the ionic liquid dried for 5 h at 70 °C *in vacuo*. Yield: 51.5 g, (173 mmol, 65%) as a pale-yellow liquid that solidifies upon storage. ^{1}H NMR (200 MHz, CD$_3$COCD$_3$): δ 7.39 (d, 1H, *J* 1.83 Hz, CH$_3$–N–CHC*H*–N), 7.36 (d, 1H, *J* 1.83 Hz, CH$_3$–N–C*H*CH–N), 4.14 (t, 2H, *J* 7.32 Hz, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.81 (s, 3H, C*H*$_3$–N), 2.62 [s, 3H, N–C(C*H*$_3$)–N], 1.79 (m, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.37 (m, 2H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.92 (t, 3H, *J* 7.32 Hz, NCH$_2$CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, CD$_3$COCD$_3$): δ 146.2 [N–*C*(CH$_3$)–N], 123.7 (CH$_3$–N–CH*C*H–N), 122.3 (CH$_3$–N–*C*HCH–N), 49.5 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 35.9 (NCH$_2$-*C*H$_2$CH$_2$CH$_3$), 33.0 (*C*H$_3$–N), 20.6 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.6 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 10.0 [N–C(*C*H$_3$)–N].

Typical procedure for the preparation of polynorbornene in the two phase ionic liquid–toluene system

1-Butyl-2,3-dimethylimidazolium hexafluorophosphate (2.5 mL) was melted and transferred using a pre-heated syringe. The ruthenium allenylidene complex (11 mg, 12 μmol) was added and the reaction mixture stirred at 40 °C for 10 min. Freshly distilled toluene (10 mL) and 0.38 g (4 mmol) of norbornene were added. After 30 min the stirring was stopped and the two phases were separated. The toluene upper phase was collected and the ionic liquid phase washed with 10 mL of toluene. The toluene phase was then poured into 300 mL of methanol containing 0.1 mol % of BHT (2,6-di-*tert*-butyl-*p*-cresol) resulting in the precipitation of the polymer as a white solid. The polymer was collected and dried. A new portion of toluene and norbornene was added to the ionic liquid and stirred for 30 min at 40 °C. The treatment procedure was repeated several times.

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