Selective hydrogen transfer reduction of ketones by recyclable ruthenium complex catalysts containing a 'ROMP polymer-attached' ligand

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Abstract

Various pyridine and 2,2′-bipyridyl ligands attached to the polymer chain end of ring-opened poly(norbornene) were prepared by living ring-opening metathesis polymerization (ROMP) using $Mo(CHCMe_2Ph)(N$-2,6-$^iPr_2C_6H_3)(O^tBu)_2$. The prepared pyridine and 2,2′-bipyridyl derivatives were examined for their use as ligands for catalytic hydrogen transfer reduction of cyclohexanone in the presence of $Ru(acac)_3$ (in toluene/^iPrOH in the presence of NaO^iPr, at 50 °C, acac: acetylacetonato). The catalytic activity increased upon addition of the above polymer as the ligand, and the prepared catalyst could be recovered by filtration as the precipitate, by pouring the reaction mixture into methanol. The recovered catalyst could be reused without decrease in the activity. Since the olefinic double bond in the ROMP polymer was not hydrogenated under these reaction conditions, exclusive reduction of carbonyl group in various ketones, such as acetophenone, 5-hexen-2-one, 2-allylhexanone could be achieved in this catalysis.
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Keywords: Ruthenium; Hydrogen transfer reduction; Polymer supported catalyst; ROMP; Selective reduction; Recyclable catalyst
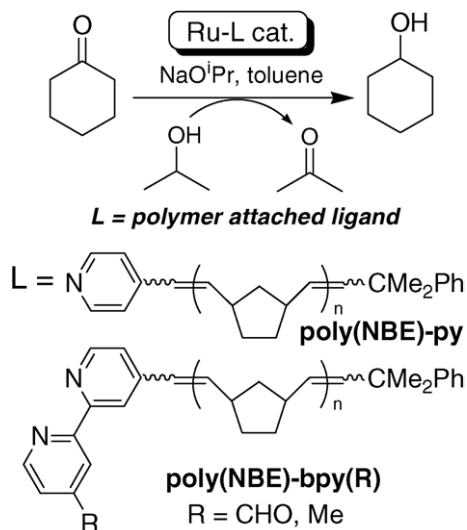
1. Introduction

Particular attention has been devoted to studies concerning polymer [1,2] or dendrimer [3] supported catalysts, not only because that there are practical concerns in using homogeneous catalysts such as separation of the products from the catalyst and ligand [4], but also because that these supported catalysts play a crucial role in combinatorial and parallel synthesis. Traditionally, insoluble polymer resins such as divinylbenzene, cross-linked polystyrene have been used as a support for homogeneous catalysts as well as for reactants since they can easily be isolated by filtration [1a]. However, several shortcomings such as nonlinear kinetic behavior, unequal distribution and/or access to the chemical reaction, solution problems, etc. still remain due to the heterogeneous reaction conditions.

As an attempt to combine the advantages and to minimize the disadvantages associated with homogeneous and heterogeneous catalysts, use of soluble polymer supported ligands has attracted considerable attention [2]. However, examples for using ligands attached to the polymer chain end and/or the synthesis of ligands by the controlled living polymerization technique still have been limited so far. We focused on using the ring-opening metathesis polymerisation (ROMP) technique [5], because quantitative introduction of reactive functionality into the polymer chain end can be easily achieved by adopting the living ROMP technique especially using the Schrock type molybdenum-alkylidene initiator [6–10]. The nice characteristics enable us not only to prepare poly(macromonomer)s by repeating ROMP technique [9], but also to prepare various amphiphilic block copolymers by grafting poly(ethylene glycol) to end-functionalized block ROMP copolymers in quantitative yields [10].

We communicated previously that the catalytic activity for the hydrogenation of an aldehyde increased upon the addition of the pyridine ligand attached to the chain end of ring-opened poly(norbornene) that was prepared by the living ROMP using $Mo(CHCMe_2Ph)(N$-2,6-$^iPr_2C_6H_3)(O^tBu)_2$, whereas the activity decreased upon the addition of pyridine, 4-methylpyridine, or poly(4-vinylpyridine) [11]. The prepared catalyst could be easily recovered by pouring the reaction mixture into methanol, and could be reused without decreasing the activity [11]. Since we also reported exclusive reduction of aromatic nitro group under CO/H_2O conditions [12], we have thus combined these methods

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Scheme 1.

and explored the possibility to expand this ROMP technique for the synthesis of ligand attached to the polymer chain end. In this paper, we wish to introduce our results for exclusive reduction of the carbonyl group in ketones by selective hydrogen transfer reduction catalyzed by recyclable ruthenium complexes containing 'ROMP polymer-attached' pyridine and 2,2'-bipyridyl ligand (Scheme 1) [13–17].

2. Results and discussion

2.1. Synthesis of 'polymer-attached' ligand

Ring-opening metathesis polymerization (ROMP) of norbornene (NBE) using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$ was performed in toluene at 25 °C, and 4-pyridinecarboxaldehyde (**A**), 4,4'-diformyl-2,2'-bipyridyl (**B**) [18], or 4-formyl-4'-methyl-2,2'-bipyridyl (**C**) [19] was added in excess amounts after consumption of NBE not only

to terminate the polymerization quantitatively, but also to introduce a pyridine or bipyridyl moiety into the chain end of ring-opened poly(NBE) quantitatively (Scheme 2). This is an established method as we demonstrated for synthesis of poly(macromonomer)s by repeating the ROMP [9], and the pyridine moiety could be introduced by cleaving the polymer-metal bond via a Wittig-like reaction with the aldehyde [6–10]. The yields were thus very high in all cases (>90%), and the resultant polymer could be isolated as a white precipitate by pouring the reaction mixture into cold methanol, because the resultant polymer was insoluble in methanol. The resultant polymer was also identified by its ^1H NMR spectrum as the ring-opened structure containing a mixture of *cis*-and *trans*-olefinic double bonds.

As shown in Table 1, the M_n value measured by GPC versus polystyrene standard increased linearly by varying the norbornene/Mo molar ratios, whereas the M_w/M_n values were narrow ($M_w/M_n = 1.07–1.21$) in all cases. These results clearly indicate that the present polymerization took place in a living manner as established previously [6–10], and that the molecular weight of the polymer ligand can be simply modified only by varying the monomer/initiator molar ratios. The M_n values estimated by GPC versus polystyrene standards were somewhat higher than those calculated based on the NBE/initiator molar ratio, however, the M_n values estimated by ^1H NMR spectra (integration ratios of olefinic protons versus pyridine or bipyridyl) were in good agreement with the calculated values [20], as reported previously by the ROMP of NBE terminated with $p\text{-}Me_3SiO\text{-}C_6H_4CHO$ [9,10,21]. The results also indicate that the present ROMP took place with quantitative initiation efficiency, as reported previously [6–10].

2.2. Hydrogen transfer reduction of cyclohexanone catalyzed by ruthenium complexes in the presence of poly(NBE)s

Hydrogen transfer reduction of cyclohexanone in the presence of a ruthenium catalyst was chosen as the model reaction
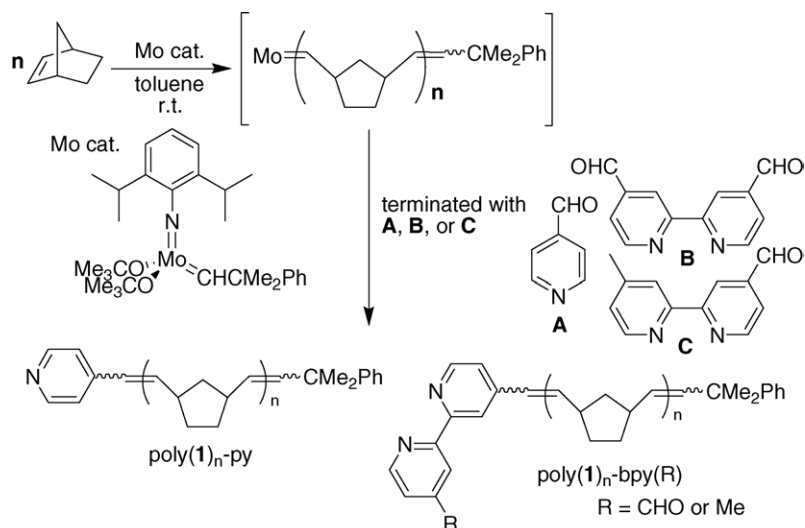
Scheme 2.

Table 1
Synthesis of poly(norbornene)s prepared by ring-opening metathesis polymerization (ROMP) initiated with Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ and terminated with **A**, **B** or **C**[a]

Run no.	Mo (μmol)	NBE/Mo[b]	Terminator[c]	M_n (calcd)[d] ($\times 10^{-4}$)	M_n (GPC)[e] ($\times 10^{-4}$)	M_w/M_n (GPC)[e]	Yield[f] (%)
1	50.0	50	**A**	0.49	0.91	1.21	>95
2	25.0	50	**A**	0.49	0.89	1.17	>95
3	25.0	100	**A**	0.96	1.73	1.09	>95
4	25.0	100	**A**	0.96	1.73	1.08	>95
5	25.0	100	**B**	0.97	2.15	1.07	>90
6	12.5	100	**C**	0.97	1.51	1.18	>90
7	16.7	150	**A**	1.43	2.65	1.07	>95
8	16.7	150	**A**	1.43	2.59	1.08	>95

[a] Conditions: toluene 7.8 g (runs 1–5) or 4.4 g (run 6) or 8.9 g (runs 7, 8), 25 °C, 30 min.
[b] Molar ratio of NBE/Mo.
[c] Aldehydes shown in Scheme 2.
[d] Calculated value based on monomer/Mo molar ratio according to Scheme 2.
[e] GPC data in THF vs. polystyrene standards.
[f] Isolated yields.

to explore the utility for using these polymer-attached ligands. The results for the hydrogen transfer reduction in toluene/^{i}PrOH at 50 °C under various base (NaO^{i}Pr) concentration conditions are summarized in Table 2. The reduction by Ru(acac)$_3$ (acac: acetylacetonato) did not take place in the absence of NaO^{i}Pr (run 9), and the activity increased upon increasing the base (NaO^{i}Pr) concentration (runs 10, 11). The addition of pyridine slightly increased the activity (runs 11, 14), and the activity seemed slightly increasing upon addition of the polymer ligand, poly(**1**)$_{100}$-py (run 11 versus 17). The increase of the NBE repeating unit did not affect the observed catalytic activity (runs 17, 18), and the activity increased upon increasing NaO^{i}Pr concentration (run 19). The activity in the presence of both pyridine and poly(**1**)$_{100}$-py showed the similar activity in the presence

of pyridine (run 20). The activity increased upon addition of 2,2-bipyridyl (run 21), and the use of the polymer ligands, poly(**1**)$_{100}$-bpy(R) (R: CHO, Me) were also found to be effective (runs 21–24).

Since the addition of poly(**1**)$_{100}$-py seemed rather effective to improve the activity in the hydrogen transfer reduction of cyclohexanone, the reductions using other ruthenium compounds were employed as the catalysts under the same conditions. The temperature dependence toward the catalytic activities was also explored in this catalysis. The results are summarized in Table 3.

The catalytic activities in the presence of Ru(acac)$_3$ increased at higher temperature, and the reduction completed at 70 °C (runs 32–34). It should be noted that the activities of RuCl$_2$(PPh$_3$)$_4$, [RuI$_2$(p-cymene)]$_2$ increased upon addition of poly(**1**)$_{100}$-py (runs 28–31), and these results suggest that the use of present 'polymer-attached' pyridine ligand is effective as the ligand for this ruthenium catalyzed reduction.

Table 4 shows the time course dependence for the reduction in the presence of Ru(acac)$_3$-poly(**1**)$_{100}$-py. The yield increased at longer reaction hours, and, as shown in Fig. 1, a relatively linear first order relationship was observed between substrate concentration ($\log_{10}[S]_0 - \log_{10}[S]$, $[S]_0$ is the initial substrate concentration and $[S]$ is the substrate concentration at the prescribed time) and the reduction rate. The result not only clearly indicates that the reduction rate was first order dependent upon the substrate concentration, but also clearly indicates that no catalyst decomposition was observed. Table 5 summarizes the solvent effect (ratio of toluene/^{i}PrOH) toward the catalytic activity, and the activity increased upon increasing the ratio of ^{i}PrOH in the reaction medium although the reaction mixture became heterogeneous at higher ^{i}PrOH/toluene ratio.

Table 2
Effect of ligand additives, base concentration in hydrogen transfer reduction of cyclohexanone catalyzed by Ru(acac)$_3$[a]

Run	NaO^{i}Pr[b] (mmol/mL)	Ligand/additives (L/Ru)[c]	TON[d]
9	–	None	Trace
10	0.04	None	63
11	0.16	None	210
12	0.16	Pyridine (1)	218
13	0.16	Pyridine (2)	228
14	0.16	Pyridine (5)	287
15	0.04	Poly(**1**)$_{100}$-py (2)	76
16	0.08	Poly(**1**)$_{100}$-py (2)	168
17	0.16	Poly(**1**)$_{100}$-py (2)	238
18	0.16	Poly(**1**)$_{150}$-py (2)	239
19	0.32	Poly(**1**)$_{100}$-py (2)	471[e]
20	0.16	Poly(**1**)$_{100}$-py (2) + pyridine (5)	284
21	0.16	2,2′-bpy (1)	374
22	0.16	2,2′-bpy (5)	377
23	0.16	Poly(**1**)$_{100}$-bpy(CHO) (2)	283
24	0.16	Poly(**1**)$_{100}$-bpy(Me) (2)	291

[a] Conditions: Ru(acac)$_3$ 0.002 mmol, cyclohexanone 1.0 mmol, ^{i}PrOH 1.5 mL, toluene 1.0 mL, 50 °C, 5 h.
[b] Initial NaO^{i}Pr conc. mmol/mL.
[c] Molar ratios Ligand/Ru.
[d] TON = (product in mmol)/Ru(mmol).
[e] 94% Yield.

2.2.1. ^{1}H and ^{31}P NMR spectra for catalyst solutions and recovered catalyst

Since the pyridine-attached ring-opened poly(NBE) was found to be effective as a ligand for the reduction of cyclohexanone in the presence of a ruthenium catalyst, we investigated the

Table 3
Ruthenium catalyzed hydrogen transfer reduction of cyclohexanone[a]

Run	Ru compound	Ligand (L/Ru)[b]	Temperature (°C)	Yield (%)	TON[c]
25	$Ru(acac)_3$	None	25	3	13
26	$Ru(acac)_3$	Pyridine (1)	25	5	26
27	$Ru(acac)_3$	Poly($\mathbf{1}$)$_{100}$-py (2)	25	6	30
11	$Ru(acac)_3$	None	50	42	210
12	$Ru(acac)_3$	Pyridine (1)	50	44	218
13	$Ru(acac)_3$	Pyridine (2)	50	46	228
17	$Ru(acac)_3$	Poly($\mathbf{1}$)$_{100}$-py (2)	50	48	238
28	$RuCl_2(PPh_3)_4$	None	50	36	181
29	$RuCl_2(PPh_3)_4$	Poly($\mathbf{1}$)$_{100}$-py (2)	50	43	216
30	$[RuI_2(p\text{-cymene})]_2$	None	50	31	157
31	$[RuI_2(p\text{-cymene})]_2$	Poly($\mathbf{1}$)$_{100}$-py (2)	50	42	212
32	$Ru(acac)_3$	None	70	96	481[d]
33	$Ru(acac)_3$	Pyridine (1)	70	99	494[d]
34	$Ru(acac)_3$	Poly($\mathbf{1}$)$_{100}$-py (2)	70	99	498[d]

[a] Conditions: Ru compound 0.002 mmol (as Ru), cyclohexanone 1.0 mmol, ^{i}PrOH 1.5 mL, toluene 1.0 mL, NaO^{i}Pr 0.40 mmol (0.16 mmol/mL), 5 h.
[b] Molar ratios Ligand/Ru.
[c] TON = (product in mmol)/Ru(mmol).
[d] Yields 96.2–99.9%.

Table 4
Time course for hydrogen transfer reduction of cyclohexanone catalyzed by Ru(acac)$_3$-poly($\mathbf{1}$)$_{100}$-py system[a]

Run	Time (h)	Yield (%)	TON[b]
35	1	21	105
36	2	27	134
37	3	42	208
17	5	48	238
38	10	73	366

[a] Conditions: Ru(acac)$_3$ 0.002 mmol, poly($\mathbf{1}$)$_{100}$-py 0.004 mmol, cyclohexanone 1.0 mmol, ^{i}PrOH 1.5 mL, toluene 1.0 mL, NaO^{i}Pr 0.4 mmol (0.16 mmol/mL).
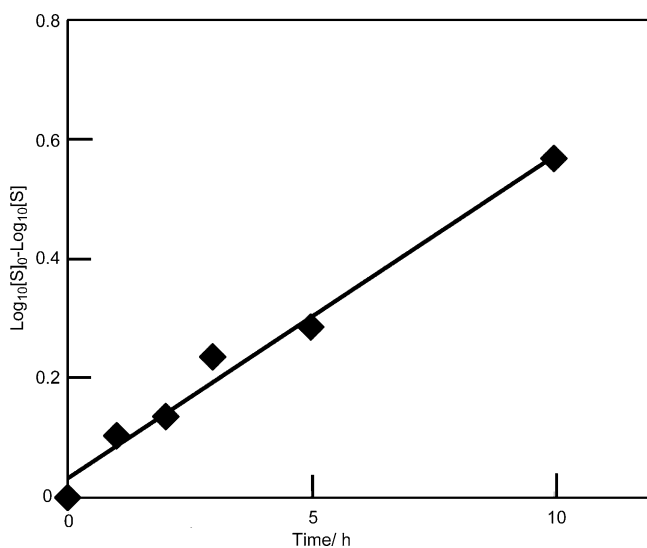[b] TON = (product in mmol)/Ru(mmol).

Fig. 1. Time course plots for the hydrogen transfer reduction of cyclohexanone catalyzed by Ru(acac)$_3$-poly($\mathbf{1}$)$_{100}$-py catalyst (detailed results are shown in Table 4). From this figure, the coefficient of 5.41×10^{-2} h^{-1} was obtained.

catalytically active species in the reaction mixture. Fig. 2 shows ^{31}P NMR spectra for (c) a mixed solution of RuCl$_2$(PPh$_3$)$_4$ and poly($\mathbf{1}$)$_{50}$-py and (d) Ru complex containing poly(NBE)$_{50}$-py [after heating in toluene/^{i}PrOH (1.0/1.5 mL) for 5 h at 50 °C] recovered by pouring the reaction mixture into methanol. The CDCl$_3$ solution containing RuCl$_2$(PPh$_3$)$_4$ (Fig. 2b) showed a mixture of the original complex and the dissociated species, RuCl$_2$(PPh$_3$)$_3$. It is clear that another PPh$_3$-coordinated species (as * in the spectra c) which is different from RuCl$_2$(PPh$_3$)$_4$ nor RuCl$_2$(PPh$_3$)$_3$ (as + in the spectrum c) was formed by the dissociation of PPh$_3$ and the resonance was the same as that in the recovered catalyst (d). The fact would also be supported by the reported facts that RuCl$_2$(PPh$_3$)$_3$ was reacted with norbornadiene (NBD), acetonitrile (MeCN) to afford the corresponding RuCl$_2$(PPh$_3$)$_2$(L)$_2$ (L: NBD, MeCN) in high yields [22–24]. Moreover, the ^{1}H NMR spectrum for the ruthenium complex, which was recovered as the precipitate after the reaction, consisted of mixed resonances of PPh$_3$ and ring-opened poly(NBE) [20]. Since the catalyst could be easily recovered by filtration as the precipitate, these results strongly suggest that pyridine in the poly($\mathbf{1}$)$_{100}$-py coordinates to the Ru in the reaction mixture.

Table 5
Effect of solvent for transfer hydrogenation of cyclohexanone catalyzed by Ru(acac)$_3$-poly($\mathbf{1}$)$_{100}$-py system[a]

Run	^{i}PrOH/toluene (mL/mL)	Yield (%)	TON[b]
39	0.5/2.0	17	83
40	1.0/1.5	33	164
17	1.5/1.0	48	238
41	2.0/0.5	52	261

[a] Conditions: Ru(acac)$_3$ 0.002 mmol, poly($\mathbf{1}$)$_{100}$-py 0.004 mmol, cyclohexanone 1.0 mmol, ^{i}PrOH + toluene total 2.5 mL, NaO^{i}Pr 0.4 mmol (0.16 mmol/mL).
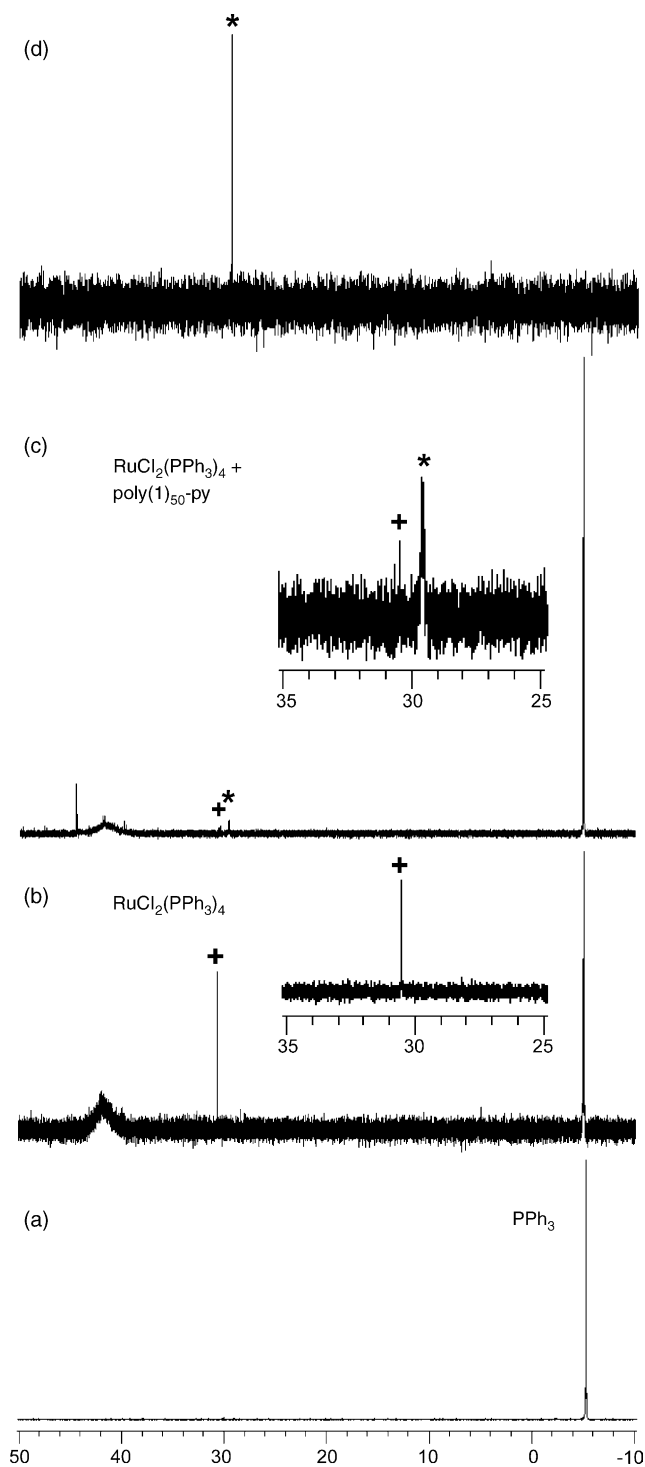[b] TON = (product in mmol)/Ru(mmol).

Fig. 2. ^{31}P NMR spectra (in CDCl$_3$ at 25 °C) for (a) free PPh$_3$, (b) RuCl$_2$(PPh$_3$)$_4$, (c) RuCl$_2$(PPh$_3$)$_4$ + poly(NBE)$_{50}$-py (2.0 equiv.), and (d) recovered Ru complex containing poly(NBE)$_{50}$-py [after heating in toluene/^{i}PrOH (1.0/1.5 mL) for 5 h at 50 °C, Ru(acac)$_3$ 0.004 mmol, 2 equiv. of poly($\mathbf{1}$)$_{50}$-py].

Moreover, the ^{1}H NMR spectrum (Fig. 3) for the recovered catalyst containing poly($\mathbf{1}$)$_{100}$-py after the reduction of cyclohexanone with Ru(acac)$_3$ showed that no olefinic double bonds were hydrogenated during this catalytic reaction [20]. This result may suggest that the present reduction took place not by hydrogenation with dihydrogen once formed by dehydrogenation of
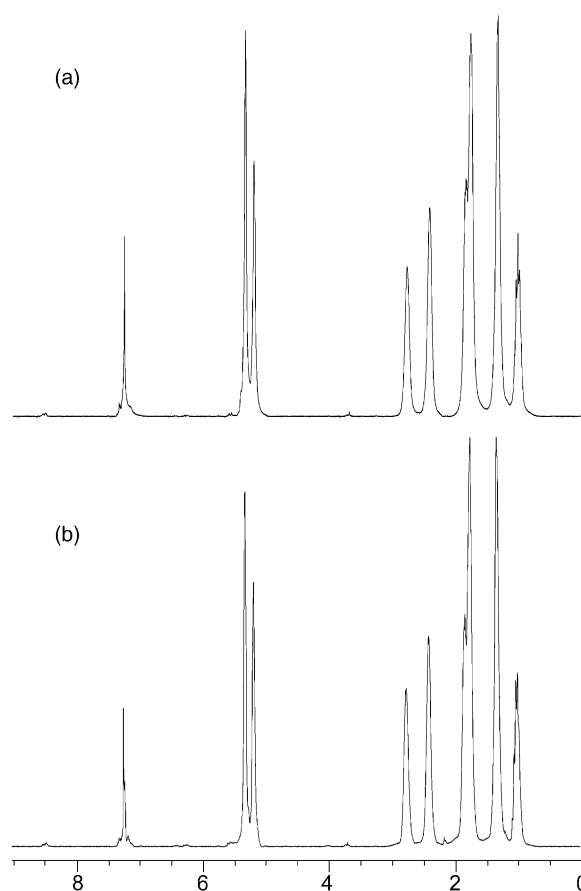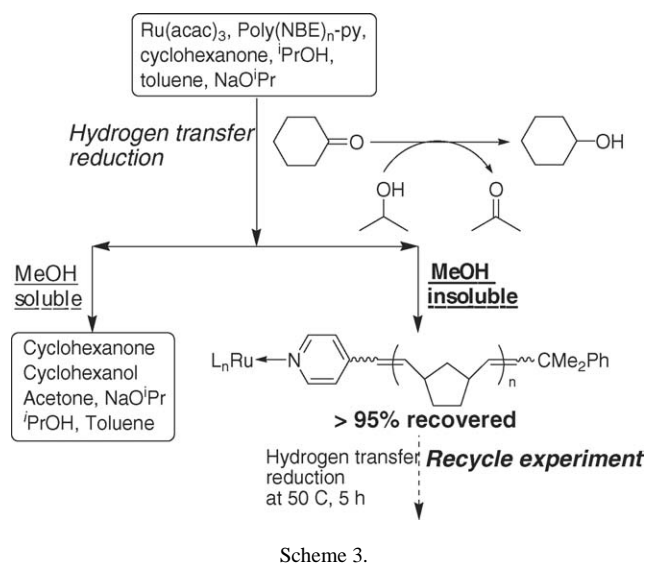

Fig. 3. ^{1}H NMR spectra for (a) ring-opened poly(NBE)$_{100}$-py and (b) the recovered catalyst after the reduction of cyclohexanone in the presence of Ru(acac)$_3$.

^{i}PrOH but by hydrogen transfer reduction generally proposed under these conditions. Since the olefinic double bonds in the ROMP polymer were not hydrogenated under these conditions, the result strongly suggests the possibility of exclusive reduction of carbonyl group in ketones in this recyclable catalysis, as described below.

2.3. Recycle experiment for hydrogen transfer reduction of cyclohexanone

As described above, the resultant ROMP polymer ligand was effective as the ligand for the catalytic hydrogen transfer reduction of cyclohexanone with Ru(acac)$_3$, RuCl$_2$(PPh$_3$)$_4$, or [RuI$_2$(p-cymene)]$_2$ in ^{i}PrOH/toluene in the presence of NaO^{i}Pr, and the activity increased upon the addition of the ligand. As also described above, the catalyst can be recovered by filtration as the precipitate by pouring the reaction mixture into a methanol solution (Scheme 3). The recovered yields were ca. 95% [25], and the catalyst can be reused without further purification after removing methanol in vacuo.

The results for the recycled experiments in the transfer hydrogenation of cyclohexanone in the presence of Ru(acac)$_3$ and poly($\mathbf{1}$)$_{100}$-py are summarized in Table 6 [26]. Several reaction runs were performed to check the reproducibility of these experimental runs (runs 17, 42–46) as well as to perform the reaction

Scheme 3.

Fig. 4. Recycled experiments for hydrogen transfer reduction of cyclohexanone with Ru(acac)$_3$-poly(**1**)$_{100}$-py (runs 42–52, Table 6).

with the same amount of catalyst in the recycled experiments. Fig. 4 shows the plot of TON values in each of the experimental runs for the transfer hydrogenation of cyclohexanone. It is clear that the TON values did not change significantly by reusing

Table 6
Hydrogenation transfer reduction of cyclohexanone catalyzed by Ru(acac)$_3$-poly(**1**)$_{100}$-py system[a]

Run	Catalyst (molar ratio to Ru)[b]	NaO^{i}Pr (mmol)	TON[c]
17	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.4	238
42	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.4	237
43	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.4	238
44	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.4	210
45	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.4	241
46	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.4	239
47	Recycled from runs 42–45 (2nd cycle)	0.4	219
48	Recycled from runs 42–45 (2nd cycle)	0.4	208
49	Recycled from runs 47–48 (3rd cycle)	0.4	210
50	Recycled from runs 47–48 (3rd cycle)	0.4	241
51	Recycled from runs 49–50 (4th cycle)	0.4	221
52	Recycled from runs 46, 51 (5th cycle)[d]	0.4	218
19	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.8	471[e]
53	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.8	471[e]
54	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	0.8	481[e]
55	Recycled from runs 53–54 (2nd cycle)	0.8	158
20	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)/py (5)	0.4	284
55	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)/py (5)	0.4	258
56	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)/py (5)	0.4	316
57	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)/py (5)	0.4	306
58	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)/py (5)	0.4	290
59	Recycled from runs 55–58 (2nd cycle)	0.4	234
60	Recycled from runs 55–58 (2nd cycle)	0.4	280
61	Recycled from runs 55–58 (2nd cycle)	0.4	200
62	Recycled from runs 59–61 (3rd cycle)	0.4	240
63	Recycled from runs 59–61 (3rd cycle)	0.4	216
64	Recycled from runs 62–63 (4th cycle)	0.4	243

[a] Conditions: Ru cat. 0.002 mmol, cyclohexanone 1.0 mmol, ^{i}PrOH 1.5 mL, toluene 1.0 mL, 50 °C, 5 h.
[b] Molar ratios for additives (ligand)/Ru.
[c] TON = (product in mmol)/Ru(mmol).
[d] Recycled catalyst from run 51 and small amount of catalyst recovered from run 46.
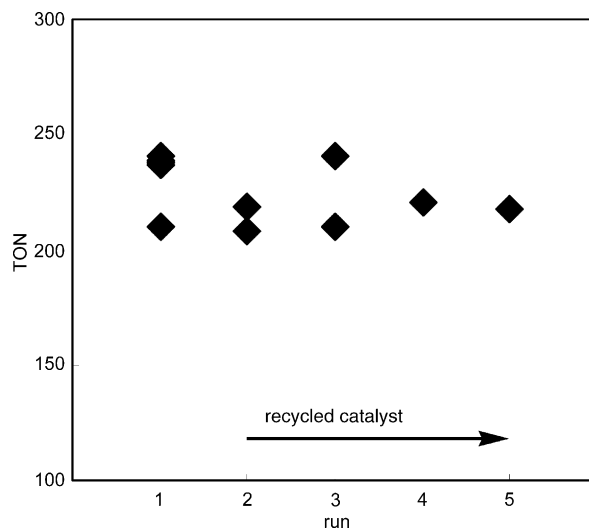[e] Yields 94–96%.

the catalyst (runs 42–52 in Table 6). Although the reduction completed under high NaO^{i}Pr concentration conditions (NaO^{i}Pr 0.80 mmol, run 53–55), the activity using the recovered catalyst decreased probably due to partial decomposition. As described in Table 2, further addition of pyridine increased the catalytic activity (runs 20, 55–58), and the TON values in the recycled runs (runs 59–64) reached those obtained in the absence of pyridine (runs 47–52) probably due to the dissociation of additional pyridine (not the polymer attached ligand) from the ruthenium. These results suggest that the pyridine ligand attached to the ROMP polymer chain end strongly coordinates to ruthenium. Taking these results into account, the present ruthenium catalyst can be easily reused without deactivation. Since the molecular weight for the supported catalyst can be tuned by varying the monomer/initiator molar ratio in the living polymerization step, we believe the catalyst system presented here is a promising candidate that possesses unique characteristics for designing efficient recyclable catalytic systems.

2.4. Application to chemoselective catalytic reduction of unsaturated ketones

As described above, the possibility for chemoselective reduction of the carbonyl group of ketones was suggested in this catalysis, because the olefinic double bond in the ROMP polymer was not hydrogenated under these reaction conditions (Fig. 3). Therefore, the reduction of various ketones using the Ru(acac)$_3$-poly(**1**)$_{100}$-py catalyst were explored under the same conditions as for cyclohexanone. The results are summarized in Table 7.

The catalytic activity slightly increased upon addition of the polymer ligand, poly(**1**)$_{100}$-py, in the reduction of acetophenone, and the reaction product formed was 1-phenylethanol exclusively. In addition, the chemospecific reduction of carbonyl group in 5-hexen-2-one proceeded to afford 5-hexen-2-ol in this catalysis, and the activity increased upon the addition of the polymer ligand. Moreover, the reduction of 2-allyl-cyclohexanone under the same conditions afforded 2-allyl-cyclohexanol with

Table 7
Hydrogen transfer reduction of various ketones[a]

Run	Catalyst (molar ratio to Ru)[b]	Substrate	Product	TON[c]
65	Ru(acac)$_3$	PhCOCH$_3$	PhCH(OH)CH$_3$	126
66	Ru(acac)$_3$/pyridine (1)	PhCOCH$_3$	PhCH(OH)CH$_3$	133
67	Ru(acac)$_3$/pyridine (2)	PhCOCH$_3$	PhCH(OH)CH$_3$	139
68	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	PhCOCH$_3$	PhCH(OH)CH$_3$	141
69	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2) + py (5)	PhCOCH$_3$	PhCH(OH)CH$_3$	154
70	Ru(acac)$_3$	5-Hexen-2-one	5-Hexen-2-ol	91
71	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	5-Hexen-2-one	5-Hexen-2-ol	175
72	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	5-Hexen-2-one	5-Hexen-2-ol	197
73	Ru(acac)$_3$	2-Allyl-cyclohexanone	2-Allyl-cyclohexanol	104
74	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	2-Allyl-cyclohexanone	2-Allyl-cyclohexanol	124
75	Ru(acac)$_3$/poly(**1**)$_{100}$-py (2)	2-Allyl-cyclohexanone	2-Allyl-cyclohexanol	125
76	Recycled from runs 74–75	2-Allyl-cyclohexanone	2-Allyl-cyclohexanol	125

[a] Conditions: Ru(acac)$_3$ 0.002 mmol, substrate 1.0 mmol, ^{i}PrOH 1.5 mL, toluene 1.0 mL, NaO^{i}Pr 0.4 mmol (0.16 mmol/mL), 50 °C, 5 h.
[b] Molar ratio of ligand additive/Ru.
[c] TON = (product in mmol)/Ru(mmol).
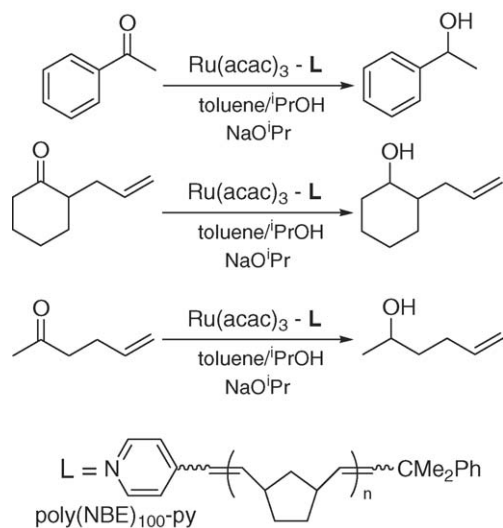
Scheme 4.

exclusive reduction of the carbonyl group, and the catalyst can be reused without decrease in the activity (runs 74–76). These results clearly indicate that selective reduction of carbonyl group can be achieved in the present catalysis (Scheme 4).

3. Concluding remarks

We have introduced a new type of polymer soluble ligand that possesses a ligand moiety only at the polymer chain end prepared by the living ROMP technique using the well-defined molybdenum-alkylidene initiator. The prepared pyridine ligand was effective for ruthenium catalyzed hydrogen transfer reduction of cyclohexanone, and the catalyst can be recovered by filtration and can be reused without decreasing the catalytic activity. Moreover, the exclusive reduction of carbonyl groups can be achieved in this catalysis. Since the molecular weight of the polymer ligand can be simply modified only by varying

the monomer/initiator molar ratios, also since the polymer main chain will also be modified not only by use of substituted norbornene but also by using the block copolymerization in this living ROMP chemistry, we certainly believe that the present approach should introduce a new insight to study polymer supported catalysis chemistry.

4. Experimental section

4.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres dry-box or using standard Schlenk techniques. All chemicals used were of reagent grade and were purified by the standard purification procedures. Polymerization grade toluene was distilled from sodium and benzophenone, stored over sodium/potassium alloy in the dry-box, and was then passed through an alumina short column prior to use. NaO^{i}Pr was prepared by treating ^{i}PrOH with Na under nitrogen atmosphere, and isolated as a white solid. Ru(acac)$_3$ (acac: acetylacetonato), RuCl$_2$(PPh$_3$)$_4$ were purchased from STREM and were used as received. [RuI$_2$(*p*-cymene)]$_2$ was prepared according to the previous report [27]. The molybdenum initiators of the type (ArN)Mo(CHCMe$_2$Ph)(O^{t}Bu)$_2$ (Ar: 2,6-^{i}Pr$_2$C$_6$H$_3$) was prepared according to the literature [28], and 4-pyridinecarboxaldehyde (Aldrich) was used without further purification. 4,4′-diformyl-2,2′-bipyridyl (B) [18], or 4-formyl-4′-methyl-2,2′-bipyridyl [19] were also prepared according to the literature.

All ^{1}H-and ^{13}C-NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (^{1}H, 399.65 MHz; ^{13}C, 100.40 MHz), and were obtained in the solvent indicated at 25 °C, with all chemical shifts quoted in ppm and referenced to SiMe$_4$. HPLC grade THF was used for GPC and was degassed prior to use. GPC were performed at 40 °C on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns

(ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm φ) were calibrated versus polystyrene standard samples.

4.2. Polymer synthesis

Typical polymerization procedure is as follows: a certain amount of toluene solution containing Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ (80 μmol in toluene 1.0 g) was added in one portion to a rapidly stirred toluene solution (4.4–8.9 g, shown in Table 1) containing the prescribed amount of norbornene at 25 °C, and the reaction mixture was stirred for 30 min. The polymerization was quenched by adding 4-pyridinecarboxaldehyde in excess amount after the consumption of monomers, and stirred for 1 h for completion. The resultant solution was poured drop wise to stirred cold methanol (∼200 mL), affording white–pale yellow precipitates. The polymer was collected by filtration, and was then dried in vacuo. Yield >95%. ^{1}H NMR (CDCl$_3$): δ 5.18 and 5.32 (m, 2H olefinic), 2.76 and 2.37 (br.s, 2H), 1.85 and 1.04 (m, 2H), 1.78 and 1.33 (m, 4H). Peaks corresponding to the polymer chain end could also be observed: δ 8.52 and 8.47 (d, pyridine), 6.42 (m, Py–CH=CH–), 6.24 (dd, Py–CH=CH–), 5.56 (d, PhMe$_2$CCH=CH–), and 5.33 (m, PhMe$_2$CCH=CH–). Other resonances corresponding to phenyl group were also observed.

Syntheses of other ligands were also prepared by the living ROMP terminated with 4,4′-diformyl-2,2′-bipyridyl, and with 4-formyl-4′-methyl-2,2′-bipyridyl under the same conditions. ^{1}H NMR (CDCl$_3$) for poly(NBE)-bpy(CHO): δ 5.19 and 5.32 (m, 2H olefinic), 2.77 and 2.41 (br. s, 2H), 1.84 and 1.02 (m, 2H), 1.84 and 1.33 (m, 4H), 8.91 and 8.90 (d, 2H 2,2′-bipyridine), 8.64 and 8.61 (d, 2H 2,2′-bipyridine), 8.42 and 8.32 (s, 2H 2,2′-bipyridine), 10.18 (s, CHO). ^{1}H NMR (CDCl$_3$) for poly(NBE)-bpy(Me): δ 5.19 and 5.32 (m, 2H olefinic), 2.77 and 2.41 (br. s, 2H), 1.84 and 1.02 (m, 2H), 1.84 and 1.33 (m, 4H), 8.58 and 8.32 (d, 2H 2,2′-bipyridine), 8.53 and 8.21 (s, 2H 2,2′-bipyridine).

4.3. Catalytic hydrogen transfer reduction of ketones

The catalytic reductions were typically carried out as follows: into an Schlenk tube (50 mL) Ru(acac)$_3$ (acac: acetylacetonato), ligand, toluene, ^{i}PrOH, and cyclohexanone (substrate) were charged under nitrogen atmosphere. The reaction mixture was stirred under N$_2$ at 50 °C for the prescribed time (5 h). The reaction product was then determined by GLC using an internal standard and was identified by using GLC by co-injection with the authentic samples under different conditions (Column: DB-1 30 m, 0.25 mm φ × 0.25 μm), and GC-MS (GC-MS QP 5000, Shimazu Co. Ltd.). After the reaction, the solution was poured into cold methanol (50 mL), and the resultant precipitate was collected by filtration, and the recovered catalyst was dried in vacuo, and was reused without further purification. Recycled experiments were carried out by using the recovered catalyst mixed with independent runs to compare the catalyst performance under the same conditions [26], and we used the recycled catalyst with the same amount of poly(**1**)$_{100}$-py [calculated as C$_{716}$H$_{1018}$N, F_w: 9639, 0.004 mmol (39 mg)] we charged in the first experiments, because the molecular weight for ring-opened poly(NBE) being much higher than those for others (ruthenium, etc.).

Appendix A. Supplementary data

Supplementary data such as (1) ^{1}H NMR spectra (in CDCl$_3$ at 25 °C) for poly(NBE)s prepared by Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ terminated with various aldehydes, (2) ^{1}H NMR spectra (in CDCl$_3$ at 25 °C) for RuCl$_2$(PPh$_3$)$_4$, RuCl$_2$(PPh$_3$)$_4$ + poly(NBE)$_{50}$-py (1.0 equiv.), and the recovered Ru complex. These supplementary data associated with this article can be found in the online version, at doi:10.1016/j.molcata.2005.09.047.

References

[1] For example:
  (a) T.W. Ford, Polymeric Reagents and Catalysts ACS Symposium Series 308, American Chemical Society Washington, DC, 1986, p. 1;
  (b) R.B. Merrifield, Angew. Chem. 97 (1985) 801.
[2] Reviews concerning soluble polymer ligands:
  (a) D.J. Gravert, K.D. Janda, Chem. Rev. 97 (1997) 489;
  (b) P. Wentworth Jr., K.D. Janda, Chem. Commun. (1999) 1917;
  (c) P.H. Toy, K.D. Janda, Accounts Chem. Res. 33 (2000) 546;
  (d) P.H. Toy, T.S. Reger, K.D. Janda, Aldrichim. Acta 33 (2000) 87;
  (e) C.W. Hartwig, D.J. Gravert, K.D. Janda, Chemtracs 12 (1999) 1;
  (f) D.E. Bergbreiter, Med. Res. Rev. 19 (1999) 439;
  (g) D.E. Bergbreiter, in: P.T. Anastas, L.G. Heine, T.C. Williamson (Eds.), Green Chemical Syntheses and Processes, ACS Symposium Series 767, American Chemical Society, Washington, DC, 2000, p. 182;
  (h) D.E. Bergbreiter, J. Polym. Sci. Part A: Polym. Chem. 39 (2001) 2351;
  (i) S. Borman, Chem. Eng. News June 4 (2001) 49;
  (j) T.J. Dickerson, N.N. Reed, K.D. Janda, Chem. Rev. 102 (2002) 3325;
  (k) D.E. Bergbreiter, Chem. Rev. 102 (2002) 3345.
[3] For example (dendrimer):
  (a) J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, Nature 372 (1994) 659;
  (b) M.A. Hearshaw, J.R. Moss, Review Chem. Commun. (1999) 1;
  (c) R.M. Crooks, M. Zhao, L. Sun, V. Chechik, L.K. Yeung, Accounts Chem. Res. 34 (2001) 181.
[4] For example: D.E. Bergbreiter, Catal. Today 42 (1998) 389.
[5] Use of ROMP polymer as the ligand, for example:
  (a) M.R. Buchmeiser, K. Wurst, J. Am. Chem. Soc. 121 (1999) 11101;
  (b) M.R. Buchmeiser, Chem. Rev. 100 (2000) 1565;
  (c) A.G.M. Barrett, B.T. Hopkins, J. Kobberling, Chem. Rev. 102 (2002) 3301;
  (d) A.M. Harned, M. Zhang, P. Vedantham, S. Mukherjee, R.H. Herpel, D.L. Flynn, P.R. Hanson, Aldrichim. Acta 38 (2005) 3.
[6] Examples as the pioneering works:
  (a) G.C. Bazan, E. Khosravi, R.R. Schrock, W.J. Feast, V.C. Gibson, M.B. O'Regan, J.K. Thomas, W.M. Davis, J. Am. Chem. Soc. 112 (1990) 8378;
  (b) G.C. Bazan, J.H. Oskam, H. Cho, L.Y. Park, R.R. Schrock, J. Am. Chem. Soc. 113 (1991) 6899.

[7] For example:
(a) R.R. Schrock, in: Y. Imamoglu (Ed.), Metathesis Polymerization of Olefins and Polymerization of Alkynes, NATO ASI Series, Kluwer Academic Publishers, 1998, p. pp. 1, 357;
(b) R.R. Schrock, A. Fürstner (Eds.), Alkene Metathesis in Organic Synthesis, Springer-Verlag, Berlin Heidelberg, 1998, p. 1.

[8] G.C. Bazan, R.R. Schrock, H. Cho, V.C. Gibson, Macromolecules 24 (1991) 4495.

[9] K. Nomura, S. Takahashi, Y. Imanishi, Macromolecules 34 (2001) 4712.

[10] J.J. Murphy, T. Kawasaki, M. Fujiki, K. Nomura, Macromolecules 38 (2005) 1075.

[11] K. Nomura, H. Ogura, Y. Imanishi, J. Mol. Catal. A 185 (2002) 311.

[12] (a) K. Nomura, Chem. Lett. (1991) 1679;
(b) K. Nomura, J. Mol. Catal. 73 (1992) L1;
(c) K. Nomura, J. Mol. Catal. A 95 (1995) 203;
(d) K. Nomura, J. Mol. Catal. A 130 (1998) 1 (Review).

[13] Part of these results have been previously presented: Y. Kuromatsu, M. Fujiki, K. Nomura, International Symposium on Catalysis and Fine Chemicals 2004, Hong Kong, 2004, p. 9.

[14] Examples for reviewing articles for (asymmetric) transfer hydrogenation;
(a) G. Zassinovich, G. Mestroni, S. Gladiali, Chem. Rev. 92 (1992) 1051;
(b) R. Noyori, S. Hashiguchi, Accounts Chem. Res. 30 (1997) 97;
(c) T. Naota, H. Takaya, S.-I. Murahashi, Chem. Rev. 98 (1998) 2599;
(d) M.J. Palmer, M. Wills, Tetrahedron Asymmetry 10 (1999) 2045;
(e) J.-E. Bäckvall, J. Organomet. Chem. 652 (2002) 105;
(f) K. Everaere, A. Mortreux, J.F. Carpentier, Adv. Synth. Catal. 345 (2003) 67;
(g) H.-U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner, M. Studer, Adv. Synth. Catal. 345 (2003) 103.

[15] Selected examples for transfer hydrogenation of ketones;
(a) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A.F. England, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. 37 (1998) 1703;
(b) M. Yamakawa, H. Ito, R. Noyori, J. Am. Chem. Soc. 122 (2000) 1466;
(c) K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J.N. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104.

[16] Recent examples for transfer hydrogenation in the presence of 2-(aminometyl)pyridine-phosphine ruhtnium(II) complexes, W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, Organometallics 24 (2005) 1660.

[17] Recent examples for (asymmetric) transfer hydrogenation of ketones using recyclable ruthenium catalysts;
(a) P.N. Liu, P.M. Gu, F. Wang, Y.Q. Tu, Org. Lett. 6 (2004) 169;
(b) S. Bastin, R.J. Eaves, C.W. Edwards, O. Ichihara, M. Whittaker, M. Wills, J. Org. Chem. 69 (2004) 5405.

[18] L. Della Ciena, W.J. Dressick, A. von Zelewsky, J. Heterocycl. Chem. 27 (1990) 163.

[19] L. Della Ciena, I. Hamachi, T.J. Meyer, J. Org. Chem. 54 (1989) 1731.

[20] Detailed results (selected ^{1}H NMR spectra for estimation of the Mn values, ^{1}H NMR spectra for the catalyst solution, recovered catalyst) are shown in the Supplementary data.

[21] The same trend was also seen if 4-Me$_3$SiC$_6$H$_4$CHO was used in place of 4-pyridinecarboxaldehyde, and the exact molecular weights were almost identical with those based on the initial molar ratios, which were confirmed from both the ^{1}H NMR spectra and MALDI-TOF mass spectrometry.

[22] For example, S. Komiya, M. Hirano, in: S. Komiya (Ed.), Synthesis of Organometallic Compounds: Practical Guide, John Wiley and Sons Ltd., Baffins Lane, England, 1997, p. 159.

[23] Reaction with norbornadiene, S.D. Robinson, G. Wilkinson, J. Chem. Soc. A (1965) 843.

[24] Reaction with MeCN, D.J. Cole-Hamilton, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1979) 1283.

[25] This is due to the fact that a trace amount of polymer was lost during the filtration/precipitation process to recover the catalyst (ca. 39 mg) from the reaction mixture (total 50 mL).

[26] We used the recycled catalyst with the same amount of poly($\mathbf{1}$)$_{100}$-py [calculated as C$_{716}$H$_{1018}$N, F_w: 9639, 0.004 mmol (39 mg)] which we used in the first experiments, because the molecular weight for ring-opened poly(NBE) being much higher than those for others (ruthenium, etc.).

[27] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.

[28] (a) G.C. Bazan, E. Khosravi, R.R. Schrock, W.J. Feast, V.C. Gibson, M.B. O'Reagan, J.K. Thomas, W.M. Davis, J. Am. Chem. Soc. 112 (1990) 8378;
(b) G.C. Bazan, J.H. Oskam, H. Cho, L.Y. Park, R.R. Schrock, J. Am. Chem. Soc. 113 (1991) 6899.