ORGANOMETALLICS
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Use of Pyridine-Coated Star-Shaped ROMP Polymer As the Supporting Ligand for Ruthenium-Catalyzed Chemoselective Hydrogen Transfer Reduction of Ketones

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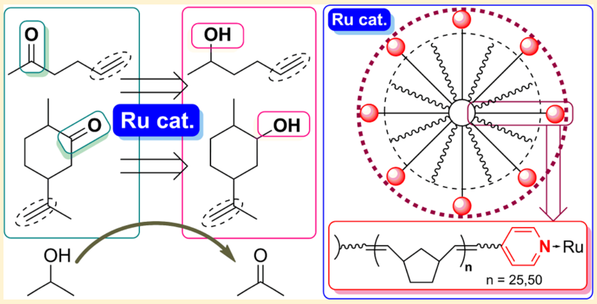
S *Supporting Information*

ABSTRACT: "Soluble" star-shaped polymers containing a pyridine ligand at the chain ends, prepared by adopting sequential living ring-opening metathesis polymerizations (ROMP) of norbornene and a cross-linking reagent using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ via a "core-first" approach, have been employed as ligands for Ru-catalyzed chemoselective hydrogen transfer reductions of various ketones (cyclohexanone, 5-hexen-2-one, 2-allylhexanone, 5-isopropenyl-2-methylcyclohexanone). The activity increased upon addition of the above polymer as the ligand: the prepared catalyst could be recovered quantitatively and reused without decreasing in both activity and selectivity.



INTRODUCTION

Precise control over macromolecular structure is a fascinating goal in polymer synthesis, and unique characteristics of living polymerizations (absence of chain transfer and termination, etc.), such as ring-opening metathesis polymerization (ROMP), controlled radical polymerization, and anionic polymerization, present techniques for accomplishing this purpose.[1] Star polymers containing multiple linear arms connected at a central branched core represent one of the simplest nonlinear polymers,[1,2] and ROMP[3,4] has also been used for the synthesis of cross-linked polymers.[5−8] We recently demonstrated a controlled synthesis of "soluble" star polymers by the living ROMP technique using a Mo-alkylidene initiator by simple sequential additions of norbornene (NBE) and the cross-linker (CL).[7] An exclusive introduction of functionality into the ROMP polymer chain end can be easily achieved through a cleavage of the ROMP polymer−metal double bonds (of Schrock-type Mo-alkylidene) with aldehyde, yielding a carbon−carbon double bond via a Wittig-like reaction.[4,6e,7,9]

Use of soluble polymer-supported ligands (instead of insoluble polymer resins such as divinylbenzene, cross-linked polystyrene[10]) for preparation of supported transition metal complex catalysts that maintain unique characteristics in the homogeneous analogues has been recognized as one of the most attractive subjects in the field of catalysis and synthetic organic chemistry.[11−14] We previously reported that ring-opened poly(NBE) containing pyridine or 2,2′-bipyridyl moieties at the chain end, prepared by living ROMP using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(O^tBu)_2$ terminated with the corresponding aldehyde(s), can be used as "ROMP polymer-attached" ligands for catalytic hydrogen transfer reduction of cyclohexanone in the presence of ruthenium compounds.[15−17] Exclusive reductions of the carbonyl group in various ketones (for example, acetophenone, 5-hexen-2-one, 2-allylhexanone) could be achieved in this catalysis, and the recovered catalyst could be reused without decreases in both the activity and selectivity (although, as described below, the recovered yields from the mixture were not perfect).[15] Moreover, we also demonstrated that a half-titanocene containing an aryloxide ligand immobilized on the chain end of ring-opened poly(NBE)s exhibited similar catalyst performances (activity, monomer reactivity) to the nonsupported, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ for ethylene/1-hexene copolymerization in the presence of methylaluminoxane (MAO).[18] Since we believe that the approach should be promising for immobilization of homogeneous catalysts, in this paper, we thus present the synthesis of pyridine-modified star-shaped ring-opened poly(NBE) and its application as the polymer-supported ligand for ruthenium-catalyzed chemoselective hydrogen transfer reduction of various ketones.[19−21]

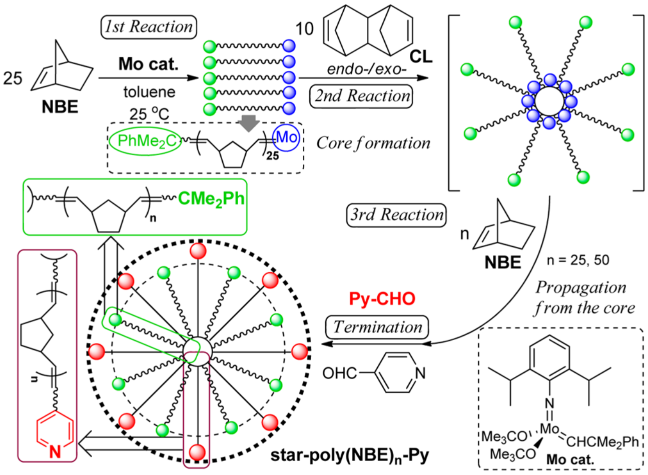
RESULTS AND DISCUSSION

1. Synthesis of Pyridine-Modified Star-Shaped Ring-Opened Poly(norbornene) and Measurement of Spherical Aggregates by Transmission Electron Microscopy.

According to our previous communication (Scheme 1),[7a] high molecular weight ring-opened star-shaped polymers, defined as

Received: May 15, 2012
Published: July 2, 2012

Scheme 1. Synthesis of Soluble star-shaped ROMP polymers employed in the present study



star-poly(NBE)$_{25}$-Py, with unimodal molecular weight distributions (M_n = (8.03−8.46) × 10^4, M_w/M_n = 1.21−1.34, runs 1−3, Table 1) could be prepared by adopting the sequential living ring-opening metathesis polymerizations of norbornene and a cross-linking reagent (1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphthalene) (CL, *exo*:*endo* = 0.17:1.00)[22] using Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$.[23] As reported previously, the present approach enables synthesis of star-shaped polymers that are soluble in common organic solvents, because the molybdenum catalyst shows markedly higher reactivity toward *strained* cyclic olefins than the internal olefins (in the ring-opened polymers),[9c,d] and the core is covered with ROMP polymers (Scheme 1). 4-Pyridine carboxaldehyde was chosen to terminate the living ROMP as well as to introduce the pyridine moiety at the polymer chain end, and the resultant polymers are highly soluble in ordinary organic solvents such as toluene, THF, dichloromethane, and chloroform. The M_n values in the resultant polymers increased upon increasing the amount of NBE in the third polymerization (25 → 50 equiv to Mo, runs 1−4). The observed increase in the M_n value [ca. 39 500 (by GPC vs polystyrene standards) from runs 1−4] was much higher than those in the linear poly(NBE) [increased 25 NBE repeating units, 2354 by molecular weight], suggesting that the resultant ROMP polymers are star-shaped polymers consisting of a core and NBE branching (first and third polymerization).[24]

Table 1. Synthesis of Pyridine Modified Star-Shaped ROMP Polymers, star-poly(NBE)$_n$-Py^a

	third reaction				
run	NBE/Mo (n)^b	time/min	M_n^{c} × 10^{-4}	M_w/M_n^{c}	yield^d/%
1	25	15	8.45	1.23	99
2	25	15	8.46	1.21	97
3	25	15	8.03	1.34	99
4	50	20	12.4	1.39	99

^{a}Conditions: toluene (total 10.0 g) at 25 °C, Mo cat. 1.0 × 10^{-2} mmol, 1st NBE 0.25 mmol, CL 0.10 mmol (detailed conditions, see Supporting Information).[23] ^{b}Starting feedstock ratio (n in Scheme 1). ^{c}GPC data in THF vs polystyrene standards. ^{d}Isolated yields.

Figure 1 shows selected transmission electron microscopy (TEM) micrographs of thin films prepared by casting the resultant ROMP polymers [**star-poly(NBE)$_n$-Py**, run 3 (left and middle, n = 25) and run 4 (right, n = 50)] on a plastic (perforated polymer, polyvinyl formal) coated Cu grid.[23] The resulting micrographs depict formation of uniform spherical images with average diameters of 58 nm (run 3) or 106 nm (run 4).[23] The diameter is similar to that reported previously (52 nm),[7a] and seems to correspond to those consisting of the arm and a core.[23] The results thus suggest that the observed micrographs should be ascribed to a single star (ball)-shaped polymers prepared by adopting the present ROMP methodology.

2. Hydrogen Transfer Reduction of Cyclohexanone Using RuCl$_2$(PPh$_3$)$_4$ −Polymer Ligand Catalysts. On the basis of our previous report,[15] hydrogen transfer reduction of cyclohexanone using RuCl$_2$(PPh$_3$)$_4$ was conducted to explore the performance of **star-poly(NBE)$_{25}$-Py** as the ligand in this catalysis (Scheme 2). A linear ROMP polymer containing pyridine at the chain end, **poly(NBE)$_{100}$-Py**,[15,23] was also used for comparison. The results are summarized in Table 2 (and Tables S6 and S7 in the Supporting Information (SI)).[25] As reported previously (and shown in Table S5 in the SI),[15,25] the activity was affected by NaO^{i}Pr concentration and also increased upon addition of a small amount of pyridine (1.0 equiv to Ru, run 6; **poly(NBE)$_{100}$-Py**, run 7).[26]

Note that the activity increased upon addition of the star-ROMP polymer, **star-poly(NBE)$_{25}$-Py**, and that the activities were not affected by the chain length employed (runs 8−10 in Table 2, the NBE/Mo molar ratio in the third reaction), which corresponds to the size of the star ROMP polymer shown in Figure 1. The observed activities were close to those in the

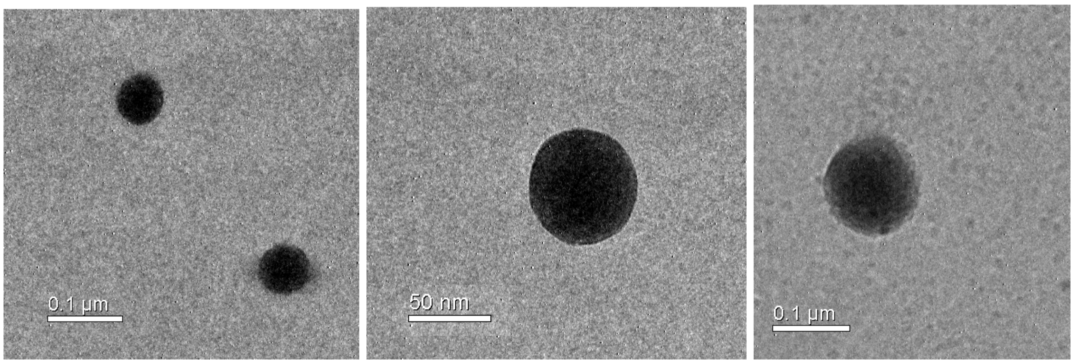


Figure 1. TEM micrographs of thin films prepared by casting **star-poly(NBE)$_{25}$-Py** (left and middle, run 3, Table 1) and **star-poly(NBE)$_{50}$-Py** (right, run 4, Table 1) on a plastic-coated copper grid at a concentration of 10^{-5} mg/mL at varying magnification.[23]

Scheme 2

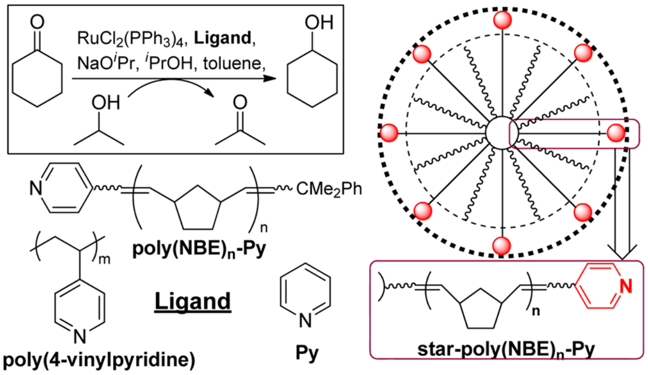


Table 2. Hydrogen Transfer Reduction of Cyclohexanone by RuCl$_2$(PPh$_3$)$_4$ star-poly(NBE)$_{25}$-Py and poly(NBE)$_{100}$-Py Catalysts[a]

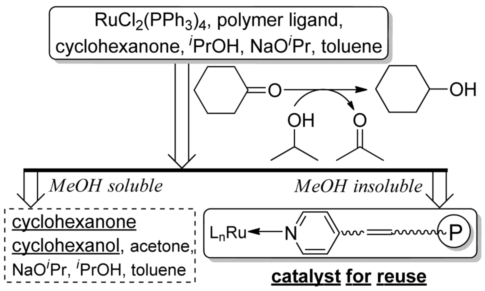
run	ligand (L/Ru)[b]	TON[c] (yield in %)[d]
5		177 (59)
6	Py (1)	249 (83)
7	**poly(NBE)$_{100}$-Py** (1)	243 (81)
8	**star-(polyNBE)$_{25}$-Py** (1)	248 (83)
9	**star-(polyNBE)$_{50}$-Py** (1)	252 (84)
10	**star-(polyNBE)$_{50}$-Py** (1)	234 (78)
11	poly(4-vinylpyridine) (1)	33 (11)
12	poly(4-vinylpyridine) (50)	18 (6)
13	poly(4-vinylpyridine) (100)	6 (2)

[a] Conditions: 50 °C, 5 h, cyclohexanone 3.0 mmol, RuCl$_2$(PPh$_3$)$_4$ 0.01 mmol, NaO^{i}Pr 0.8 mmol, ^{i}PrOH 3.0 mL, toluene 2.0 mL. [b] Molar ratios of L/Ru (L = pyridine). [c] TON = (product in mmol)/Ru (mmol). [d] Yield estimated by GC using internal standard.

linear polymer, **poly(NBE)$_{100}$-Py** (run 7, Table 2) and free pyridine (run 6). These results clearly indicate that use of the present "star polymer-attached" pyridine ligand is potentially effective in this ruthenium catalysis. In contrast, the activity decreased upon addition of poly(4-vinylpyridine): the activity decreased by further addition (runs 11–13).

The catalyst supported on **star-(polyNBE)$_{25}$-Py** could be separated from the reaction products and recovered by filtration as the precipitate by pouring the reaction mixture into a methanol solution (Scheme 3). The recovered yields were quantitative in all cases. This is an interesting contrast to the fact that the recovered yields were 89–95% in the linear polymers, **poly(NBE)$_{100}$-Py**,[25] due to loss of a trace amount of polymer during the filtration/precipitation process: the recovered yields decreased (ca. 70–80% yields) when **poly(NBE)$_{25}$-Py** at low NBE repeating units was used as the ligand due to the improved solubility in methanol.

Scheme 3



We conducted the recycled experiments using the recovered catalyst without further purification (removal of methanol *in vacuo* after filtration), because we assumed that the pyridine moiety on the star polymer would be strongly coordinated to Ru on the basis of our previous results.[15] The results are summarized in Table 3.[25] Several reaction runs were performed to check the reproducibility, and the results in detail are summarized in Table S6 in the SI.[25] The experiments using **poly(NBE)$_{100}$-Py** were also conducted for comparison. Figure 2 shows plots of the TON values in each of the experimental runs.[25]

Table 3. Hydrogen Transfer Reduction of Cyclohexanone by RuCl$_2$(PPh$_3$)$_4$/star-poly(NBE)$_{25}$-Py or poly(NBE)$_{100}$-Py Catalysts: Selected Results for the Catalyst Recycle Experiments[a]

catalyst	time/h	TON[b] (yield in %)[c]
RuCl$_2$(PPh$_3$)$_4$ + **star-poly(NBE)$_{25}$-Py**	5	249 (83)
recycled runs (first recycle)	5	240 (80)
recycled runs (second recycle)	5	255 (85)
recycled runs (third recycle)	5	246 (82)
recycled runs (fourth recycle)	5	249 (83)
recycled runs (first recycle)	10	291 (97)
recycled runs (second recycle)	10	282 (94)
recycled runs (fourth recycle)	10	288 (96)
RuCl$_2$(PPh$_3$)$_4$ + **poly(NBE)$_{100}$-Py**	5	243 (81)
recycled runs (first recycle)	5	246 (82)
recycled runs (second recycle)	5	252 (84)
recycled runs (third recycle)	5	255 (85)
recycled runs (fourth recycle)	5	243 (81)
recycled runs (fourth recycle)	10	282 (94)

[a] Conditions: 50 °C, cyclohexanone 3.0 mmol, RuCl$_2$(PPh$_3$)$_4$ 0.01 mmol, NaO^{i}Pr 0.8 mmol, ^{i}PrOH 3.0 mL, toluene 2.0 mL, 1.0 equiv of pyridine moiety was added to Ru. [b] TON = (product in mmol)/Ru (mmol). [c] Yield estimated by GC using internal standard. Recycle yields >99% [**star-poly(NBE)$_{25}$-Py**]; 89–95% [**poly(NBE)$_{100}$-Py**]. More data are shown in the SI.[23]

It is clear that no significant decreases in the TON values were observed by reusing the catalyst in both cases [catalysts consisting of RuCl$_2$(PPh$_3$)$_4$ and linear **poly(NBE)$_{100}$-Py** or **star-poly(NBE)$_{25}$-Py**]. The reaction yields reached completion when the reactions were conducted for 10 h, and the trend did not change after several recycle runs (Table 3). As described above, the star polymer-supported catalyst could be recovered quantitatively, whereas the recovered yields were 89–95% in the case of **poly(NBE)$_{100}$-Py**. Taking these results into account, the present Ru catalyst can be easily reused without deactivation. We believe that the catalyst system presented here is a promising candidate that possesses unique characteristics for designing efficient recyclable catalytic systems.

^{1}H and ^{31}P NMR Spectra for a CDCl$_3$ Solution Containing the Recovered Catalyst . ^{31}P NMR spectra of the CDCl$_3$ solution containing recycled catalysts [RuCl$_2$(PPh$_3$)$_4$ and **poly(NBE)$_{100}$-Py** or **star-poly(NBE)$_{25}$-Py**, after precipitation from MeOH] showed a sharp resonance at 28.0 ppm, and the observed resonance was different from those observed in the CDCl$_3$ solution containing RuCl$_2$(PPh$_3$)$_4$ (Figure S7 in the SI).[28] The results thus suggest formation of another PPh$_3$-coordinated species, as previously demonstrated for exclusive

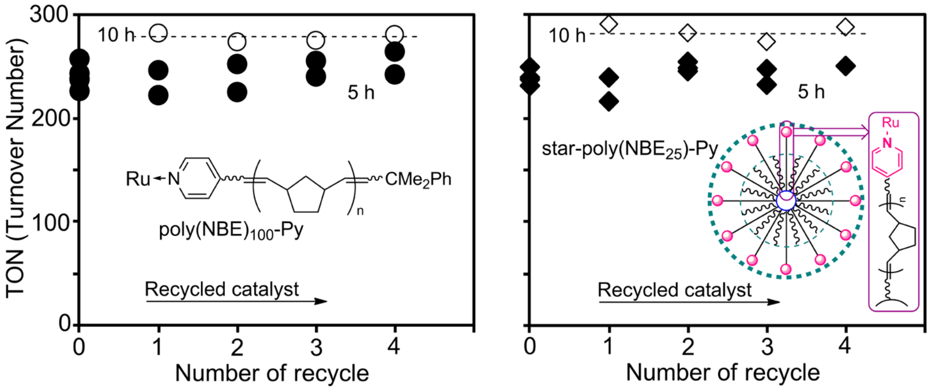
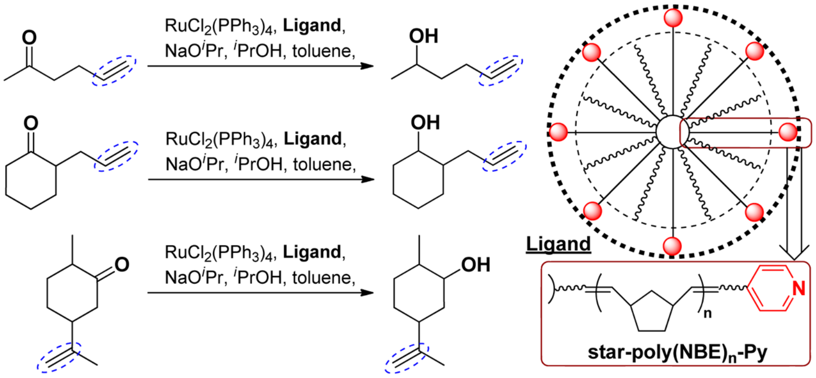


Figure 2. Recycling experiments for hydrogen transfer reduction of cyclohexanone catalyzed by $RuCl_2(PPh_3)_4$/**poly(NBE)$_{100}$-Py** or **star-poly(NBE)$_{25}$-Py** (Table 3 and Tables S6, S7).[25]

Scheme 4



formations of $RuCl_2(PPh_3)_2(L)_2$ [L = norbornadiene, MeCN] from $RuCl_2(PPh_3)_3$.[29,30] The catalyst could be easily recovered by filtration, suggesting that pyridine in **star-poly(NBE)$_{25}$-Py** strongly coordinates to Ru.

Moreover, the ^1H NMR spectrum for the $CDCl_3$ solution containing recovered catalyst was very close to that of the original star-shaped ROMP polymer, and the intensity of the olefinic protons was unchanged before/after the reaction (Figure S8 in the SI).[28] This suggests that the present reduction took place by hydrogen transfer reduction (not by hydrogenation with dihydrogen once formed) generally proposed under these conditions.[16,17] 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 the carbonyl group in this catalysis.[15]

3. Chemoselective Hydrogen Transfer Reduction of Various Ketones by $RuCl_2(PPh_3)_4$/Star Polymer-Supported Ligand Catalysts. As described above, a possibility for exclusive reduction of the carbonyl group was suggested in this catalysis. The reductions of various ketones using the $RuCl_2(PPh_3)_4$/**star-poly(NBE)$_{25}$-Py** catalyst were thus explored under the same conditions (Scheme 4). The results are summarized in Table 4.[25]

Note that the reaction products from 5-hexen-2-one, 2-allylcyclohexanone, and 5-isopropenyl-2-methylcyclohexanone (dihydrocarvone) were 5-hexen-2-ol, 2-allyl-cyclohexanol, and 5-isopropenyl-2-methylcyclohexanol (dihydrocarveol), respectively, as the sole products (Scheme 4): the exclusive reduction of the carbonyl group has thus been achieved in this catalysis. High product yields were attained if these reactions were conducted for long reaction times and/or under rather high catalyst concentration (Table 4). Moreover, as demonstrated above, the catalyst can be easily recycled according to a procedure shown in Scheme 3: the catalyst can be reused without decrease in activity (Figure 3). These results clearly indicate that the present catalyst [$RuCl_2(PPh_3)_4$/**star-poly(NBE)$_{25}$-Py**] can be used as an efficient recyclable catalyst for exclusive reduction of the carbonyl group in various ketones.

We have shown that pyridine-modified, "soluble", star-shaped polymers have been prepared in a precisely controlled manner by adopting the living ROMP technique using the molybdenum-alkylidene initiator. The resultant polymer, **star-poly(NBE)$_n$-Py** ($n = 25, 50$), can be used as an effective ligand for ruthenium-catalyzed chemoselective hydrogen transfer reduction of various ketones. The activity of $RuCl_2(PPh_3)_4$ increased upon addition of the star polymer ligand, and exclusive reduction of the carbonyl groups in cyclohexanone, 5-hexen-2-one, 2-allylcyclohexanone, and 5-isopropenyl-2-methylcyclohexanone (dihydrocarvone) has been demonstrated in this catalysis. The catalyst can be quantitatively recovered by pouring the reaction mixture into methanol and can be reused without further purification. Moreover, both activity and selectivity did not decrease in several recycle runs. The present method for synthesis of modified star-shaped ROMP polymers should be facile, and many applications (syntheses of various ligands, applications for catalytic reactions) can be thus considered. Therefore, we highly believe that the present approach of using recyclable spherical supported catalysts for efficient organic transformations should thus introduce a new insight to study polymer-supported catalysis chemistry.

Table 4. Chemoselective Hydrogen Transfer Reduction of Various Ketones (Selected Results[25]) Catalyzed by $RuCl_2(PPh_3)_4$ and star-poly(NBE)$_{25}$-Py[a]

catalyst/ligand[b]	substrate	time/h	yield /%[c]	TON[d]
$RuCl_2(PPh_3)_4$ + **star-poly(NBE)$_{25}$-Py**	5-hexen-2-one	5	58	174
recycled runs (first recycle)	5-hexen-2-one	5	64	192
recycled runs (second recycle)	5-hexen-2-one	5	60	180
recycled runs (third recycle)	5-hexen-2-one	5	61	183
recycled runs (fourth recycle)	5-hexen-2-one	5	59	177
recycled runs (fourth recycle)[e]	5-hexen-2-one	15	90	270
$RuCl_2(PPh_3)_4$ + **star-poly(NBE)$_{25}$-Py**	2-allylcyclohexanone	5	42	126
recycled runs (first recycle)	2-allylcyclohexanone	5	41	123
recycled runs (second recycle)	2-allylcyclohexanone	5	42	126
recycled runs (second recycle)[d]	2-allylcyclohexanone	15	93	140
$RuCl_2(PPh_3)_4$ + **star-poly(NBE)$_{25}$-Py**	5-isopropenyl-2-methylcyclohexanone	5	69	138
recycled runs (first recycle)	5-isopropenyl-2-methylcyclohexanone	5	69	138
recycled runs (second recycle)	5-isopropenyl-2-methylcyclohexanone	5	70	140
recycled runs (second recycle)	5-isopropenyl-2-methylcyclohexanone	15	90	180

[a]Conditions: $RuCl_2(PPh_3)_4$ 0.01 mmol, substrate 3.0 mml (dihydrocarvone 2.0 mmol), NaO^iPr 0.8 mmol, ^iPrOH 3.0 mL, toluene 2.0 mL. [b]1.0 equiv of pyridine (moiety) to Ru. [c]Yield estimated by GC using internal standard. [d]TON = product (mmol)/Ru (mmol). [e]Ru 0.02 mmol. Recycle yields >99% [**star-poly(NBE)$_{25}$-Py**], and more data are shown in the SI.[23]

■ EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All ^1H and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^1H, 125.77 MHz for ^{13}C), and all chemical shifts are given in ppm and are referenced to $SiMe_4$. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C. HPLC grade THF (Wako Pure Chemical Ind., Inc.) was used for GPC and was degassed prior to use. GPC was performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu 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.

All chemicals used were of reagent grade and were purified by standard purification procedures. Polymerization grade toluene was stored over sodium/potassium alloy in a drybox and was then passed through a short alumina column prior to use. Anhydrous grade toluene (Kanto Kagaku Co. Ltd.) for polymerization (before storage in the presence of sodium/potassium alloy) was transferred into a bottle containing molecular sieves (mixture of 3A, 4A 1/16, and 13X) in the drybox. $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$[31] and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphtalene (CL, *exo*:*endo* = 0.17:1.00)[22] were prepared according to the literature. NaO^iPr was prepared by treating ^iPrOH with Na under a nitrogen atmosphere and isolated as a white solid. $RuCl_2(PPh_3)_4$ (STREM) and 4-pyridinecarboxaldehyde (Aldrich) were used as received.

Transmission electron microscopy measurements were conducted on thin films, prepared by evaporating a THF solution of the polymer samples on an Okenshoji Co. Ltd. copper grid, which was covered with a perforated polymer (polyvinyl formal) film and coated with carbon on all sides (diameter 3 mm), at concentrations of 10^{-5} or 10^{-6} mg/mL (THF). They were then analyzed with a JEOL JEM-3100FEF electron microscope (gun type: field emission), at an accelerate voltage of 300 kV, a column vacuum of 1.0 × 10^{-5} Pascals, and at a magnification of 20 000×. All pictures were energy-filtered TEM images, which were taken with an Omega energy filter for zero-loss images (cut inelastic scattered electrons). The temperature was set to 22 °C, and the relative humidity was set to 50%.

General Polymerization Procedure. A toluene solution (0.5 g) containing $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2C_6H_3)(O^tBu)_2$ (1.82 × 10^{-5} mol) was added in one portion to a rapidly stirred toluene solution (9.5 g) containing the norbornene (25 equiv to Mo) at room temperature (25 °C), and the solution was stirred for 4 min. The second monomer, 10 equiv of cross-linker, 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphtalene (CL, *exo*:*endo* = 0.17:1.00), was then added into the solution, and the mixture was stirred for 50 min. The third monomer (norbornene) in toluene (1.0 g) was then added in one portion, and the reaction mixture was further stirred for prescribed time. The polymerization was quenched by adding pyridine carboxaldehyde (ca. >10 mg, excess), and the solution was stirred for 1 h until completion. The mixture was then removed *in vacuo*, and the resultant solid was dissolved in the minimum amount of THF. The solution was poured dropwise into methanol to afford off-white precipitates. The polymer was then collected by filtration and dried *in vacuo*. ^1H NMR ($CDCl_3$): δ 5.19 and 5.32 (br m, 2H olefinic), 2.76 and 2.40 (br s, 2H), 1.85 and 1.04 (m, 2H), 1.77 and 1.33 (m, 4H), 8.52 and 8.55 (d, pyridine).

Catalytic Hydrogen Transfer Reduction of Ketones. The typical procedure is as follows:[15] into a Schlenk tube (50 mL), $RuCl_2(PPh_3)_4$, ligand, toluene, ^iPrOH, NaO^iPr, and cyclohexanone (substrate) were charged under a nitrogen atmosphere. The reaction mixture was stirred under N_2 at 50 °C for the prescribed time (5 h).

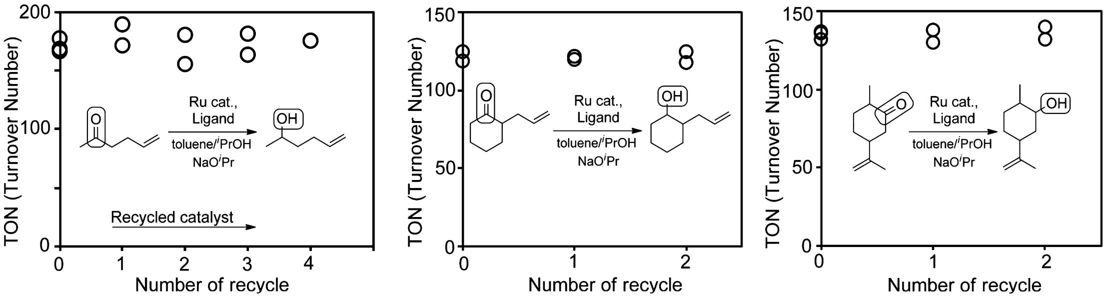


Figure 3. Recycling experiments for hydrogen transfer reduction of 5-hexen-2-one (left), 2-allylcyclohexanone (middle), and 5-isopropenyl-2-methylcyclohexanone (dihydrocarvone, right) catalyzed by $RuCl_2(PPh_3)_4$/**star-poly(NBE)$_{25}$-Py** (Table 4, and Tables S8−10). More data are shown in the SI.[25]

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). After the reaction, the solution was poured into cold methanol (50 mL), 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.

■ ASSOCIATED CONTENT

Supporting Information

Text giving additional data for polymer synthesis (including ^{1}H NMR spectra), measurement of spherical aggregates (shape polymers) by TEM, additional (recycled) results for chemoselective hydrogen transfer reduction of various ketones by ruthenium catalysts, and ^{1}H and ^{31}P NMR spectra of CDCl$_3$ solutions containing recycled catalyst. This information is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The project was partly supported by a Grant-in-Aid for Challenging Exploratory Research (No. 21656209). K.N. and K.T. express their thanks to Prof. Michiya Fujiki (NAIST) for discussion and to Mr. Shohei Katao (NAIST) for help in TEM measurements with S.F.

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(25) Detailed results in the transfer hydrogenation of cyclohexanone and various ketones including their recycled experiments are shown in the SI.

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