Transfer Hydrogenation of Ketones Catalyzed by PEG-Armed Ruthenium-Microgel Star Polymers: Microgel-Core Reaction Space for Active, Versatile and Recyclable Catalysis

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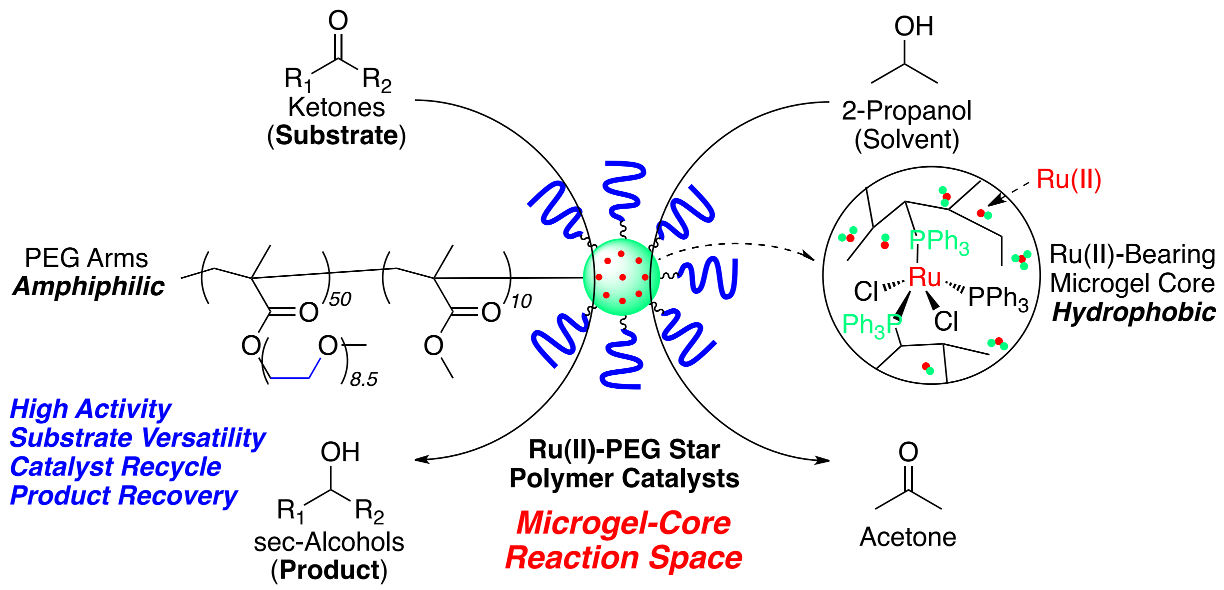
Abstract

PEG-armed Ru(II)-bearing microgel-core star polymer catalysts were employed for the transfer hydrogenation of ketones. The star catalysts [Ru(II)-PEG Star] were one-pot synthesized by ruthenium-catalyzed living radical polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and a sequential linking reaction with ethylene glycol dimethacrylate (**1**) and diphenylphosphinostyrene (**2**). The polymers efficiently and homogeneously reduced acetophenone into 1-phenylethanol in 2-propanol coupled with K_2CO_3 at a high yield, despite a low catalyst feed ratio to the substrate [Ru(II)/substrate = 1/1000]. Importantly, the catalytic activity was higher than that of the original $RuCl_2(PPh_3)_3$, as well as that of similar polymer-supported Ru(II) catalysts, such as poly (methyl methacrylate) (PMMA)-armed star-, polystyrene gel-, and random polymer-supported catalysts. Ru(II)-PEG Star is applicable to various substrates, including para-substituted aromatic, aliphatic, and bulky ketones, where Ru(II)-PEG Star's activity is generally higher than that of $RuCl_2(PPh_3)_3$. For example, the turn-over frequency for 4-chloroacetophenone and cyclohexanone reached approximately 1000 h^{-1}, and the reduction rate of cyclopentanone and 3-methyl-5-heptanone was twice as high as that of $RuCl_2(PPh_3)_3$. The star catalyst also showed high catalyst recyclablity, independent of the substrate species. These features most likely arise from its unique reaction space, which consists of a ruthenium-embedded, hydrophobic microgel-core surrounded by amphiphilic and polar PEGMA arms.



O
R1 R2
Ketones
(Substrate)
OH
2-Propanol
(Solvent)
Ru(II)
PEG Arms
Amphiphilic
50
10
8.5
PPh3
Cl
Ru
PPh3
Ph3P
Cl
Ru(II)-Bearing
Microgel Core
Hydrophobic
High Activity
Substrate Versatility
Catalyst Recycle
Product Recovery
OH
R1 R2
sec-Alcohols
(Product)
Ru(II)-PEG Star
Polymer Catalysts
Microgel-Core
Reaction Space
O
Acetone

Introduction

The design of a reaction space around a catalytic center is an intriguing possibility for innovations in catalysis. Owing to their design versatility, macromolecules are attractive materials for providing catalysts with unique and desirable functions. Thus far, macromolecules have been used as supporting agents for metal catalysts, where the main objectives are focused on practicability in catalysis such as the recoverability of products and the recyclability of catalysts.[1-4] The representative materials are insoluble heterogeneous polymer-supported catalysts typically produced using cross-linked polystyrene gel and silica gel. Unfortunately, these materials often exhibit inferior catalytic activity and substrate selectivity compared to homogeneous catalysts, owing to the substrate's reduced accessibility to the catalytic center. Although soluble polymer-supported catalysts have also been developed to improve activity, they sometimes leach the catalysts from the supporting agents, eventually leading to inferior product recovery and catalyst recyclability. In contrast, dendrimers,[5-7] amphiphilic block copolymers for micellar catalysis,[8,9] and polymersomes[10,11] are examples of macromolecular scaffolds that provide well-designed reaction spaces for a unique catalytic performance. They serve to segment the reaction space isolated from the outer environment, as viewed by an enzyme, to accelerate catalysis[7,9] and realize cascade reactions.[11] However, they normally require multi-step synthesis and/or complex optimization in catalytic conditions.

Microgel-core star polymers[12-23] are a new category of macromolecule-based scaffolds for enclosing catalysts.[15-23] The star polymer carries a unique microgel core covered by linear arms in the center of the polymer. This promising environment encouraged us to produce metal-bearing microgel core star polymer catalysts by ruthenium-catalyzed living radical polymerization.[24-28] Here, the living polymers (arms) were linked with a divinyl compound (**1**) and $RuCl_2(PPh_3)_3$ in the presence of a phosphine ligand-bearing monomer (diphenylphosphinostyrene: **2**) (Scheme 1).[15-19] Importantly, the ligand monomer directly encapsulates the ruthenium polymerization catalyst into a microgel core via ligand exchange during the arm-linking reaction to produce ruthenium-bearing microgel core star polymers. Namely, a ruthenium catalyst with triphenylphosphine is transformed into a star polymer-supported ruthenium catalyst in one-pot synthesis. Based on this efficient synthetic procedure, we can also successfully introduce hydrophilic, amphiphilic, and thermosensitive functions to ruthenium-carrying star polymers in conjunction with poly(ethylene glycol) methyl ether methacrylate (PEGMA) as an arm monomer (Scheme 1).[17,18] This allows the one-pot transformation of "hydrophobic polymerization catalysts" into "amphiphilic and thermosensitive star polymer catalysts". The resultant star catalyst is completely soluble in various solvents (e.g., toluene, alcohol, and water) owing to the presence of poly(ethylene glycol) (PEG) in the arms, whereas the microgel core comprising multiple phosphine ligands and ruthenium is hydrophobic and cross-linked. Owing to the core-reaction pocket covered by the amphiphilic and thermosensitive arms, the star polymer catalysts induce phase-transfer catalysis in water with a unique activity and stability.[18]

Scheme 1

Herein, we investigate the homogeneous transfer hydrogenation of ketones[29-35] catalyzed by ruthenium-bearing microgel core star polymers with PEG arms [Ru(II)-PEG Star][17] coupled with K_2CO_3 in 2-propanol (Scheme 2). In this catalysis, it is expected that the unique structure of the star polymer catalysts will allow effective accessibility of a hydrophobic substrate (ketone) to the hydrophobic reaction space (core) and smooth diffusion of the resultant hydrophilic product (alcohol) from the core to the polar arm parts achieving high activity. Additionally, the cross-linked core enhances the stability of catalysts, thus improving recycle efficiency. These features will be discussed in comparison to similar polymer-supported catalysts and the original $RuCl_2(PPh_3)_3$.

Scheme 2

Experimental Section

Materials for polymer synthesis

Poly(ethylene glycol) methyl ether methacrylate (PEGMA: $M_n \approx 475$, Aldrich) was purified by column chromatography with an inhibitor remover (Aldrich) and degassed by reduced pressure before use. Methyl methacrylate (MMA: Tokyo Kasei, purity >99%) was dried overnight over calcium chloride and purified by double distillation from calcium hydride before use. $(MMA)_2$-Cl (initiator) was prepared according to the literature.[36] Ethylene glycol dimethacrylate (**1**: Aldrich, purity >98%) was purified by distillation from calcium hydride before use. Diphenylphosphinostyrene (**2**), kindly supplied by Hokko Chemical (purity >99.9%), and polystyrene cross-linked with divinylbenzene, diphenylphosphinated **[**PPh_3-Gel (**3**): polystyrene cross-linked with 2% divinyl benzene; 3 mmol phosphine/g-resin; Aldrich], were degassed by reduced pressure and purged by argon before use. 2,2'-Azobis(isobutyronitrile) (Wako, purity >98%) was used as received. $RuCl_2(PPh_3)_3$ (Aldrich, purity >97%) was used as received and handled in a glove box under a moisture- and oxygen-free argon atmosphere (H_2O <1 ppm, O_2 <1 ppm). *n*-Bu_3N (Tokyo Kasei, purity >98%) was bubbled with argon for 15 min immediately before use. Internal standards for gas chromatography (*n*-octane for MMA, tetralin for **1**) were dried over calcium chloride overnight and distilled twice from calcium hydride. Toluene (solvent) was purified by passing through a purification column [Solvent Dispensing System; HANSEN&CO., LTD.] before use. Hexane (Wako, dehydrated) for polymer purification was used as received. The solvents were bubbled with argon for more than 15 min immediately before use.

Materials for hydrogenation

Substrates (**S1**: acetophenone, Aldrich, purity >99%; **S2**: *p*-chloroacetophenone, Wako, purity >95%; **S3**: 4-methoxyacetophenone, Aldrich, purity >99%; **S4**: *p*-butylacetophenone, Aldrich, purity >95%; **S5**: valerophenone, Aldrich, purity >99%; **S6**: 1-indanone, Aldrich purity >99%; **S7**: cyclopentanone, Wako >95%; **S8**: cyclohexanone, Wako >99%; **S9**: 2-hexanone, Wako, purity >95%; **S10**: 2-octanone, Wako, purity, >98%; **S11**: 2-dodecanone, AVOCADO, purity >99%; **S12**: 5-methyl-3-heptanone, TCI, purity >95%) were degassed by reduced pressure and purged by argon or bubbled with argon for more than 15 min before use. K_2CO_3 (Wako, >99.5%) and 2-propanol (Wako, dehydrated) were degassed by reduced pressure and purged by argon before use.

Characterization

The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were measured by SEC in DMF containing 10 mM LiBr at 40 ^{o}C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L; exclusion limit = 4×10^6; particle size = 10 μm; pore size = 5000 Å; 0.8 cm i.d. × 30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/Vis detector set at 270 nm. The columns were calibrated against ten standard poly(MMA) samples (Polymer Laboratories; M_n = 1000–1200000; M_w/M_n = 1.06–1.22). The ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at 25 ^{o}C on a JEOL JNM-LA500 spectrometer operating at 500.16 MHz. The ^{31}P NMR spectra were recorded with $(C_2H_5O)_2POH$ (12 ppm) as an internal standard in toluene-d_8 at 25

^{o}C on a JEOL JNM-LA500 spectrometer operating at 500.16 MHz. The absolute weight-average molecular weight (M_w) of the star polymer catalysts was determined by multi-angle laser light scattering coupled with SEC (SEC-MALLS) in DMF containing 10 mM LiBr at 40 ^{o}C on a Dawn E instrument (Wyatt Technology; Ga-As laser, λ = 690 nm). The refractive index increment (*dn/dc*) was measured in DMF at 40 ^{o}C on an Optilab DSP refractometer (Wyatt Technology; λ = 690 nm, c < 2.0 mg/mL). UV-Vis spectra to determine the ruthenium contents of the star polymer catalysts were collected in CH_2ClCH_2Cl at room temperature on a Shimadzu MultiSpec 1500. The core-bound Ru(II) content was determined by the absorbance at 475 nm and a calibration plot made for $RuCl_2(PPh_3)_3$ (0.10–2.0 mM solution) at the same wavelength. The core-bound Ru(II) content was further estimated by inductively coupled plasma atomic emission spectrometry (ICP-AES; Thermo Fisher Scientific IRIS Intrepid II XDL Radial).

Synthesis of Ru(II)-PEG Star (C1-C3)

Ru(II)-PEG Star (**C1**)[17] was synthesized by a syringe technique under dry argon in baked glass tubes equipped with a three-way stopcock. $RuCl_2(PPh_3)_3$ (0.09 mmol, 86.3 mg) was first placed in a 50-mL round-bottomed flask. Then, toluene (6.45 mL), *n*-Bu_3N (0.18 mmol, 0.45 mL of 400 mM solution in toluene), PEGMA (4.5 mmol, 1.98 mL), and $(MMA)_2$-Cl (0.09 mmol, 0.12 mL of 773 mM solution in toluene) were sequentially added in that order to the flask at 25 ^{o}C under argon. The total volume of the mixture was thus 9 mL. Immediately after mixing, the mixture was placed in an oil bath at 80 ^{o}C. The polymerization reached over ca. 90% conversion in 10 h; subsequently, MMA (0.9 mmol, 0.096 mL) and *n*-octane (0.024 mL) were added to the unquenched solution. The MMA conversion reached over ca. 78% in 24 h, after which a solution of **1** (1.35 mmol, 0.63 mL of 2159 mM solution in toluene), **2** (0.11 mmol, 0.11 mL of 1000 mM solution in toluene), tetralin (0.09

mL), and $RuCl_2(PPh_3)_3$ (86.3 mg) in toluene (3.68 mL) was added to the unquenched arm-polymer solution (SEC: M_n = 34,800, M_w/M_n = 1.47). After 25 h, the reaction was terminated by cooling the mixture to -78 °C. The conversions of PEGMA, MMA, **1**, and **2** were 98%, 94%, 84%, and 100%, respectively, as determined by ^{1}H NMR with an internal standard of tetralin (PEGMA, **2**) and gas chromatography with *n*-octane (MMA) and tetralin (**1**) as internal standards. The yield of the star polymers was 76%, as calculated from the area ratio of the arm residue and the star polymers using SEC curves. The quenched mixture was precipitated into hexane under argon to remove the remaining monomers and an amine additive. The precipitate was further purified by column chromatography with silica gel (Wako Gel 200) and toluene as an eluent under argon to remove free ruthenium complexes. The eluted solutions were evaporated to give the final products, which were subsequently dried overnight under vacuum at room temperature before analysis and catalysis. SEC-MALLS (DMF): M_w = 770,000 g/mol; 16 arms per star polymer; R_g = 15.1 nm. ^{1}H-NMR (500 MHz, CD_2Cl_2, 25 °C): δ 7.4-7.7 (aromatic), 4.2-4.0 (-$CO_2C\underline{H}_2CH_2$-), 3.9-3.4 (-OC_2H_4O-), 3.4-3.2 (-OCH_3), 2.2-1.7 (-CH_2-), 1.6-0.8 (-CCH_3). UV-Vis (CH_2ClCH_2Cl, 25 °C, $RuCl_2(PPh_3)_3$ calibration at 475 nm): 24 μmol Ru/g-polymer (**C1**). ICP-AES: 27 μmol Ru/g-polymer (**C1**). Other Ru(II)-PEG Stars (**C2**, **C3**) were also prepared by the same procedure coupled with a different volume of **2** and were similarly characterized, as shown in Table 1.

Synthesis of Ru(II)-MMA Star (C4)

Ru(II)-MMA Star (**C4**) was synthesized by the linking reaction of PMMA arms (conversion of MMA = 93%, 60 h, M_n = 8300, M_w/M_n = 1.19) with **1** and **2** using $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization for an 88% yield of star polymers (conversion of MMA/**1**/**2** = 98/90/100%, +20 h).[15,16] SEC-MALLS (DMF): M_w = 600,000; 40 arms per star polymer; R_g = 11.6 nm. ^{1}H-NMR

(500 MHz, CD_2Cl_2, 25 °C): δ 7.4-7.7 (aromatic), 3.6-3.5 (-OCH_3), 2.2-1.7 (-CH_2-), 1.6-0.8 (-CCH_3). UV-Vis (CH_2ClCH_2Cl, 25 °C, $RuCl_2(PPh_3)_3$ calibration at 475 nm): 29 μmol Ru/g-polymer (**C4**).

Synthesis of Ru(II)-Gel (C5)

In a 50-mL round-bottomed flask, $RuCl_2(PPh_3)_3$ (0.24 mmol, 230 mg) in toluene (24 mL) was added to polymer-supported triphenylphosphine (**3**) (1.2 mmol phosphine, 0.4 g) under argon. The mixture was stirred at 80 °C for 28 h under dispersion to give a red-brown Ru(II)-supported powder with a colorless supernatant. The obtained powder was washed three times by toluene under argon. The supernatant exhibited no UV-Vis absorption derived from $RuCl_2(PPh_3)_3$, indicating quantitative immobilization of Ru(II) complexes onto **3**. UV-Vis (CH_2ClCH_2Cl, 25 °C, $RuCl_2(PPh_3)_3$ calibration at 475 nm); feed ratio of $RuCl_2(PPh_3)_3$ and **3**: 420 μmol Ru/g-polymer (**C5**).

Synthesis of Ru(II)-Random (C6)

2,2'-Azobis(isobutyronitrile) (0.3 mmol, 51.5 mg) was placed in a 50-mL round-bottomed flask. Then, toluene (4.08 mL), MMA (39.8 mmol, 4.24 mL), and **2** (2.09 mmol, 2.15 mL of 975 mM toluene solution) were sequentially added to the flask at 25 °C under argon. The mixture was placed in an oil bath at 80 °C for 25 h. The reaction was terminated by cooling the mixture to -78 °C (conversion of MMA/**2** = 99%/100%). The solution was precipitated to hexane three times, and the resulting phosphine-bearing random copolymer (**4**) was dried under vacuum. SEC (DMF, PMMA standards): M_n = 16700, M_w/M_n = 2.24. ^{1}H-NMR (500 MHz, CD_2Cl_2, 25 °C): δ 7.0-7.4 (aromatic), 3.6-3.4 (-OCH_3), 2.2-1.7 (-CH_2-, -CHPh-), 1.6-0.8 (-CCH_3). ^{31}P-NMR (500 MHz, toluene-d_8, 25 °C): δ -0.9 (PPh_3). **4**-bound-phosphine ligands calculated from the monomer conversion in **4**: 0.457 μmol/g-polymer.

In a 50-mL round-bottomed flask, a solution of $RuCl_2(PPh_3)_3$ (0.23 mmol, 217 mg) in toluene

(23 mL) was added to **4** (1.13 mmol of **4**-bound phosphine, 2.48 g) under argon. The mixture was placed in an oil bath at 80 ^{o}C for 23 h. After the reaction was terminated by cooling the mixture to -78 ^{o}C, the product (**C6**) was purified by column chromatography with silica gel (Wako Gel 200) and toluene as an eluent under argon and was dried overnight under vacuum at room temperature before analysis and catalysis. SEC (DMF, PMMA standards): M_n = 20700, M_w/M_n = 2.94. ^{1}H-NMR (500 MHz, CD_2Cl_2, 25 ^{o}C): δ 7.0-7.4 (aromatic), 3.6-3.4 (-OCH_3), 2.2-1.7 (-CH_2-, -CHPh-), 1.6-0.8 (-CCH_3). ^{31}P-NMR (500 MHz, toluene-d_8, 25 ^{o}C): δ -0.9 (PPh_3). UV-Vis (CH_2ClCH_2Cl, 25 ^{o}C, $RuCl_2(PPh_3)_3$ calibration at 475 nm): 50 μmol/g-polymer (**C6**).

Transfer Hydrogenation of Ketones Catalyzed by Ru(II)-PEG Star (C1)

The typical procedure of **C1**-catalyzed transfer hydrogenation of a ketone was as follows: K_2CO_3 (1 mmol, 138 mg) was placed in a baked 50-mL round-bottomed flask equipped with a condenser and a three-way stopcock, and the flask was purged with argon. A solution of **C1** (0.42 g: $[\text{core-Ru(II)}]_0$ = 0.01 mmol) and acetophenone (**S1**: 10 mmol, 1.17 mL) in 2-propanol (10 mL) was added to the flask at 25 ^{o}C under argon. The mixture was stirred and refluxed at 100 ^{o}C. The solution was sampled at a pre-determined period by the syringe technique under argon to determine the conversion. The yield was determined by ^{1}H NMR analysis of the reaction solution.

Results and Discussion

1. Design of Ru(II)-Bearing Polymer Catalysts

Three types of poly(PEGMA)-armed star polymers with a Ru(II)-bearing microgel core (**C1**-**C3**) were employed as catalysts for the transfer hydrogenation of ketones, compared with a similar series of Ru(II)-bearing polymer catalysts (**C4**-**C6**) and $RuCl_2(PPh_3)_3$ (**C7**). Their chemical structures and characterization are given in Figure 1 and Table 1, respectively. Ru(II)-PEG Stars labeled as **C1**, **C2**, and **C3** were directly prepared by $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization of PEGMA, MMA, **1**, and **2**, according to Scheme 1.[17] Only the ratio of **2** to the initiator (r_2 = ***n*** = $[\mathbf{2}]_0$/$[\text{initiator}]_0$) was changed as follows: r_2 = 1.25 (**C1**), 2.5 (**C2**), and 5.0 (**C3**), to lead to different numbers of core-bound ruthenium (N_{Ru} = 19, 36, and 87) and different number ratios of core-bound **2** per core-bound ruthenium (N_2/N_{Ru} = 1.0, 1.8, and 2.6), respectively. The other conditions and feed ratios were uniform, such as the degree of polymerization (arm) [*DP* = ($[\text{PEGMA}]_o$+$[\text{MMA}]_o$)/$[\text{initiator}]_o$ = 60] and the ratio of **1** to the initiator (r_1 = $[\mathbf{1}]_{add}$/$[\text{initiator}]_o$ = 15). N_{Ru} and N_2/N_{Ru} increased nearly proportionally to r_2. **C1**-**C3** were well soluble in 2-propanol at temperatures over 31 ^{o}C (upper critical solution temperature).[17] **C4** [Ru(II)-MMA Star], directly synthesized by $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization of MMA, **1**, and **2**,[15] is a hydrophobic PMMA arm version of **C1** with almost the same ruthenium amount (N_{Ru}). Ru(II)-Gel (**C5**), polystyrene gel-supported Ru(II), was obtained from the immobilization of $RuCl_2(PPh_3)_3$ on phosphine-bearing cross-linked styrene gel (**3**). This was employed as a cut-out mimic of the cross-linked core of star polymer catalysts; however, it was not soluble in any solvent. Ru(II)-Random (**C6**) was also obtained from the immobilization of $RuCl_2(PPh_3)_3$ on a linear random copolymer of MMA and **2**, which was a linear analogue of the Ru(II) microgel core.

Figure 1

Table 1

2. Transfer Hydrogenation of Ketones

Effects of Catalyst Structure

To examine the effects of catalyst structure on the activity, we utilized Ru(II)-PEG Star (**C1**), Ru(II)-MMA Star (**C4**), Ru(II)-Gel (**C5**), Ru(II)-Random (**C6**), and $RuCl_2(PPh_3)_3$ (**C7**) as catalysts for the transfer hydrogenation of acetophenone (**S1**) with K_2CO_3 in 2-propanol at 100 ^{o}C (reflux) (Figure 2). The feed molar ratio of the catalyst [Ru(II)] to the substrate (**S1**) was set at [**S1**]/[Ru(II)] = 1000/1.[31] Owing to its high solubility in 2-propanol at temperatures over 31 ^{o}C, **C1** efficiently and homogeneously catalyzed the transfer hydrogenation of acetophenone, with an 86% yield in 4 h. The final turnover frequency (TOF) was 215 (h^{-1}). The reduction rate for **C1** was faster than that for the conventional and homogenous **C7**. Although the hydrophobic PMMA-armed star catalyst (**C4**) and its gel counterpart (**C5**) were also effective for reduction (**C2**: 80%, **C3**: 72%), their rates were lower than those obtained with **C1** and **C7** owing to the lower solubility of **C4** and **C5** in the reaction mixture (**C4**: not completely soluble, **C5**: insoluble). Additionally, the linear counterpart (**C6**) exhibited low catalytic activity (14% yield in 4 h). From these results, **C1** was determined to be the most active among all of the catalysts, including the original ruthenium catalyst (**C7**).

Figure 2

Large quantities of conventional cross-linked polymer-supported catalysts (insoluble type) are generally required to achieve sufficient activity, because the active catalyst sites are just located on the surface.[34] Even soluble polymer-supported catalysts often show lower activity than the original non-supported catalysts, owing to the steric hindrance and/or low mobility of the polymer backbone.[15,19,37] However, Ru(II)-PEG Star (**C1**) induced the reduction of **S1** faster than the original $RuCl_2(PPh_3)_3$ (**C7**) with the same and rather small amount of ruthenium ([**S1**]/[Ru(II)] = 1000/1), even though the star catalyst has bulky and crowded PEG side chains. This acceleration is most likely a result of the unique environment around the catalytic center,[7,9] where ruthenium catalysts are enclosed in the hydrophobic microgel-core covered by the amphiphilic and polar poly(PEGMA) arms. The high activity may be explained by the following possibility (Scheme 2). Because 2-propanol works as a hydrogen donor in this reaction, the efficient catalytic cycle naturally requires a sufficient supply of solvent at the ruthenium center. In this case, the hydrogen source is effectively donated to the core-bound ruthenium owing to the homogeneous solubility of the star catalyst originating from the affinity between the amphiphilic PEG-based arms and 2-propanol (Scheme 2A). Additionally, the hydrophobic acetophenone (**S1**) can easily enter the reaction space, comprising a hydrophobic Ru(II)-bearing microgel core, while 1-phenylethanol, the product from **S1**, can efficiently escape because the alcohol product favors the polar PEG-based arm area over the hydrophobic microgel core (Scheme 2B). Such a polarity difference between the core and arms of the star catalysts might effectively diffuse the substrate and the product around the microgel-core reaction space, contributing to higher catalytic activity. This effect is further supported by the results of the reverse reaction: **C1**-catalyzed oxidation of 1-phenylethanol via the hydrogen transfer reaction in acetone (Figure S1), where the activity was much lower than that of $RuCl_2(PPh_3)_3$ (**C7**). In this case, Ru(II)-PEG Star (**C1**) would be structurally undesirable for efficient catalysis because the alcohol substrate favors the arm part and the ketone product as well as the hydrophobic core (reaction space).

Effects of Core-Bound Ru(II)

To investigate the effects of the Ru number per star polymer (N_{Ru}) on the catalytic activity, Ru(II)-PEG Stars containing various Ru(II) amounts [N_{Ru} = 19 (**C1**), 36 (**C2**), 87 (**C3**)] were employed for the hydrogenation of **S1** (Figure 3). Here, the total ruthenium concentration was kept constant ([**S1**]/[Ru(II)] = 1000/1), meaning that a higher N_{Ru} corresponds to a smaller number of star polymer molecules employed for the reaction. All Ru(II)-PEG Stars efficiently reduced **S1** to

1-phenylethanol at high yields [86% (**C1**), 88% (**C2**), and 81% (**C3**)] in 4 h. Uniquely, the rate was dependent on N_{Ru}, increasing with decreasing N_{Ru}. This tendency is explained by the following three causes (i, ii, iii). (i) The reaction rate relies on the number of stars available for the reaction (ii) The amount of core-bound ruthenium molecules effectively contributing to the reaction is critical to the reaction rate. Namely, the distribution and location of core-phosphine ligands (ruthenium catalysts) determine the activity. Owing to the electron-donating phosphine, **2,** at a small feed ratio to **1** ([initiator]/[**1**]/[**2**] = 1/15/1.25), was consumed faster than **1** during the copolymerization of **1** and **2** in the arm-linking reaction for **C1**, although **2** was consumed at almost the same rate as **1** for **C3** ([initiator]/[**1**]/[**2**] = 1/15/5.0). As a result, the phosphine ligands and ruthenium catalysts in the **C1** core would be mainly located on the core surface in contrast to those in the **C3** core with a homogeneous distribution of phosphine ligands. Thus, the ruthenium complexes in **C1** would be more accessible to the substrate than those in **C3**. (iii) The number ratio of core-bound ligands per core-bound ruthenium (N_2/N_{Ru}) in **C1** to **C3** increased from 1.0 to 2.6 with increasing N_{Ru}. In other words, a single Ru(II) complex in **C1** is supported by one phosphine ligand anchored in the core and has two non-bound (free) triphenylphosphines, while a Ru(II) complex in **C3** is bound by about three phosphine ligands in the core. Thus, as N_{Ru} increased, the mobility of the core-bound ruthenium would decrease and the catalytic site would be sterically hindered. These effects of N_{Ru} and N_2/N_{Ru} on the catalytic activity are consistent with the oxidation of sec-alcohols catalyzed by ruthenium-bearing microgel star polymers with poly(MMA) arms.[15,19]

Figure 3

Substrate Versatility

The high solubility of Ru(II)-PEG Star (**C1**)[17] encouraged us to apply various substrates to

C1-mediated transfer hydrogenation. Table 2 summarizes the reaction time, yield, and turnover frequency (TOF) for each reaction in comparison to those obtained with $RuCl_2(PPh_3)_3$ (**C7**: parentheses).

Table 2

C1 efficiently hydrogenated all ketones (**S1**-**S12**) to their corresponding alcohols. In comparison to acetophenone (**S1**: non-substituted), the para-substituted acetophenone derivatives (**S2**, **S3**, **S4**) exhibited different TOFs depending on their substituents. **S2,** with an electron-withdrawing substituent (Cl), was more rapidly reduced than **S1**, with a high yield (93%) and a high TOF (930 h^{-1}) at 1 h. In contrast, **S3** (OCH_3), a ketone with an electron-donating substituent, led to a lower yield (65%) and lower TOF (81 h^{-1}) at 8 h as compared to **S1**. Among **S1** to **S4**, the TOFs increased in the order of their substituents: OCH_3 (**S3**: 81 h^{-1}) < *n*-C_4H_9 (**S4**: 198 h^{-1}) < H (**S1**: 215 h^{-1}) < Cl (**S2**: 930 h^{-1}). These results indicate that the turnover-limiting step is the hydride transfer from a ruthenium hydride (metal center) to the carbonyl carbon of a ketone (substrate) coordinating onto the ruthenium.[38-40] The reduction of a long alkyl-aryl ketone (**S5**) by **C1** proceeded with a relatively high yield (82%), whereas the TOF (103 h^{-1}) was much smaller than that of **S1**, owing to the steric hindrance of **S5**. For aromatic substrates (**S1-S6**), the yields with **C1** exhibited values similar to those of **C7**. These results demonstrate that the catalytic property of ruthenium bound by **C1** to the substrate is the same as that of **C7**, with only the surroundings around the core ruthenium differing from those of **C7**.

For non-aromatic substrates (**S7-S12**), **C1** showed a higher yield than **C7** under the same conditions. The TOF for cyclohexanone (**S8**) with **C1** also almost reached 1000. **C1** completely induced a homogeneous reaction for non-aromatic ketones owing to the affinity between the

PEG-based arms and the various substrates and products. In contrast, **C7** was sometimes precipitated in the latter stage, because the non-aromatic alcohol products are often poor solvents for $RuCl_2(PPh_3)_3$. Therefore, the high solubility and stability of **C1** also afford higher yields and TOFs than **C7**.

Relative Catalytic Activity of Ru(II)-PEG Star and $RuCl_2(PPh_3)_3$

To examine the reaction rate, the half-life periods of the substrates (time to reach 50% yield: $T_{1/2}$) with PEG-Ru (II) Star (**C1**) were compared with those of $RuCl_2(PPh_3)_3$ (**C7**). Figure 4 shows the relative reduction rate [$R_{1/2}$(Star/Ru) = $T_{1/2}$(**C7**)/$T_{1/2}$(**C1**)] for aromatic (**S1**-**S6**) and non-aromatic (**S7**-**S12**) substrates. The $R_{1/2}$(Star/Ru) results are almost 1.0 and over 1.0, indicating that **C1** exhibited almost the same and/or superior activity to **C7** depending on the substrates. The large value of $R_{1/2}$(Star/Ru) tended to be more distinct for non-aromatic ketones such as cyclopentanone (**S7**) and 5-methyl 3-heptanone (**S12**) [$R_{1/2}$(Star/Ru) > 2.0]. The high activity is due to the affinity of the substrates to the core and that of the products to the arms, respectively. The respective compatibility led to the stable homogeneity of the star catalyst and the efficient diffusion cycle during the reaction, in which a substrate goes into the microgel core and the resultant product goes out from the reaction space. Therefore, the star polymer catalyst (**C1**) showed high substrate versatility in the transfer hydrogenation of ketones including aliphatic ones that were sometimes unfavorable for the conventional $RuCl_2(PPh_3)_3$ (**C7**).

Figure 4

Catalyst Recyclability

One of the attractive advantages of polymer-supported catalysts is catalyst recyclability and easy catalyst separation from the products.[1-4,34,35] Thus, the reusability of **C1** was examined for the transfer hydrogenation of acetophenone (**S1**) and 2-octanone (**S10**) (Figures 5A and 5B). The catalyst recycling was performed in three steps: (1) after a reaction, the solvent (2-propanol) was evaporated to give the catalyst, K_2CO_3, and non-volatile organic compounds such as the unreacted substrate and resultant products; (2) the catalyst and the base were washed twice with hexane under argon to remove the non-volatiles; (3) the substrate and solvent were recharged for the next run. As shown in Figure 5A, **C1** more efficiently reduced **S1** for three cycles [yield (8 h): 89% (1st); 80% (2nd); 81% (3rd)] compared to **C7** [yield (8 h): 88% (1st); 74% (2nd); 46% (3rd)]. Furthermore, **C1** performed the reduction of **S10** without any loss of activity for three cycles (Figure 5B). The solvent (hexane) exhibited no color (transparent) and no UV-Vis absorption from ruthenium complexes after washing **C1** during the recycle experiments. This strongly indicates that the ruthenium complexes are steadily supported by the microgel-core and do not leach from the core.[18,19,41] Thus, the almost-pure product was easily recovered from the precipitation of the reaction solution, followed by filtration and evaporation. The superior catalyst reusability and product recovery are due to the effective protection and immobilization of the ruthenium complexes by the cross-linked microgel core in **C1**.

Figure 5

Conclusion

We have demonstrated the transfer hydrogenation of various ketones with Ru(II)-PEG star polymer catalysts in 2-propanol. The star catalysts were directly obtained from Ru(II)-catalyzed living radical polymerization of PEGMA and a sequential cross-linking reaction in the presence of a phosphine ligand monomer. Importantly, although the ruthenium complexes were placed in the core and shielded from the outside region, the star polymers efficiently and homogeneously reduced aromatic and non-aromatic ketones into their corresponding alcohols, in a manner superior to that of other polymer-bound catalysts and the original one. This high activity most likely arises from the unique "reaction space", which consists of a ruthenium-embedded hydrophobic microgel core and amphiphilic and polar PEG-bearing arm polymers. Not only are the star polymers completely soluble in 2-propanol (solvent) but the arms and the core also exhibit a high affinity for products and substrates, respectively. The design around the catalytic site leads to high homogeneity during catalysis, independent of the substrate species, and smooth diffusion of the substrate and the resultant product around the microgel-core. Furthermore, a PEG-star catalyst can be reused three times, which is better than conventional ruthenium, in addition to facile recovery of almost-pure products from the star catalyst. These reaction properties are also a result of the encapsulation and protection of the ruthenium complexes by the microgel core. Therefore, a PEG-armed ruthenium-bearing microgel star polymer catalyst provides a catalyst-enclosed reaction space that achieves high activity, versatility, and catalyst recyclability in the transfer hydrogenation of ketones.

Acknowledgments

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Figure and Scheme Captions

Scheme 1 One-pot synthesis of Ru(II)-PEG star polymer catalysts via Ru(II)-catalyzed living radical polymerization.

Scheme 2 Microgel-core reaction space of Ru(II)-PEG star catalysts for the transfer hydrogenation of ketones: (a) supply of a hydrogen donor (2-propanol) to core-bound Ru(II) and (b) diffusion of substrates (ketones) and products (sec-alcohols) around the microgel-core reaction space.

Figure 1 Structures of Ru(II)-bearing polymer catalysts.

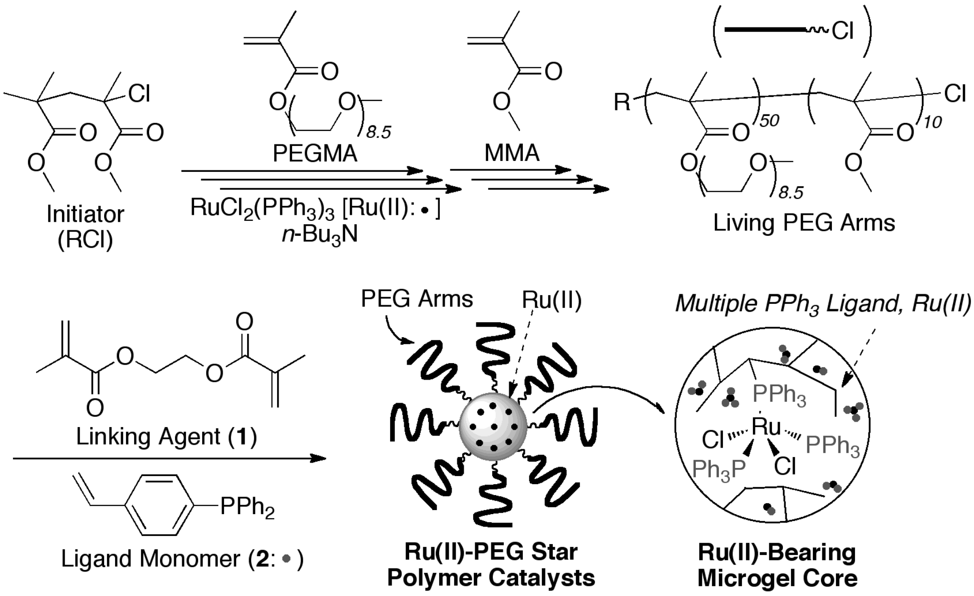
Figure 2 Transfer hydrogenation of acetophenone (**S1**) catalyzed by various Ru(II) complexes: Ru(II)-PEG Star (**C1**: filled squares); Ru(II)-MMA Star (**C4**: filled circles); Ru(II)-Gel (**C5**: filled triangles); Ru(II)-Random (**C6**: filled diamonds); $RuCl_2(PPh_3)_3$ (**C7**: open circles). Conditions: **S1**/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in 2-propanol (10 mL) at 100 ^{o}C.

Figure 3 Effects of Ru(II) number (N_{Ru}) per a Ru(II)-PEG star molecule [**C1** (filled squares), **C2** (open circles), **C3** (filled triangles)] on the transfer hydrogenation of acetophenone (**S1**): **S1**/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in 2-propanol (10 mL) at 100 ^{o}C.

Figure 4 Catalytic activity of **C1** to **C7** evaluated for the relative reduction rate [$R_{1/2}$(Star/Ru)] of various substrates (**S1-S12**). $R_{1/2}$(Star/Ru) = $T_{1/2}$(**C7**)/$T_{1/2}$(**C1**). $T_{1/2}$(**C7** or **C1**): half-life periods of substrates catalyzed by **C7** or **C1**, respectively. Conditions: substrate/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in 2-propanol (10 mL) at 100 ^{o}C. **S6**: $R_{1/2}$(Star/Ru) calculated from the respective yields (**C1**, **C7** = 22%) at 8 h.

Figure 5 (**a**) Recycle experiments of **C1** (light gray) and **C7** (dark gray) for the hydrogenation of **S1**. (**b**) Recycle experiments of **C1** for the hydrogenation of **S10** [cycle: 1st (open squares), 2nd (open circles), 3rd (filled triangles)]. Conditions: **S1** or **S10**/Ru(II)/K_2CO_3 = 15/0.015/1.5 mmol in 2-propanol (15 mL) at 100 ^{o}C for 8 h.

Schemes and Figures



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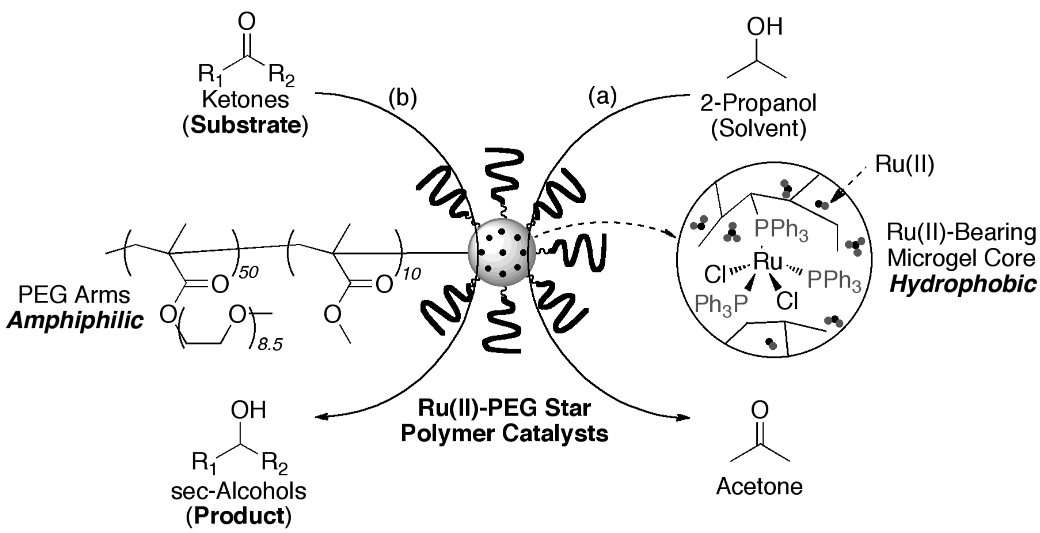

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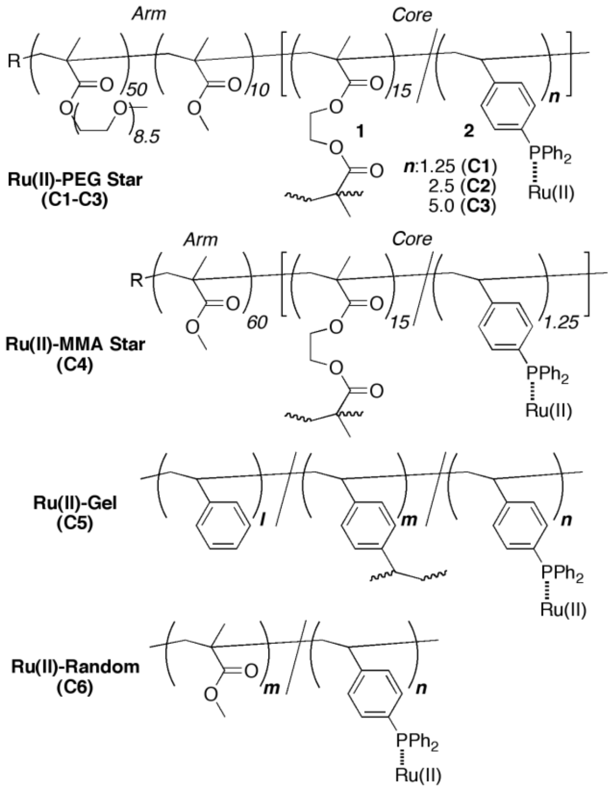

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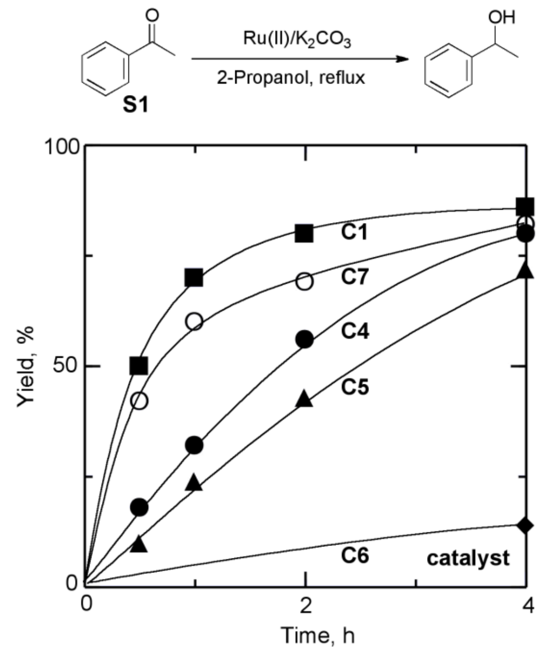

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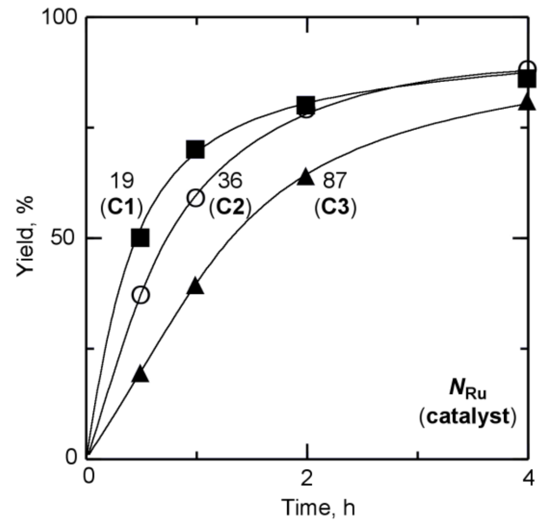

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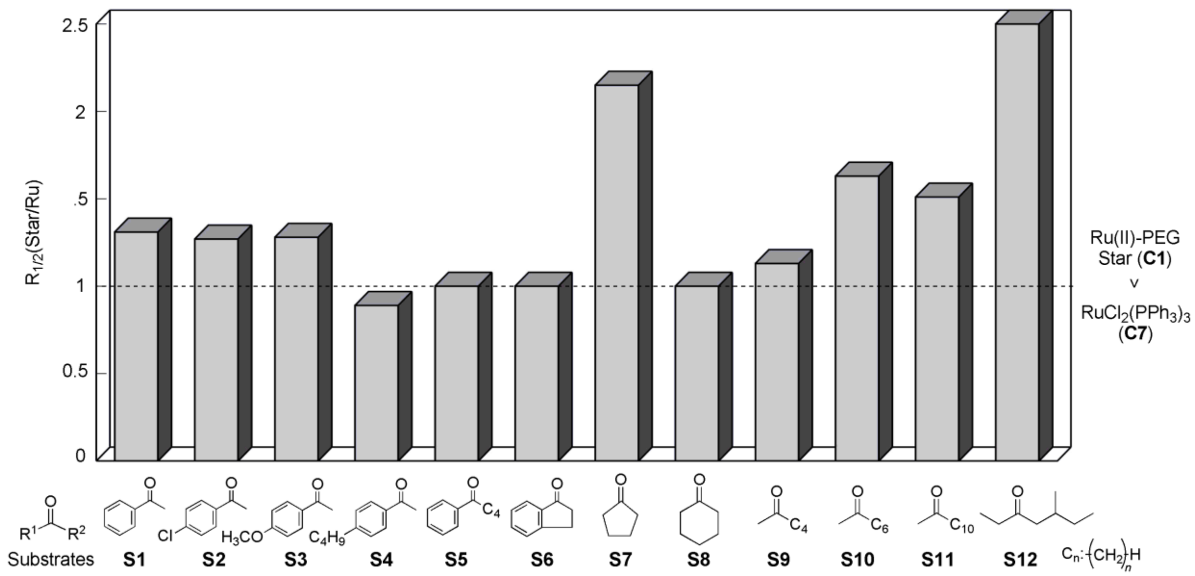

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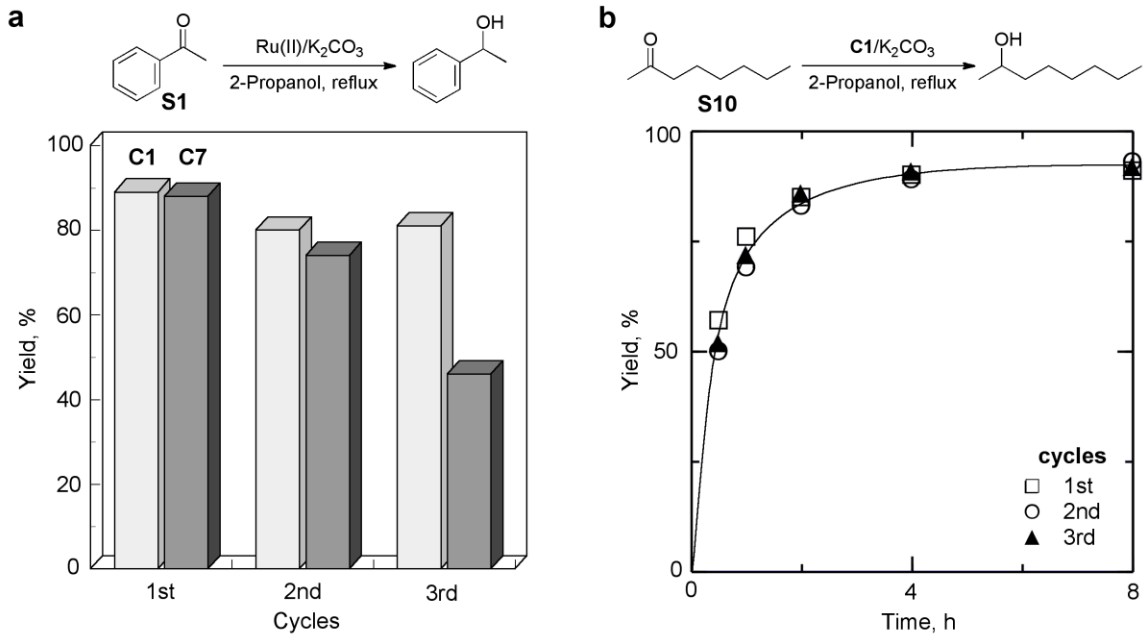

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Table 1 Characterization of Ru(II)-Bearing Polymer Catalysts[a]

Code	Arm	*DP*	r_2	M_w[b]	f[c] (No. of arms)	R_g[d] (nm)	N_2[e] (No. of **2**)	Ru[f] (μmol/g)	N_{Ru}[g] (No. of Ru)	N_2/N_{Ru}[h]
C1	PEGMA-*b*-MMA	60	1.25	772,000	16	15	20	24	19	1.0
C2	PEGMA-*b*-MMA	60	2.5	1,190,000	25	17	63	30	36	1.8
C3	PEGMA-*b*-MMA	60	5.0	2,220,000	45	22	225	39	87	2.6
C4	MMA	60	1.25	600,000	40	12	50	29	17	2.9
C5	-		–	–	–	–	–	420	–	–
C6	-		-	20,700	–	–	–	50	1.0	–

[a] Ru(II)-PEG Stars (**C1**-**C3**) were prepared by $RuCl_2(PPh_3)_3$ [Ru(II)]-catalyzed living radical polymerization of PEGMA, MMA, **1** and **2**: *DP* ([PEGMA]/[initiator] + [MMA]/[initiator]) = 50 + 10 = 60; r_1 ([**1**]/[initiator]) = 15; r_2 ([**2**]/[initiator]) = 1.25 (**C1**), 2.5 (**C2**), 5.0 (**C3**). Ru(II)-MMA Star (**C4**) was prepared by Ru(II)-catalyzed living radical polymerization of MMA, **1** and **2**: *DP* ([MMA]/[initiator]) = 60; r_1 = 15; r_2 = 1.25. Ru(II)-Gel (**C5**) was prepared by the immobilization of $RuCl_2(PPh_3)_3$ onto a phosphine-bearing cross-linked polystyrene (**3**). Ru(II)-Random (**C6**) was prepared by free radical polymerization of MMA and **2**, followed by the immobilization of $RuCl_2(PPh_3)_3$.

[b] **C1**-**C4**: Absolute weight-average molecular weights determined by SEC-MALLS in DMF; **C6**: weight-average molecular weights determined by SEC in DMF (M_w/M_n = 2.94).

[c] The number of arms per polymer molecule: f = (weight fraction of arms) x $M_w/M_{w,\ arm}$ [**C1-C3**: $M_{w,\ arm}$ (MALLS) = 40900; **C4**: $M_{w,\ arm}$ (SEC) = 9800].

[d] Gyration radius determined by SEC-MALLS in DMF.

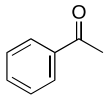
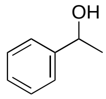
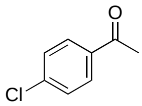
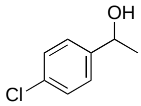
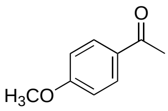
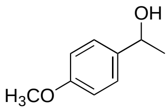
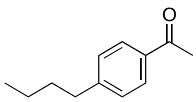
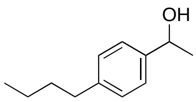
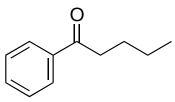
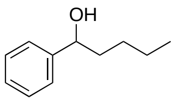
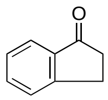
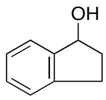
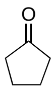
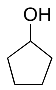
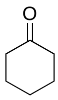
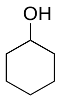
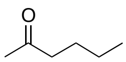
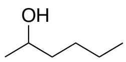
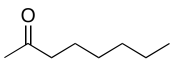
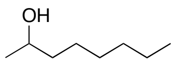
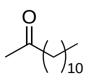
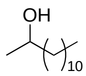
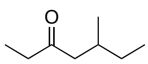
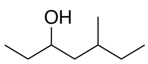
[e] The number of core-bound **2** molecules per a star polymer molecule: $N_2 = f \times r_2$.

[f] The amount of polymer-bound Ru(II) determined by UV-Vis with $RuCl_2(PPh_3)_3$ calibration at 475 nm.

[g] The number of core-bound Ru complexes per a star polymer molecule: N_{Ru} = Ru (μmol/g) x M_w.

[h] The number of **2** molecules per a Ru complex in the core.

Table 2 Ru(II)-PEG Star (C1)-Catalyzed Transfer Hydrogenation of Ketones[a]

Code	Substrate	Product	*t* (h)	Yield[b] (%)	TOF[c] (h^{-1})
S1			4	86 (82)	215
S2			1	93 (94)	930
S3			8	65 (63)	81
S4			4	79 (78)	198
S5			8	82 (87)	103
S6			8	22 (22)	28
S7			8	92 (79)	115
S8			1	98 (95)	980
S9			4	92 (81)	230
S10			4	88 (72)	220
S11			8	87 (82)	109
S12			16	66 (50)	41

[a] Substrate/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in 2-propanol (10 mL) at 100 ^{o}C.

[b]The product yields were determined by ^{1}H NMR. The data in parentheses are product yields obtained with $RuCl_2(PPh_3)_3$.

[c]Turnover frequency: [Product]/([Ru(II)]×*t*).