

Oxidation of Olefins Using Rhenium Supported by Imidazole-Functionalized Amphiphilic Copolymers

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Abstract Well-defined amphiphilic EO_{45} - b - MA_m block copolymers modified with aminopropyl-imidazole groups are used as a support for methyltrioxorhenium. This material appears to be a good catalyst for the oxidation of olefins into the corresponding diols and can be recycle-used.

Keywords Oxidation of olefin · Amphiphilic block copolymer · Recycle catalyst · Rhenium

1 Introduction

The use of micelle systems, which are capable of dissolving organic molecules in water, in obtaining product formation has received much attention and provokes chemist to examine the potential micelles as reaction media [1, 2]. In this context, it has been demonstrated that polymer supports undergo self-assemble in water to form micellar aggregates with a hydrophobic environment providing reactivity better than conventional micelles based on small molecule surfactant [1, 2]. Soluble polymeric supports involve polystyrene, poly(ethylene glycol), and dendritic/hyperbranched polymers [3–7].

In our previous work, we have found that polymers of poly(ethylene glycol)- b -(methyl acrylate) [denoted as EO_n - b - MA_m] are excellent agents to form uniformly micellar aggregates in water with a hydrophobic core and water-soluble shell, thus templating the synthesis of mesoporous silicas [8–10]. Inspired by polymer-support catalysis, we

intended to use EO_n - b - MA_m for preparation of a core-shell-type nano-reactor where the hydrophobic core provides a favorable environment for the metal complex and the reactant, while the hydrophilic shell allows these reactors to be water soluble. Here we describe the preparation of well-defined amphiphilic copolymers (EO_n - b - MA_m) with imidazole units covalently attached to the polymer. The rhenium complexes with this copolymer are studied for the aqueous two-phase oxidation of alkenes.

2 Experimental

All reaction steps for polymerization were performed under a dry nitrogen atmosphere. Dichloromethane was dried with CaH_2 and distilled under nitrogen. $[CH_3(OCH_2CH_2)_{45}NH_2]$, $N[CH_2CH_2N(CH_3)_2]_3$ (Metren), and macro-initiator **MI** were prepared according to the method reported in literature [10]. Nuclear magnetic resonance spectra were recorded on a Bruker AVANCE 400 spectrometer. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pallets. Gel permeation chromatography (GPC) data were obtained from a Waters Model 590 liquid chromatograph installed with a Lab Alliance RI 2000 detector using THF as eluant (at the rate 1 mL/min) at 40 °C and polystyrene calibration curve for analyses.

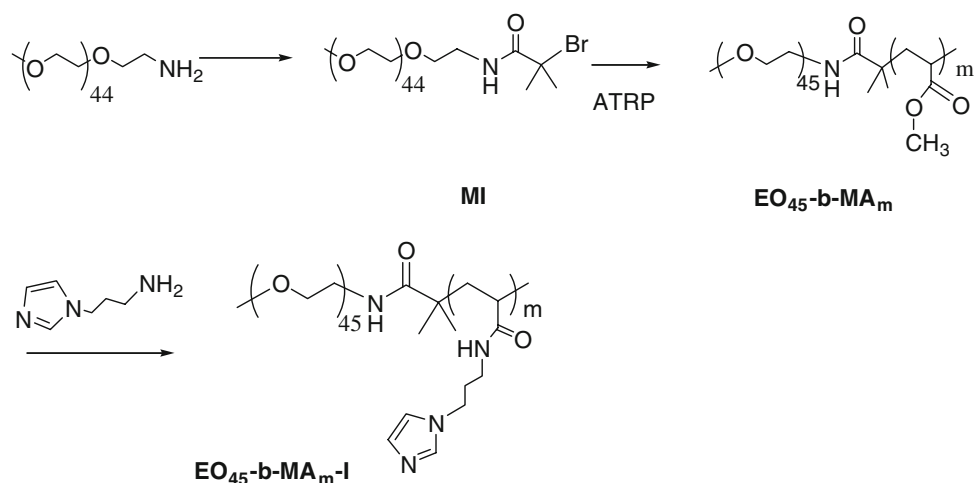
2.1 Synthesis and Characterization (Scheme 1)

2.1.1 Diblock Copolymer (EO_{45} - b - MA_m)

A mixture of **MI** (5.0 g, 2.3 mmol) and CuBr (85 mg, 0.46 mmol) was placed in a 50 mL flask sealed with a septum. The flask was evacuated and flashed with nitrogen

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Scheme 1



three times. Methyl acrylate (15.5 mL, 173 mmol) was syringed into the above mixture with stirring. Metren (175 μL , 0.46 mmol) was then added and the polymerization took place immediately. After stirring 30 min, the reaction was quenched by the addition of THF (30 mL). The reaction mixture was filtered through silica gel to remove the catalyst. Upon concentration and re-precipitation in ether/methanol, the obtained copolymer was dried under vacuum overnight (19.3 g, 99%). ^1H NMR (400 MHz, CDCl_3) δ 3.82–3.60 (255 H, br, $-\text{OCH}_3$), 3.62 (180 H, br, $-\text{OCH}_2\text{CH}_2-$), 3.40 (s, 3H, $-\text{OCH}_3$), 2.40–2.20 (85 H, br, $-\text{CHCH}_2-$), 2.00–1.40 (170 H, br, $-\text{CH}-\text{CH}_2-$), 1.14 (3H, s, $-\text{C}(\text{CH}_3)_2$), 1.12 (3H, s, $-\text{C}(\text{CH}_3)_2$). GPC: $M_N = 9,800$, PDI = 1.13. IR (KBr): $1,744\text{ cm}^{-1}$ ($\nu_{\text{C}=\text{O}}$).

2.1.2 Modification of Copolymer ($\text{EO}_{45}\text{-b-MA}_{85}\text{-I}$)

A mixture of $\text{EO}_{45}\text{-b-MA}_{85}$ (1.0 g, 0.12 mmol) and *N*-(3-aminopropyl)imidazole (1 mL) was heated at $140\text{ }^\circ\text{C}$ for 20 h. Excess of imidazole was removed under vacuum and the residue was dissolved in methanol. Addition of THF to the above solution gave the desired product as white precipitates (1.21 g). ^1H NMR (400 MHz, D_2O) δ 8.20–7.60 (br, 85 H, imidazole-H), 7.40–7.00 (br, 170 H, imidazole-H), 4.22–4.00 (br, 170 H, $-\text{N}-\text{CH}_2-$), 3.80–3.50 (br, 180 H, OCH_2CH_2-), 3.40 (3 H, $-\text{OCH}_3$), 3.30–2.95 (br, 255 H, $-\text{CONCH}_2-$ and $\text{CO}-\text{CH}-\text{CH}_2-$), 1.80–1.15 (170 H, $-\text{CH}-\text{CH}_2-$). IR: (KBr) $3,481\text{ cm}^{-1}$ ($\nu_{\text{N}-\text{H}}$), $1,652\text{ cm}^{-1}$ ($\nu_{\text{C}=\text{O}}$), $1,552\text{ cm}^{-1}$ ($\nu_{\text{C}=\text{N}}$, imidazole).

2.1.3 Preparation of $\text{EO}_{45}\text{-b-MA}_{85}\text{-Re}$

To a solution of $\text{EO}_{45}\text{-b-MA}_{85}\text{-I}$ (50 mg) in ethanol (5 mL) was added a solution of MeReO_3 (30 mg, 0.12 mmol) in 0.5 mL of ethanol. The resulting mixture was stirred at room temperature for several hours. Yellow-brown color precipitation was deposited on the flask, which was obtained by

filtration. This solid was washed with ethanol and ether several times and then dried under vacuum for 2 h. By the analysis of ICP Mass, per gram of this material contained 164 mg of Re. IR $3,481\text{ cm}^{-1}$ ($\nu_{\text{N}-\text{H}}$), $1,649\text{ cm}^{-1}$ ($\nu_{\text{C}=\text{O}}$), $1,548\text{ cm}^{-1}$ ($\nu_{\text{C}=\text{N}}$, imidazole), 912 cm^{-1} ($\nu_{\text{Re}=\text{O}}$).

2.2 Catalysis

2.2.1 Typical Procedure for Oxidation of Cyclohexene

A mixture of cyclohexene (5 mmol), KHSO_5 (10 mmol), and $\text{EO}_{45}\text{-b-MA}_{85}\text{-Re}$ in a mixture of ethyl acetate/water (1:1, 20 mL) was stirred at room temperature for 12 h. The reaction was monitored by GC analysis to check the consume of reactant. Upon standing for 12 h, the organic product was obtained by separation of organic layer. The organic portions was dried and concentrated. Product analysis was performed by GC and ^1H NMR spectroscopic methods. ^{13}C NMR (100 MHz, CDCl_3) δ 75.6, 33.0 and 24.4 ppm, which are all essentially identical to those reported for *trans*-cyclohexanediol [14].

2.2.2 Recycle Use of Catalyst

A mixture of cyclohexene (5 mmol), KHSO_5 (10 mmol), and $\text{EO}_{45}\text{-b-MA}_{85}\text{-Re}$ in a mixture of ethyl acetate/water (1:1, 20 mL) was stirred at room temperature for 12 h. Upon the separation of organic layer, the aqueous portion was added to a mixture of cyclohexene (5 mmol) and KHSO_5 (10 mmol) in ethyl acetate (10 mL). The resulting mixture was stirred for another run.

3 Results and Discussion

The synthesis of linear diblock copolymers ($\text{EO}_{44}\text{-b-MA}_m$) has been accomplished by using the ATRP (Atom transfer

Table 1 Preparation of diblock copolymers^a

Entry	[MA]/[MI]	M _N	PDI	EO:MA ^b
1	85	9800	1.13	45:82
2	45	6100	1.15	45:44
3	30	4800	1.14	45:30

^a Reaction conditions: **MI** (2.3 mmol), [(Me₂NCH₂CH₂)₃N] (0.46 mmol), CuBr (0.46 mmol) and monomer at room temperature

^b Units of EO versus MA

radical polymerization) method [10]. Preparation of the functionalized copolymer is summarized in scheme 1. Macro-initiator (**MI**), which obtained from the condensation of CH₃(OCH₂CH₂)₄₅NH₂ with 2-bromoisobutyryl bromide, was subjected to connect the poly(methyl acrylate) chain by the ATRP [11]. A typical procedure is as follows: a mixture of **MI**, CuBr (20 mol%) and methyl acrylate (MA) forming a homogeneous solution in a 25 mL flask was degassed. [(Me₂NCH₂CH₂)₃N] (20 mol%) was then added. After stirring at room temperature for 1 h, the reaction mixture was diluted with THF. The reaction mixture was passed through silica gel to remove the copper complexes. The filtrate was concentrated to give the desired polymer. By manipulation molar ratio of [MI]/[monomer], a series of polymers EO₄₅MA_m with different chain length of poly-acrylate were obtained (Table 1).

Based on the GPC and ¹H NMR integration, the polymerization degree of MA is estimated, which is consistent with the molar ratio of monomers in the reaction (Table 1). In all instances, all monomers were completely converted into polymers. Infrared spectrum of the copolymer shows a characteristic absorption at 1,744 cm⁻¹ for the carbonyl stretching of acrylate. Under refluxing conditions, treatment of EO₄₅-b-MA_m with excess of 1-(3-aminopropyl)imidazole yielded the imidazole-bound copolymers (EO₄₅-b-MA_m-I). The infrared spectrum of EO₄₅-b-MA_m-I presents a distinctive carbonyl stretching at 1,648 cm⁻¹ with the diminishing peak at 1744 cm⁻¹, indicating that all ester functionalities of the copolymer are converted into the amide linkage. In addition, the ¹H NMR spectrum of EO₄₅-b-MA₈₅-I shows that signals of all methyl groups corresponding to methyl ester are disappeared accompanied with the new shifts at 7.0–7.4 (br) and 7.6–8.2 (br) for the imidazole-hydrogens. Both spectral data are consistent with the formation of the desired functionalized copolymers.

Complexation of rhenium oxide with EO₄₅-b-MA_m-I was achieved by mixing the polymer EO₄₅-b-MA₈₅ and methyltrioxorhenium in ethanol solution. The obtained material (EO₄₅-b-MA₈₅-Re) is a light brown powder solid. Analysis of IR spectra of EO₄₅-b-MA₈₅-Re confirms the coordination of imidazole toward metal ions due to the presence of the expected C=N stretching at 1,548 cm⁻¹.

The loading level of metal ions is determined to be 164 mg per gram of polymer via the ICP Mass analysis. Further evidence for the formation of rhenium complex with imidazole comes from the Raman bands. Raman spectrum of EO₄₅-b-MA₈₅-Re shows the band corresponding to the asymmetric Re=O stretching vibrations at 912 cm⁻¹, which is similar to that for CH₃ReO₃(N–N) [12].

To check the potency of EO₄₅-b-MA₈₅-Re for the oxidation reaction, cyclohexene was treated with oxidants in aqueous two-phase at room temperature (Table 2). It is quite obvious that the oxidation proceeds smoothly under phase-transfer conditions, better than in an organic solvent. Without the use of surfactants (CTAB), MeReO₃ does not show good catalytic activity on the oxidation (entry 2 versus 3). Obviously, the good activity of the EO₄₅-b-MA₈₅-Re is because of the amphiphilic supporting and the imidazole ligand accelerated catalysis. From NMR spectroscopy, the product obtained is the 1,2-cyclohexanediol instead of the epoxide. The ¹³C shifts of the diol product shows δ 75.6, 33.0 and 24.4 ppm, which are consistent with the *trans*-isomer [13]. Apparently, this catalytic reaction provides the epoxide as the initial product, which is subsequently hydrolyzed into the *trans*-diol. This result is quite different from the work reported by Saladino and coworkers [14]. They reported that microencapsulated Lewis base adduct of MeReO₃ with amine ligands was an efficient catalyst for the epoxidation of olefins in organic solvent. However, we learned that the catalytic system in our study was quite acidic and pH value reached up to 2–3, which might explain the production of the diol instead of the epoxide.

To optimize the reaction conditions, the oxidation reactions were performed under various conditions using at EO₄₅-b-MA₈₅-Re. Both CH₂Cl₂/water and ethyl acetate/water are good solvent systems for carrying out the oxidation (Table 2, entries 5 and 7). Higher oxidation yields were obtained with ethyl acetate and dichloromethane because they are good solvents for reactants and diffuse easily in the polymer. However, the use of hexane/water as the solvents leads the failure of the catalysis, which might be due to the insoluble nature of the polymer in hexane.

The ability of different oxidants such as O₂, H₂O₂, KHSO₅ and urea–H₂O₂ (UHP) was examined in the oxidation of cyclohexene at room temperature. The results showed that in the presence of EO₄₅-b-MA₈₅-Re catalyst, KHSO₅ was the best oxygen source due to good oxidation conversions. Other oxidants in ethyl acetate/water did not show any good activity. The temperature effect was less pronounced as observed from conversions of 45% at room temperature, 44% at 40 °C and 46% C at 60 °C.

In view of the above results, the catalytic system renders the best yield in oxidation of cyclohexene into *trans*-1,2-cyclohexanediol and was followed in the subsequent

Table 2 Results of the oxidation of cyclohexene in the presence of $\text{CH}_3\text{ReO}_3^{\text{a}}$

Entry	Catalyst	Oxidant	Solvent	T (°C)	t (h)	Conv. (%) ^b	Yield (%) ^c	TON ^d
1	None	KHSO ₅	EA/H ₂ O	rt	24	7	7	80
2	CH ₃ ReO ₃	KHSO ₅	EA/H ₂ O	rt	12	45	45	513
3	CH ₃ ReO ₃ /CTAB ^e	KHSO ₅	EA/H ₂ O	rt	12	100	100	1140
4	EO ₄₅ MA ₈₅ -Re	KHSO ₅	EA/H ₂ O	rt	5	45	44	502
5	EO ₄₅ MA ₈₅ -Re	KHSO ₅	EA/H ₂ O	rt	12	100	100	1140
6	EO ₄₅ MA ₈₅ -Re	KHSO ₅	Ether/H ₂ O	rt	48	34	33	376
7	EO ₄₅ MA ₈₅ -Re	KHSO ₅	CH ₂ Cl ₂ /H ₂ O	rt	12	100	100	1140
8	EO ₄₅ MA ₈₅ -Re	KHSO ₅	Hexane/H ₂ O	rt	48	0	–	–
9	EO ₄₅ MA ₈₅ -Re	KHSO ₅	EA/H ₂ O	40 °C	5	44	43	490
10	EO ₄₅ MA ₈₅ -Re	KHSO ₅	EA/H ₂ O	60 °C	5	46	46	524
11	EO ₄₅ MA ₈₅ -Re	O ₂	EA/H ₂ O	rt	48	0	–	–
12	EO ₄₅ MA ₈₅ -Re	H ₂ O ₂	EA/H ₂ O	rt	12	30	–	–
13	EO ₄₅ MA ₈₅ -Re	UHP	EA/H ₂ O	rt	48	30	–	–

^a Reaction conditions: cyclohexene (5 mmol), catalyst (5 mg) and oxidant (10 mmol) in solvent (10 mL; 1:1 by volume). [cyclohexene]:[Re] = 1,140

^b Determined by GC

^c *trans*-1,2-Cyclohexanediol; yield based on NMR integration with mesitylene as the internal standard in CDCl₃

^d TON = per mol product/per mol Re catalyst

^e CTAB = Cetyltrimethylammonium bromide

Table 3 Conversion of alkenes into its corresponding diol^a

Entry	Alkenes	Solvents	Time (h)	Yield (%)	TON ^d
1	1-methylcyclohexene	EA/water	5	100	1140
2	1-methylcyclohexene	CH ₂ Cl ₂ /water	5	96	1090
3	1-acetylcyclohexene	EA/water	5	–	–
4	4-vinylcyclohexene	EA/water	12	86 ^b	980
5	1-ethynylcyclohexene	EA/water	24	85	970
6	Limonene	EA/water	48	62 ^c	706
7	Styrene	EA/water	48	79	900
8	Cyclooctene	CH ₂ Cl ₂ /water	48	81	923
9	1-hexene	EA/water	12	–	–

^a Reaction conditions: olefin (5 mmol), KHSO₅ (10 mmol), catalyst (5 mg), solvent (10 mL) and water (10 mL) at room temperature. [alkene]:[catalyst] = 1,140

^b 4-vinylcyclohexane-1,2-diol as the product

^c 4-isopropenyl-1-methyl-cyclohexane-1,2-diol as the product

^d TON = per mol product/per mol Re catalyst

studies. Various substituted olefins are tested under this reaction conditions and the results are summarized in Table 3. Substituted cyclohexenes when reacted with KHSO₅ via the EO₄₅-b-MA₈₅-Re catalyst afforded the corresponding diol in excellent yields except 1-acetylcyclohexene (entries 1–6). Under the reaction conditions, oxidation of 1-acetylcyclohexene gave cyclohexanone as the major product due to the hydrolysis. It is also noticed that the internal double bond of limonene is readily oxidized, but the terminal one remains intact, i.e. 4-isopropenyl-1-methyl-cyclohexane-1,2-diol was obtained

as the only product. Under the similar reaction conditions, the vinyl group of 4-vinylcyclohexene did not undergo the oxidation (entry 4), neither the double bond of 1-hexene did (entry 9). This selectivity is presumably due to the electronic effect of C=C, which is similar to other related oxidation [15].

The stability and activity of the catalyst was tested in the recycle-use experiments. Typically, a mixture of cyclohexene (5 mmol), EO₄₅-b-MA₈₅-Re (5 mg) and KHSO₅ (10 mmol) in a mixture of ethyl acetate/water (1:1, 20 mL) was stirred at room temperature for 12 h. After stop

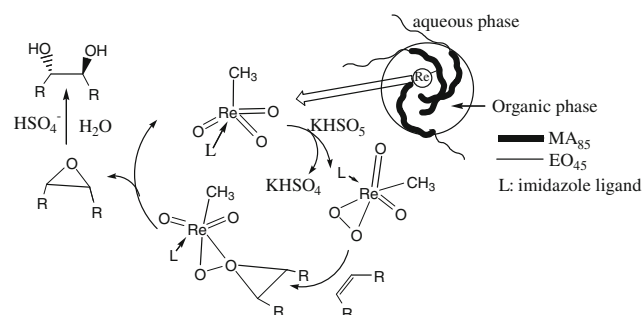
Table 4 Oxidation of cyclohexene by the recycle catalyst^a

Run	1	2	3	4	5	6	7
Yield (%)	100	96	100	100	97	98	95

^a Reaction conditions: cyclohexene (5 mmol), KHSO_5 (10 mmol), catalyst (5 mg), ethyl acetate (10 mL) and water (10 mL) at room temperature for 12 h

stirring, the organic layer was separated. Another portion of substrate and oxidant in ethyl acetate was added to the aqueous residue for the next run. Over a period of seven reaction cycles under the same conditions, a minor leaching of metal ion was detected, but no significant loss of activity. The results are listed in Table 4. By the analysis of ICP Mass, less than 5% of rhenium was leached after seven runs. After the first run, a small portion of aqueous portion was dried under vacuum and the infrared spectrum of the residue was determined. The spectrum is much more complicated than the pre-catalyst. However, the absorptions corresponding to the C=O stretching frequency ($1,645\text{ cm}^{-1}$) and C=N ($1,540\text{ cm}^{-1}$) appear in the spectrum, indicating that the copolymer remains intact during the catalysis.

Reaction mechanisms for epoxidation of an olefin catalyzed by methyltrioxorhenium complex have been proposed by Herrmann's and Espenson's groups. Pathways involve the direct oxidation of metal center to yield the corresponding monoperoxo or diperoxo species, which then undergo the oxygen transfer to yield the epoxide [16–19]. It is believed that the introduction of nitrogen donor ligand around the rhenium metal center would accelerate the catalytic reaction, which is presumably due to the stabilization of the intermediates via the coordination of N-donor ligand toward metal ions [17]. Scheme 2 shows the possible reaction pathway for the bishydroxylation of olefin catalyzed by EO_{45} -b- MA_{85} -Re system. The rhenium metal center plays the role for the oxidation. This initial oxidation results in the formation of epoxide, which is subsequently hydrolyzed by water under acidic conditions to yield the *trans*-diol.

**Scheme 2**

In the EO_{45} -b- MA_{85} -I system, the hydrophobic core provides a favorable environment for the metal complex through a coordination or chelation, which prevents the leaching of metal ion from the organic phase. Indeed, less than 5% loss of rhenium metal ions was observed after seven recycle-runs. The other advantage of this oxidation process is the use of potassium hydrogen peroxysulfate (KHSO_5) (known as Oxone), a commercial available chemical, which also provides an acidic medium during the reaction.

4 Conclusion

In conclusion, this procedure offers several advantages for the preparation of diols from the corresponding olefins such as low loading of catalyst, mild conditions, high yields, and clean reactions, which make it a useful and attractive methodology for organic synthesis. The simple workup procedure is also beneficial to this method. Further applications of this catalyst to other transformations are currently under investigation.

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