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DEVELOPMENT OF TIGHTLY CONVOLUTED POLYMERIC PHOSPHOTUNGSTATE CATALYSTS AND THEIR APPLICATION TO AN OXIDATIVE CYCLIZATION OF ALKENOLS AND ALKENOIC ACIDS

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Abstract – Tightly convoluted polymeric phosphotungstate catalysts were prepared via ionic-assembly of $H_3PW_{12}O_{40}$ and poly(alkylpyridinium)s. An oxidative cyclization of various alkenols and alkenoic acids was efficiently promoted by the polymeric phosphotungstate catalyst in *aq*. H_2O_2 in the absence of organic solvents to afford the corresponding cyclic ethers and lactones in high yield. The catalyst was reused four times without loss of catalytic activity. The polymeric phosphotungstate was unambiguously characterized by spectro- and microscopic studies (MAS $^{31}P\{^1H\}$ NMR, IR spectroscopy, elemental analysis, TEM, SEM, and EDS).

INTRODUCTION

The development of immobilized catalysts exhibiting high aquacatalytic activity[1] and recyclability[2] has become an important topic in organic chemistry today.[3,4] We have developed amphiphilic polymer resin-supported transition metal complexes and nanoparticles that catalyze various organic transformations in water under heterogeneous conditions.[5,6,7] Recently, we have also presented a novel self-assembling protocol for the preparation of solid-phase catalysts where metal species served as cross-linkers of non-cross-linked polymeric ligands as well as catalytically active centers.[8,9] Thus, for example, an ionically crosslinked polymeric phosphotungstate catalyst PWAA was prepared via salt formation of $PW_{12}O_{40}^{3-}$ with poly{[3-(acryolylamino)propyl]-dodecyldimethylammonium nitrate}-*co*-(*N*-isopropylacrylamide)$_{12}$}, a main chain of poly(*N*-isopropylacrylamide) bearing branched ammonium cation parts (Figure 1, top).[10] The polymeric phosphotungstate PWAA catalyzed the oxidation of alkenes, amines, and sulfides; however, it could not be sufficiently recycled presumably due to its physical fragility. More rigid assembling of the cationic polymer with the phosphotungstate anion might provide more stable polymeric catalysts. Here we would like to report the amphiphilic pyridinium polymer **1** bearing main-chain cationic groups constructed with a tightly convoluted pyridinium phosphotungstate salt which exhibited high catalytic activity and recyclability for oxidative cyclization of alkenols and alkenoic acids (Figure 1, bottom).[11] The polymeric pyridinium phosphotungstate was found to catalyze the oxidative cyclization of a wide variety of (*E*)- and (*Z*)-alkenols as well as (*E*)- and (*Z*)-alkenoic acids with high stereospecificity in aqueous hydrogen peroxide under organic solvent-free conditions, and was reused four times without loss of catalytic activity.

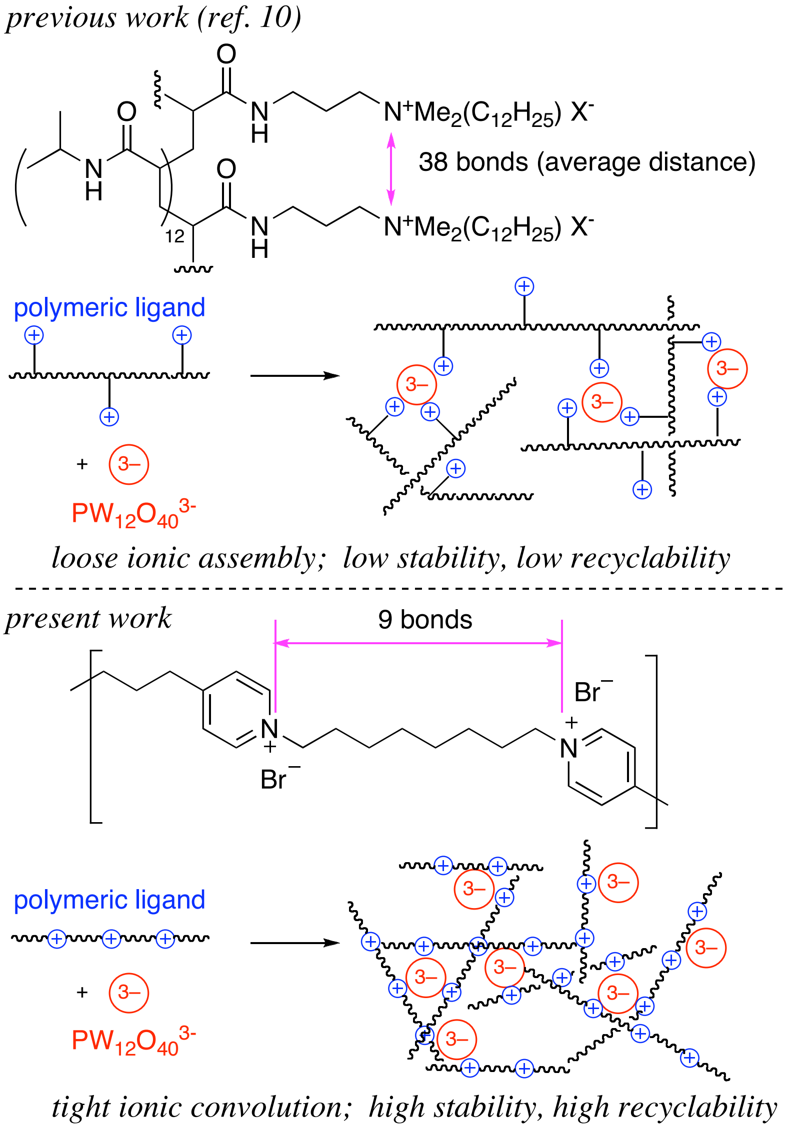


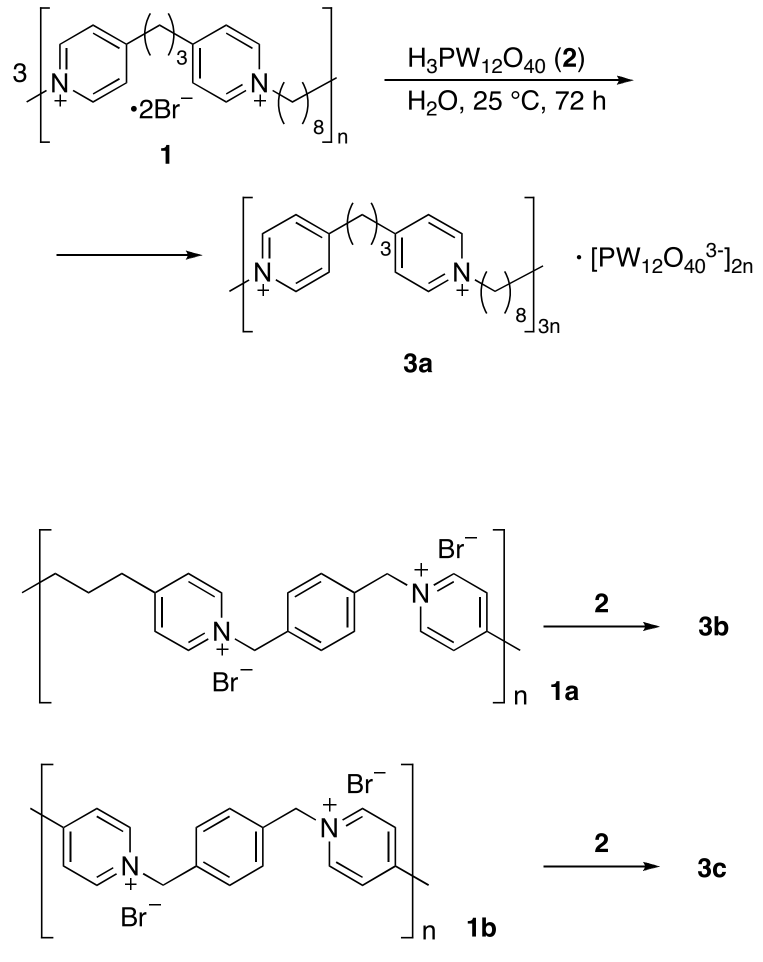
Figure 1. An assembly of $H_3PW_{12}O_{40}$ and an amphiphilic copolymer with a branched ligand (top); a tight assembly of $H_3PW_{12}O_{40}$ and a main-chain pyridinium polymer (bottom)

RESULTS AND DISCUSSION

A polymeric tungsten catalyst was readily prepared from poly[1,8-dibromooctane-*co*-1,3-di(4-pyridyl)-propane] (**1**)[12] with $H_3PW_{12}O_{40}$ (**2**)[13] according to the preparation of $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$.[14] Thus, when an aqueous solution of **2** was added to an aqueous solution of **1** at 25 °C, the ionic components assembled to give the polymeric salt **3a** as a white powder (83% yield), which was insoluble in water, ethanol, ethyl acetate, tetrahydrofuran, dichloromethane, toluene and hexane (Scheme 1). Poly[1,4-bis(bromomethyl)benzene-*co*-1,3-di(4-pyridyl)propane] (**1a**) and poly[1,4-bis(bromomethyl)-benzene-*co*-4,4'-bipyridine] (**1b**) were also reacted with **2** under similar conditions to give polymer salts **3b** and **3c**, respectively.

The polymeric phosphotungstate **3a** was unambiguously characterized by spectro- and microscopic studies (MAS $^{31}P\{^1H\}$ NMR, IR spectroscopy, elemental analysis, TEM, SEM, and EDS). Typical data are shown in Figure 2. MAS $^{31}P\{^1H\}$ NMR of the polymeric **3a** showed a narrow singlet resonance at -16.5 ppm that was identical to a phosphorus resonance of $PW_{12}O_{40}^{3-}$.[15,16]

Scheme 1. Preparation of New Generation Convoluted Polymeric Tungsten Catalysts[a]



[a] **1** (3 mol equiv of a pyridinium), **2** (1 mol equiv), water, 25 °C, 3 d.

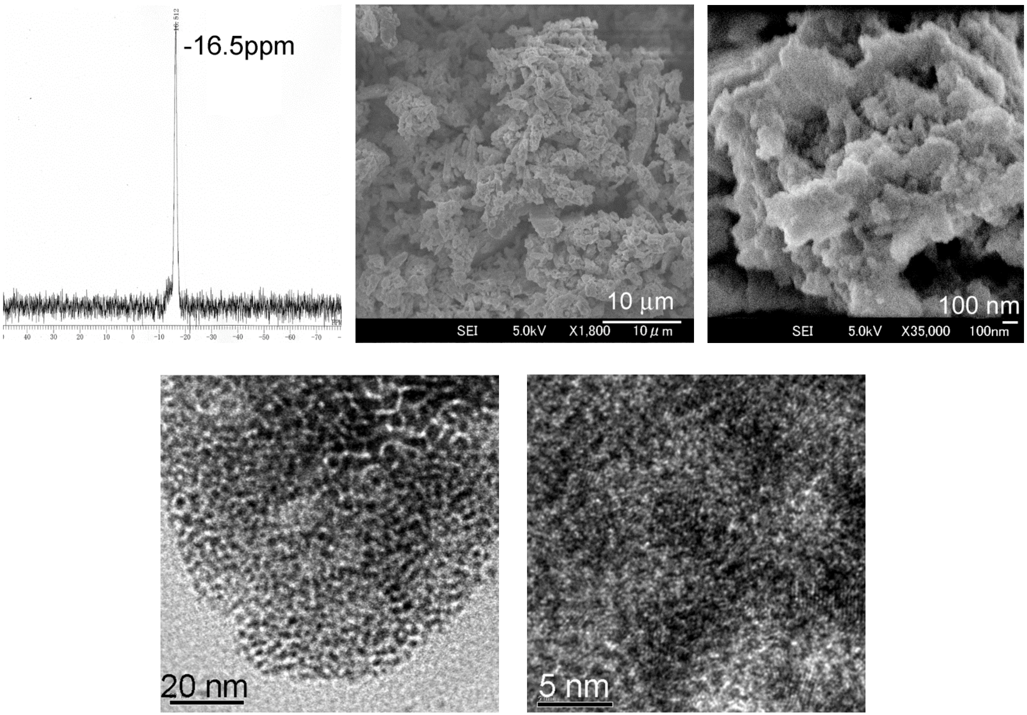


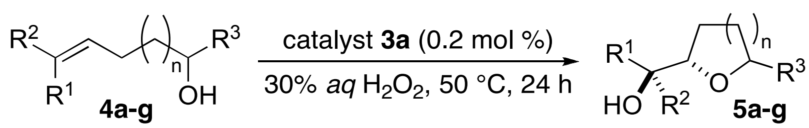
Figure 2. MAS $^{31}P\{^1H\}$ NMR (top, left), SEM (top, center; bar length = 10 μm), HR-SEM (top, right; bar length = 100 nm), and TEM (bottom; bar length = 20 nm (left), 5 nm (right)) images of the solid-phase catalyst **3a**.

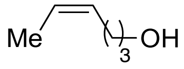
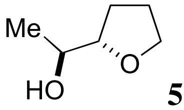
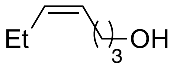
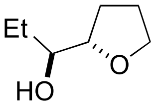
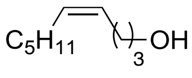
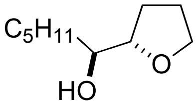
High-resolution TEM analysis of **3a** revealed that the phosphotungstate clusters were uniformly dispersed throughout the polymer matrix having a diameter of ca. 1 nm, which is consistent with the size of monomeric $PW_{12}O_{40}^{3-}$.[17] The NMR and TEM observations indicate the integrity of the monomeric structure of $PW_{12}O_{40}^{3-}$, whereas a similar phosphotungstate $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is known to form an aggregated tertiary structure ($(Cs_{2.5}H_{0.5}PW_{12}O_{40})_n$; ϕ = 100-500 nm).[12] SEM images of **3a** confirmed its dendroidal surface. The polymeric phosphotungstate **3a** was expected to exhibit good catalytic performance owing to the immense surface area of the convoluted composite **3a** and the monomeric structure of the phosphotungstate cluster.

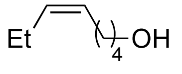
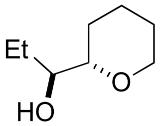
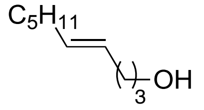
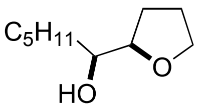
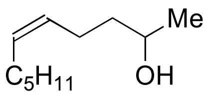
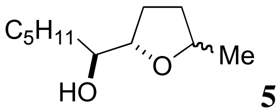
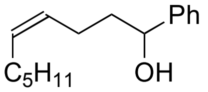
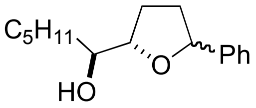
The aquacatalytic potential of the novel polymeric phosphotungstate **3a** was examined for the oxidative cyclization of alkenols with aqueous hydrogen peroxide (Table 1) producing furanyl- and pyranyl carbinols, which are the key components of biologically active compounds.[18, 19] While only homogeneous transition metal-catalysts have been developed for oxidative cyclizations so far,[20] the development of immobilized solid-phase catalysts still remains a major challenge in terms of catalytic activity and recyclability.[21] When the oxidations of the *cis*-alkenols, (*Z*)-4-hexen-1-ol (**4a**), (*Z*)-4-hepten-1-ol (**4b**), and (*Z*)-4-decen-1-ol (**4c**), were carried out with **3a** (0.2 mol % $PW_{12}O_{40}^{3-}$) in 30% aqueous H_2O_2 at 50 °C, we were pleased to find that the *threo*-1-(2-tetrahydrofuranyl)alkanols **5a**-**c** were obtained in 92-98% yield with complete diastereoselectivity (entries 1-3). The reaction of **4c** with polymeric phosphotungstates **3b** or **3c** was performed under similar conditions to give **5c** in 82% and

83% yields, respectively (entries 9 and 10). The cyclization of (*Z*)-5-octen-1-ol (**4d**) proceeded smoothly to give the *threo*-tetrahydropyranyl alcohol **5d** in 74% yield (entry 11). (*E*)-4-Decen-1-ol (**4e**) also underwent the cyclization to give the *erythro*-product **5e** in 82% yield (entry 12). These stereochemical observations indicate that the cyclization involves a stereospecific reaction pathway. The secondary alcohols **4f** and **4g** were converted to the corresponding *threo*-tetrahydrofuranols **5f** and **5g** in 86 and 82% yield, respectively, without control of the stereochemistry at the C5-position of the tetrahydrofuran (entries 13 and 14).[22]

Table 1. The Oxidative Cyclization of Alkenols and Alkenoic Acids Catalyzed by **3a** [a]



entry	substrate	product	yield (%) [b]
1	 **4a**	 **5a**	96[c]
2	 **4b**	 **5b**	98[c]
3	 **4c**	 **5c**	92[c]
4	(2nd use)		99[c]
5	(3rd use)		99[c]
6	(4th use)		94[c]
7	(5th use)		99[c]
8	(6th use)		94[b,d]
9[e]	**4c**	**5c**	82
10[f]	**4c**	**5c**	83

11	 **4d**	 **5d**	74[c]
12[g]	 **4e**	 **5e**	82
13	 **4f**	 **5f**	86 (1:1)[h]
14	 **4g**	 **5g**	82 (1:1)[h]

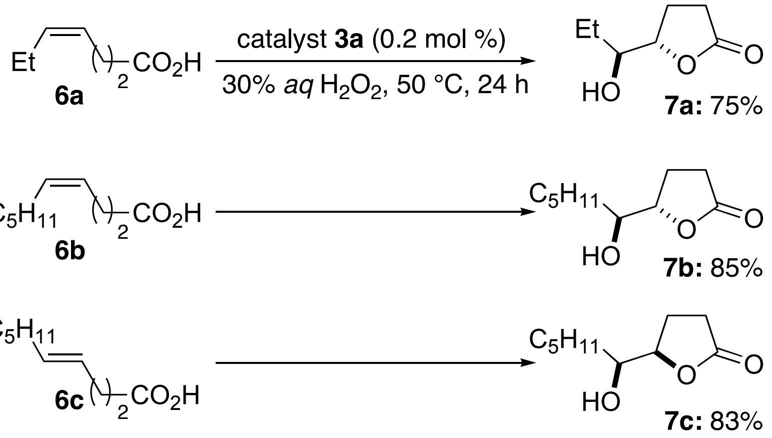
[a] All reactions were performed in the presence of **4** (1 mol equiv), 30% aq H_2O_2 (2.5 mol equiv), and **3a** (0.2 mol % phosphotungstate) at 50 °C for 24 h. [b] Isolated yields otherwise noted. [c] GC yield. [d] The catalyst was reused after being stored for 6 months. [e] The catalyst **3b** was used. [f] The catalyst **3c** was used. [g] **3a** (0.4 mol %); aq H_2O_2 (3.5 mol equiv); reaction time, 35 h. [h] Diastereomeric ratio.

Recycling experiments of the insoluble catalyst **3a** were examined in the oxidative cyclization of **4c** (entries 3-7). Thus, the first use of the catalyst afforded **5c** in 92% yield. After being recovered by filtration, washed with water and dried *in vacuo*, the catalyst was reused to give **5c** in quantitative yield. To our delight, the third, fourth and fifth uses of the recovered catalyst also provided **5c** in 99%, 94%, and 99% yields, respectively. After the fifth use (entry 7), the recovered catalyst was stored for 6 months under atmospheric conditions at ambient temperature and then subjected to the sixth run (entry 8) to give 94% yield of **5c**.

Alkenoic acids were also suitable substrates for the oxidative cyclization (Scheme 2). Thus, the oxidative cyclization of (*Z*)-4-heptenoic acid (**6a**), (*Z*)- **6b**, and (*E*)-4-decenoic acid **6c** under similar conditions proceeded stereospecifically to afford the corresponding lactones **7a-c** in 75-85% yield. By using this catalytic system, L-factor (leucomycin-inducing-factor) **7b**, isolated from *Streptomyces griseus*,[23] was obtained in 85% yield.

In conclusion, the novel tightly convoluted polymeric phosphotungstate cluster catalyst **3a** was readily prepared via the ionic self-assembly process of a main-chain polypyridinium and phosphotungstic acid. It is noteworthy that this polymeric catalyst effectively catalyzed the oxidative cyclization of a variety of alkenols and alkenoic acids in aqueous H_2O_2 under organic solvent-free conditions. The insoluble catalyst was reused without any loss of catalytic activity.

Scheme 2



EXPERIMENTAL

Preparation of Solid-phase Tungsten Catalyst **3a**

To an aqueous solution (30 mL) of poly[1,8-dibromooctane-*co*-1,3-di(4-pyridyl)propane] (**1**) (148 mg; 0.63 mmol of a pyridinium unit) was added an aqueous solution (70 mL) of $H_3PW_{12}O_{40}$ **2** (608 mg; 0.21 mmol) at 25 °C, and the resulting colorless suspension was stirred for 3 days at the same temperature. The precipitates were collected by filtration, washed with water and dried at 5 Pa for 12 h to give **3a** (624 mg; 83%) as a colorless powder.

MAS $^{31}P\{^{1}H\}$ NMR (162 MHz; $CDCl_3$): δ -16.5 ppm; IR (ATR) ν 3727, 3624, 3062, 2927, 2858, 1638, 1572, 1514, 1469, 1172, 1077, 974, 892, 792, cm^{-1}; Anal. Calcd for $(C_{63}H_{90}N_6P_2W_{24}O_{80})_n$: C, 11.32%; H, 1.36%; N, 1.26%. Found: C, 12.45%; H, 1.60%; N 1.32%.

General Procedure for the Oxidative Cyclization of Alkenols **4** or Alkenoic Acids **6**

To a suspension of **3a** (13 mg) in 30% aq H_2O_2 (5 mmol) was added **4** or **6** (2 mmol) (and mesitylene (an internal standard for the determination of a GC yield)), and the resulting suspension was stirred at 50 °C for 24 h. After the reaction mixture was cooled to 25 °C, *t*-butyl methyl ether was added, and the resultant organic layer was separated by decantation. After the addition and extraction process were carried out for three times, the combined organic layer was subjected to GC-MS analysis for the determination of a GC yield (for **5a**, **5b**, **5c** and **5d**). The organic layer was washed with sat. aqueous $Na_2S_2O_3$, dried over $MgSO_4$, dried in vacuo, and purified by silica gel column chromatography to give the cyclized product (for **5e**, **5f**, **5g**, **7a**, **7b** and **7c**). The recovered **3a** was dried in vacuo, and subjected to the next series of the reaction under similar reaction conditions.

CAS registry #:

1: 158400-75-0; **1a**: 67291-12-7; **1b**: 32168-10-8; **2**: 12501-23-4; **3a**: 158400-75-0; **4a**: 928-91-6; **4b**: 6191-71-5; **4c**: 57074-37-0; **4d**: 64275-73-6; **4e**: 10339-62-5; **4f**: 92051-77-9; **4g**: 854001-04-0; **5a**: 16765-41-6; **5b**: 33964-64-6; **5c**: 143493-19-0; **5d**: 157756-84-8; **5e**: 143264-37-3; **5f**: 144539-31-1/144539-30-0; **5g**: 854000-82-1; **6a**: 41653-95-6; **6b**: 505-90-8; **6c**: 57602-94-5; **7a**: 97101-23-0; **7b**: 82309-35-1; **7c**: 82309-34-0

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