

Polymerization and Isomerization of Oxetanes using Heteropolyacid as a Catalyst

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The reaction of oxetanes using heteropolyacids as catalysts was examined. The reaction of 3-ethyl-3-phenoxy-methyloxetane (EPMO) was examined using commercial heteropolyacid without any treatment (PW_{12-com.}) as a catalyst at 80 °C in chlorobenzene for 12 h, and the cationic ring-opening polymerization of EPMO proceeded smoothly to give the corresponding polyether poly(EPMO) in 89% yield. However, no polymer was obtained using treated heteropolyacid PW_{12-dry270} as a catalyst which is heated at 270 °C *in vacuo* before use. Furthermore, the cationic isomerization reaction of 3-acethyloxymethyl-3-ethyloxetane (AOEO) using PW_{12-dry270} was examined to give 4-ethyl-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE) in 70% yield.

KEY WORDS: Oxetane / Heteropolyacid / Catalyst / Cationic Ring-opening Polymerization / Cationic Isomerization /

Heteropolyacids (HPA's) are well-known^{1–3} as multifunctional catalysts in the organic chemistry and also act as solid acid catalysts for the cationic polymerization of olefins and cyclic ethers. It was reported⁴ that cationic polymerizations of tetrahydrofuran (THF) and 1,3,5-trioxane using HPA as a catalyst proceeded smoothly to afford the corresponding polyether and poly(oxy-methylene) with high molecular weights in high yields, respectively. Aoshima *et al.*⁵ also reported that poly(THF) with narrow molecular weight distribution could be obtained using the complex of water and HPA as a catalytic system.

Meanwhile, oxetanes with 4-membered ring are well-known^{6–13} to be polymerized very smoothly with cationic catalysts due to their high basicities. Some interesting cationic reactions of oxetane using certain catalysts have been reported. Vandenberg *et al.*¹⁰ reported the synthesis of linear polyethers by the cationic ring-opening polymerization of 3,3-bis-(hydroxymethyl)oxetane (BHO) using aluminium complexes as cationic catalysts. Hult *et al.*¹⁴ reported the synthesis of hyperbranched polyethers by the cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (EHO) using antimonate derivative as a cationic catalyst. Penczek *et al.*¹⁵ also reported the synthesis of hyperbranched polyethers by the cationic ring-opening polymerization of BHO and the copolymerization of BHO and EHO with medium molecular weight polymers in good yields. Furthermore, Motoi *et al.*^{16–21} reported that the isomerization reaction of oxetanes containing ester groups proceeded smoothly using acid catalysts to give the corresponding bicyclo ortho esters selectively. These results indicate that the cationic reactions of oxetanes are strongly affected by the structures of oxetanes and catalysts, and the combination of oxetanes with catalysts. Chen *et al.*²² reported the cationic polymerization of tetrahydrofuran using oxetane as a promoter in the presence HPA as a catalyst.

However, there are no detail study concerning the cationic organic reactions of oxetanes using HPA as a catalyst. Here, we

report the cationic isomerization and polymerization of certain oxetanes using 12-tungsto(IV)phosphoric acids (PW₁₂) as HPA catalyst.

EXPERIMENTAL

Materials

Commercial chlorobenzene was dried using CaH₂ and purified by distillation before use. Reagents grade pyridine, acetic anhydride, and HCl were used without further purification. 12-Tungsto(IV) phosphoric acid (PW_{12-com.}) was purchased from WAKO Co and used without further modification. PW_{12-com.} was heated at 200 and 270 °C *in vacuo*, to form the corresponding dried catalysts PW_{12-dry200} and PW_{12-dry270}, respectively. 3-Ethyl-3-phenoxy-methyloxetane (EPMO) and 3-ethyl-3-hydroxymethyloxetane (EHMO) (donated from Toagosei Co., Ltd.) were purified by distillation before use.

Measurements

¹H NMR and ¹³C NMR spectroscopy were recorded on a JEOL Model JNM α-500 (500 MHz for ¹H NMR and 125 MHz for ¹³C NMR) instrument in CDCl₃ using Me₄Si (TMS) as an internal standard. IR spectra were measured on a Jasco Model FT/IR-420 spectrometer. The number-average molecular weight (*M_n*) and weight-average molecular weight (*M_w*) of the polymers were estimated by size exclusion chromatography (SEC; TOSO model HLC-8020) on TSK gel Multipore Hx1-M columns calibrated by narrow molecular weight polystyrene standards and with THF as an eluent without correction with a refractive index detector.

Synthesis of 3-Acethyloxymethyl-3-ethyloxetane (AOEO)

AOEO was synthesized by the according to the reported method²³ as follows. Acetic anhydride (30.6 g, 300.0 mmol) was added slowly to the solution of EHMO (29.0 g, 250.0 mmol) and

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pyridine (23.7 g, 300.0 mmol) in THF at 0 °C and stirred at room temperature for 12 h. The reaction mixture was concentrated by a rotary evaporator. After that, ethyl acetate (400 mL) was added to the residues and washed following water with three times, the saturated aqueous solution of sodium hydrogen carbonate, hydrochloric acid solution (10% v/v), and water. The organic layer was dried over with MgSO₄ and concentrated by a rotary evaporator, followed by distillation to obtain colorless liquid AOEO. Bp = 72 °C/5 mmHg. Yield = 24.9 g (63%). IR (bulk, cm⁻¹): 1741 (ν C=O, ester), 1241 (ν C-O-C) and 983 (ν C-O-C cyclic ether). ¹H NMR (500 MHz, CDCl₃, TMS) δ (ppm) = 0.92 (t, 3.0H, *J* = 7.8 Hz, -CH₂-CH₃), 1.76 (q, 2.0H, *J* = 7.8 Hz, -CH₂-), 2.10 (s, 3H, -CH₃), 4.21 (s, 2H, -O-CH₂-), 4.41, 4.47 (dd, 4H, *J* = 6.6, *J* = 28.0 Hz, -O-CH₂- cyclic ether). ¹³C NMR (125 MHz, CDCl₃, TMS) δ (ppm) = 8.22 (-CH₂-CH₃), 20.92 (-CH₃), 26.93 (-CH₂-), 42.64 (=C=), 66.46 (-O-CH₂-), 77.96 (-O-CH₂- cyclic ether), 171.23 (>C=O carbonyl carbon).

Cationic Ring-Opening Polymerization of EP MO

Typical procedure: PW_{12-com.} (1.5 mg, 0.1 wt %) in a polymerization tube equipped with rubber septum was degassed and substituted with nitrogen at room temperature. Chlorobenzene (8 mL) and EP MO (1.54 g, 8.0 mmol) were injected by syringe and, then the solution was stirred at 80 °C for 12 h. After that, PW_{12-com.} was filtered off and washed with chloroform several times. The resulting organic phase was evaporated under reduced pressure. The residual oil was poured into large amount of methanol to precipitate the colorless high viscous oily product and then dried *in vacuo* at 60 °C for 24 h to obtain the polymer. The yield of polymer was 89% (1.36 g). *M_n* = 14400, *M_w*/*M_n* = 2.3. IR (film, cm⁻¹): 1598 and 1496 (ν C=C of aromatic), 1243 and 1106 (ν C-O-C). ¹H NMR (500 MHz, CDCl₃, TMS) δ (ppm) = 0.66–0.83 (m, -CH₂-CH₃), 1.32–1.44 (m, -CH₂-CH₃), 3.12–3.27 (m, -CH₂-O-CH₂-O-), 3.60–3.77 (m, -CH₂-OPh), 6.67–7.26 (m, aromatic). ¹³C NMR (125 MHz, CDCl₃, TMS) δ (ppm) = 8.17 (-CH₂-CH₃), 23.78 (-CH₂-CH₃), 43.63 (>C<), 69.12 (-CH₂-OPh), 71.95 (-CH₂-O-CH₂-O-), 114.93–159.87 (aromatic).

Cationic Isomerization of AOEO

Chlorobenzene (8 mL), AOEO (1.25 g, 8.0 mmol), and PW_{12-dry270} (1.3 mg, 0.1 wt %) were injected in a three-way stopcock under nitrogen by syringe, and then the solution was stirred at 80 °C for 12 h. After that, the mixture was concentrated. The residual was purified by column chromatography on alumina using mixed solvents of *n*-hexane and ethylacetate as an eluent, followed by recrystallization from the mixed solvents of *n*-hexane and ethylacetate to obtain the colorless solid, 4-ethyl-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE).²⁴ The yield of BOE was 70% (0.88 g). IR (KBr, disk cm⁻¹): 998 (ν C-O-C). ¹H NMR (500 MHz, CDCl₃, TMS) δ (ppm) = 0.81 (t, *J* = 7.5 Hz 3.0H, -CH₂-CH₃), 1.24 (q, *J* = 7.5 Hz 2.0H, -CH₂-CH₃), 1.45 (s, 3H, =C-CH₃), 3.92 (s, 6H, O-CH₂-C). ¹³C NMR (125 MHz, CDCl₃, TMS) δ (ppm) = 7.31 (-CH₂-CH₃), 22.52 (-CH₂-CH₃), 31.22 (-CH₃), 33.13 (=C=), 64.09 (-O-CH₂-), 109.44 (-C(-O-CH₂)-₃).

RESULT AND DISCUSSION

Preparation of 12-Tungsto (IV) Phosphoric Acid (PW₁₂)

When we examined the reaction of oxetane and commercial grade PW₁₂ (PW_{12-com.}) in certain solvents, the good reproducibility of the resulting polymers could not be obtained. As described in the introduction, it has been reported that water was required for the cationic polymerization system of THF using HPA as a catalyst. Therefore, we considered that the values of absorbed water on HPA should be controlled. PW_{12-com.} was heated at 200 °C and 270 °C *in vacuo* for 8 h to prepare the unhydrous catalysts such as PW_{12-dry200} and PW_{12-dry270}, respectively. Figure 1 illustrates the IR spectra of PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270} respectively, and shows the decreases of absorption peaks assignable to water around at 3500 cm⁻¹ by heating at elevated temperatures. This suggests that any waters were absorbed into PW_{12-com.}, and most of the absorbed water can be removed by heating at elevated temperature *in vacuo*. Then, we examined the following reaction of oxetanes using three types of PW₁₂ such as PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270} as solid heterogeneous catalysts.

Cationic Ring-Opening Polymerization of Oxetane; The Reaction of EP MO using PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270} as Catalysts

The cationic ring-opening polymerization of EP MO was performed using 0.1 wt % of PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270} as catalysts at various temperatures in chlorobenzene under nitrogen (Scheme 1 and Table I).

When the reaction of EP MO and PW_{12-com.} was carried out in chlorobenzene at 0 °C for 12 h, it was observed that no reaction proceeded (run 1). At room temperature for this reaction, 31% of EP MO was converted to afford the corresponding polymer with *M_n* = 14200 and *M_w*/*M_n* = 1.9 in 20% yield (run 2). Furthermore, the conversions of EP MO and yields of polymers increased with increasing reaction temperatures (runs 3–5). Consequently, it was found that the cationic ring-opening polymerization of EP MO proceeded at 80 °C quantitatively to afford the corresponding polymer with *M_n* = 14400 and *M_w*/*M_n* = 2.3 in 89% yield. (Table I).

The structure of the obtained polymers was confirmed by IR and ¹H NMR spectroscopy. Figure 2 depicts the ¹H NMR spectra of obtained polymer with *M_n* = 14400, *M_w*/*M_n* = 2.3 (run 5 in Table I) along with EP MO. Figure 2(b) shows the signals assignable to methylene and methyl protons of obtained polymer at 1.86–1.92, 4.03–4.07, 4.32–4.52 and 1.35–1.41 ppm, respectively. IR spectroscopy of the obtained polymer also supports the result of ¹H NMR analysis. SEC curves of the obtained polymers show unimodal peaks. These results mean that the cationic ring-opening polymerization of EP MO proceeded smoothly at 80 °C to give the corresponding polyether poly(EP MO) in satisfactory yield. It was also found that all of the obtained polymers were soluble in common organic solvents such as chloroform and THF.

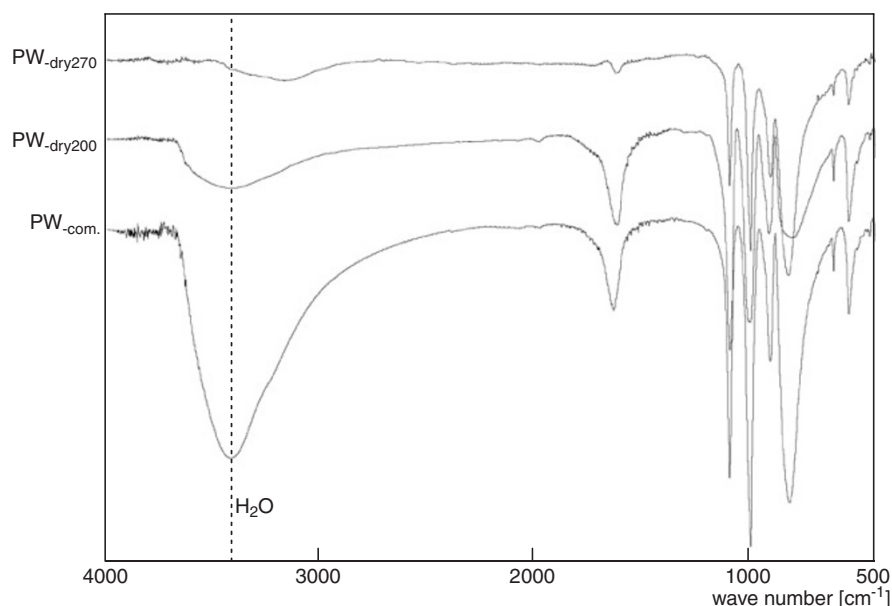
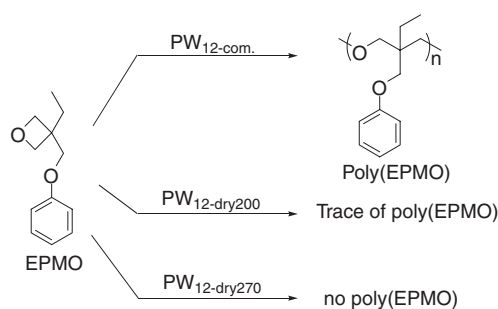


Figure 1. IR spectra of PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270}.



Scheme 1. The reaction of EPMO using PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270} as catalysts.

Furthermore, the cationic ring-opening polymerization of EPMO using PW_{12-dry200} and PW_{12-dry270} were examined in the same way as the case of PW_{12-com.}. In the case of PW_{12-dry200}, only 4% of EPMO converted to give the corresponding poly(EPMO) with $M_n = 16100$ and $M_w/M_n = 3.0$ (run 6). Furthermore, it was observed that the conversion of EPMO was trace and poly(EPMO) could not be obtained (run 7) using PW_{12-dry270} as a catalyst. These results mean that PW_{12-com.} act as a heterogeneous catalyst associated with absorbed water in PW₁₂ for the polymerization of EPMO, but PW_{12-dry200} and PW_{12-dry270} could not do without associating small water. To clear the effect of water in these catalysts, we examined the cationic ring-opening polymerization of EPMO using the catalyst PW_{12-vapor}, which was the treated PW_{12-dry270} with vapor, and it was found that the polymerization of EPMO proceeded to afford the corresponding poly(EPMO) with $M_n = 10400$ in 88% yield (run 8). That is, small water including in PW_{12-com.} acts as a co-catalyst. In addition, IR spectroscopy of PW_{12-vapor} same to that of PW_{12-com.}.

It is well known²⁵ that the cationic-ring opening polymerization of oxetane was performed using certain acids such as

Table I. The reaction of EPMO using PW_{12-com.}, PW_{12-dry200}, and PW_{12-dry270} as catalysts^{a)}

Run	Catalyst	Temperature (°C)	Conversion ^{b)} (%)	Yield ^{c)} (%)	M_n ^{d)}	M_w/M_n ^{d)}
1	PW _{12-com.}	0	<1	—	—	—
2	PW _{12-com.}	r.t.	31	20	14200	1.9
3	PW _{12-com.}	40	77	66	14300	2.2
4	PW _{12-com.}	60	>99	88	13900	2.5
5	PW _{12-com.}	80	>99	89	14400	2.3
6	PW _{12-dry200}	80	4	trace	16100	3.0
7	PW _{12-dry270}	80	<1	—	—	—
8	PW _{12-vapor}	80	>99	88	10400	2.8
9	BF ₃ ·OEt ₂	80	95	52	6000	1.7
10	SnCl ₄	80	<1	—	—	—
11	TfOH	80	<1	—	—	—
12	HClO ₄	80	<1	—	—	—
13	TsOH	80	<1	—	—	—
14	H ₂ SO ₄	80	<1	—	—	—

^{a)}The reaction conditions: EPMO (8 mmol), catalyst (0.1 wt %), in chlorobenzene (8 mL) for 12 h. ^{b)}Calculated by ¹H NMR. ^{c)}Insoluble parts in methanol. ^{d)}Estimated by SEC (THF) based on polystyrene standards.

boron trifluoride diethyl ether complex (BF₃·OEt₂), tin(IV) chloride (SnCl₄), trifluoromethanesulfonic acid (TfOH), perchloric acid (HClO₄), *p*-toluenesulfonic acid (TsOH), and conc.-H₂SO₄. These acids act as cationic catalysts on the ring-opening polymerization of oxetanes at lower temperatures than 0 °C. We re-examined the cationic polymerization of EPMO using these common acids under the same condition of PW_{12-com.} as mentioned above, and it was found that only BF₃·OEt₂ gave the corresponding poly(EPMO) with $M_n = 6000$ in 52% yield (run 9). However, the other catalysts did not produce any poly(EPMO) (runs 10–14). These mean that cationic polymerization system is strongly effect of the reaction temperature and reaction media. In general, the cationic polymerization would be performed at lower temperatures at about 0 °C to prevent the termination reaction. However, in the

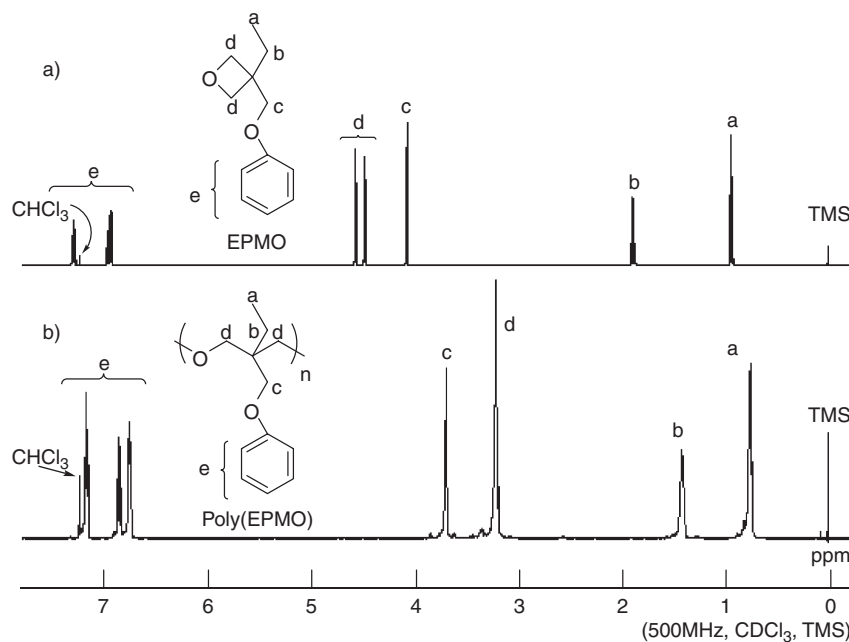


Figure 2. ^1H NMR spectra. a) EPMO. b) poly(EPMO), $M_n = 14400$, $M_w/M_n = 2.3$ obtained by the reaction of EPMO, run 5 in Table I.

case of $\text{PW}_{12\text{-com}}$, the cationic polymerization did not proceed at lower temperatures in the range between $0\text{--}25^\circ\text{C}$, and proceeded at 80°C to afford the corresponding polymer in satisfactory yield. That is, $\text{PW}_{12\text{-com}}$ can act as a superior catalyst for the cationic ring-opening polymerization of oxetane at high reaction temperature.

The Restoration of Catalytic Activity of $\text{PW}_{12\text{-com}}$ for Cationic Ring-Opening Polymerization of EPMO

Since the $\text{PW}_{12\text{-com}}$ is insoluble in common organic solvents, in this cationic polymerization system, separation of the resulting polymers and catalysts from the reaction mixtures is very easy. Therefore, after the first polymerization, $\text{PW}_{12\text{-com}}$ was recovered by the filtration, and washed with chloroform several times, and then dried *in vacuo* at room temperature for 24 h. The resulting $\text{PW}_{12\text{-cycle}}$ was reused as a catalyst for the polymerization of EPMO at 80°C , and it was found that EPMO converted in 44% to afford the corresponding poly(EPMO) in 30% yield. It seems that the activity of PW_{12} decreased by the coating of small amount of products on the surface of catalyst after the polymerization of EPMO. To revive the activity of catalyst, $\text{PW}_{12\text{-cycle}}$ was heated at 300°C for 3 h under open air. Then, the resulting catalyst $\text{PW}_{12\text{-heat}}$ was used again for the reaction of EPMO under same condition, and it was found that EPMO converted in quantitatively, affording the corresponding poly(EPMO) with $M_n = 11600$, $M_w/M_n = 2.5$ in 77% yield. These results are summarized in Table II. In addition, the IR spectroscopy of $\text{PW}_{12\text{-heat}}$ was same to that of $\text{PW}_{12\text{-com}}$.

Cationic Isomerization of AOEO: The Reaction of AOEO with $\text{PW}_{12\text{-com}}$, $\text{PW}_{12\text{-dry270}}$, and $\text{PW}_{12\text{-vapor}}$

As described in the introduction, Motoi reported^{16–21} the synthesis of bicyclo ortho ester by the isomerization of oxetane

Table II. The reaction of EPMO using $\text{PW}_{12\text{-cycle}}$ and $\text{PW}_{12\text{-heat}}$ as catalysts^{a)}

Run	Catalyst	Conversion ^{b)} (%)	Yield ^{c)} (%)	M_n ^{d)}	M_w/M_n ^{d)}
1	$\text{PW}_{12\text{-cycle}}$	44	30	10900	1.9
2	$\text{PW}_{12\text{-heat}}$	>99	77	11600	2.5

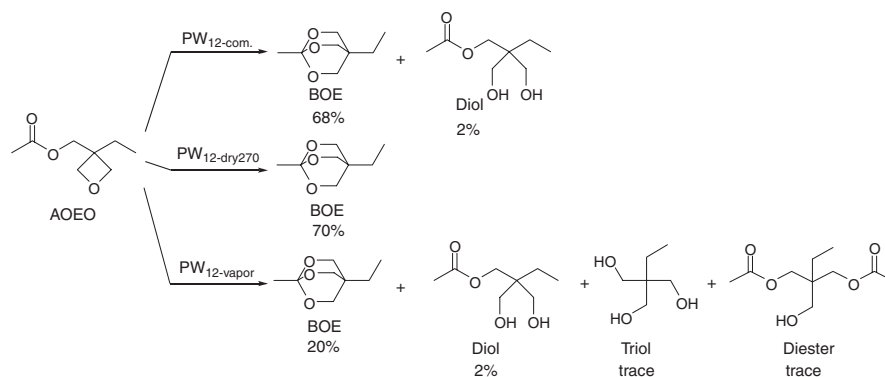
^{a)}The reaction conditions: EPMO (4 mmol), catalyst (0.1 wt%), in chlorobenzene (4 mL) at 80°C for 12 h. ^{b)}Calculated by ^1H NMR. ^{c)}Insoluble parts in methanol. ^{d)}Estimated by SEC (THF) based on polystyrene standards.

Table III. The reaction of AOEO using $\text{PW}_{12\text{-com}}$, $\text{PW}_{12\text{-dry270}}$, and $\text{PW}_{12\text{-vapor}}$ as catalysts^{a)}

Run	Catalyst	Yield			
		BOE	Diol	Triol	Diester
1	$\text{PW}_{12\text{-com}}$	68	2	0	0
2	$\text{PW}_{12\text{-dry270}}$	70	0	0	0
3	$\text{PW}_{12\text{-vapor}}$	20	2	trace	trace

^{a)}The reaction conditions: AOEO (8 mmol), catalyst (0.1 wt%), in chlorobenzene (8 mL) at 80°C for 12 h.

containing ester moiety such as AOEO using Lewis acid catalyst. In this case, cationic ring-opening polymerization did not proceed and only isomerization proceeded due to its neighboring effect of ester moiety. We also examined the cationic isomerization reaction of AOEO using $\text{PW}_{12\text{-com}}$ and $\text{PW}_{12\text{-dry270}}$ as catalysts in chlorobenzene at 80°C for 12 h. In the case of $\text{PW}_{12\text{-com}}$, AOEO converted to produce bicyclo ortho ester 4-ethyl-1-methyl-2,6,7-trioxa-bicyclo[2.2.2]octane (BOE) and 2-hydroxymethyl-2-acetyloxymethyl-1-butanol (diol) in 68% and 2% yields, respectively. The obtained products were isolated by HPLC and their structures were confirmed by IR and ^1H NMR spectroscopy. Only BOE was obtained in 70% yield using $\text{PW}_{12\text{-dry270}}$ as a catalyst. This means that $\text{PW}_{12\text{-dry270}}$ might act as a Lewis acid catalyst in this



Scheme 2. The reaction of AOEO using PW_{12-com} , $PW_{12-dry270}$, and $PW_{12-vapor}$ as catalysts.

reaction system. Furthermore, we examined this cationic isomerization using $PW_{12-vapor}$ as a catalyst, and it was found that BOE and diol were obtained in 20 and 2% yields accompany with small amount of 1,1,1-trihydroxymethylpropane (triol) and 2,2-di(acethyloxymethyl)-1-propanol (diester) as shown in Scheme 2. However, in the all cases, no polymer was obtained. Consequently, $PW_{12-dry270}$ is the most suitable catalyst for the cationic isomerization of oxetane.

All these results suggest that $PW_{12-dry270}$ act as a Lewis acid to produce only BOE. However, no reaction of EP MO was observed using $PW_{12-dry270}$ as a catalyst. That is, the cationic ring-opening polymerization was performed using PW_{12-com} and $PW_{12-vapor}$ due to their Brønstead acid active sites. It is also suggested that diol, triol, and diester were obtained by the hydrolysis or ester-exchange reaction of AOEO and resulting products with Brønstead acid active sites of PW_{12-com} and $PW_{12-vapor}$.

CONCLUSIONS

We examined the reaction behavior of two oxetanes such as EP MO and AOEO with heteropolyacids (PW_{12}) as cataionic catalysts. The reaction of oxetanes was examined using the commercial grade PW_{12} (PW_{12-com}), and anhydrous PW_{12} such as $PW_{12-dry200}$ and $PW_{12-dry270}$. As the result, it was found that PW_{12-com} acts as a cationic catalyst for the ring-opening polymerization of EP MO at high reaction temperature (80 °C) to afford the corresponding poly(EP MO) in satisfactory yield. However, $PW_{12-dry270}$ do not act as a cationic catalyst for the polymerization of EP MO. On the other hand, the isomerization reaction of AOEO proceeded using $PW_{12-dry270}$ to give bicyclo ortho ester in high yield.

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