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Heteropolyacid-conjugated chitosan matrix for triphase catalyst

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ABSTRACT

$H_3PW_{12}O_{40}$ (12-phosphotungstic acid; PWA) is efficient catalysts for the selective oxidation of alkanes, aldehydes, and perfluorinated acids. However, PWA molecules are high solubility in water and this property has been making it difficult to utilize as an industrial catalyst. In this study, the water-insoluble PWA-conjugated chitosan matrix was prepared by mixing the aqueous PWA and chitosan solutions. This conjugate matrix was constructed by the electrostatic interaction between amino group of chitosan and negative charge of PWA and showed the thermal stability at $<100\,^{\circ}C$. In addition, the PWA-conjugated chitosan matrix indicated the property for triphase catalyst as epoxidation of allylic alcohols, such as cinnamyl alcohol, farnesol, and so on. The isolated yield of epoxidation with the conjugate matrix was as same as that of pure PWA. Furthermore, since this conjugate matrix did not dissolve in water, matrices could easily separate from the reaction solvent and recycle more than 3 times. Therefore, the PWA-conjugated chitosan matrices may have a potential to utilize the novel catalyst for the epoxidation of various allylic alcohols.

1. Introduction

Chitin, *β*-1,4-poly-*N*-acetyl-*D*-glucosamine, is present in the cell wall of fungi and in the outside skeleton of crustaceans and insects. Large amounts of chitin-enriched materials, such as crab and shrimp shells, have been discarded as industrial waste around the world. Chitosan, deacetylated chitin, is a highly specialized basic biopolymer and virtually non-toxic polymer with a wide safety margin [1,2]. Moreover, chitosan is a biodegradable, biocompatible, and low cost polymer, which shows many interesting properties, such as wound healing, antibacterial activity, and binding in tissue [1,2]. Therefore, chitosan has been used for bio- or medical-materials, such as a tissue engineering material, surgical tape, and artificial skin [3–8]. Furthermore, the presence of amino groups in chitosan shows the unique properties, such as the removal of hazardous metals from dilute aqueous solutions and the storage of metal anion, such as Pt and Pd [9–12]. As a result, the preparation of metallic catalysis-immobilized chitosan materials has been reported [10]. These catalysis-immobilized chitosan has been used for the oxidation, carbonylation, and hydrogenation reactions [9,10]. Applications of chitosan in industrial process are not only interesting but also important for environmental safety. Additionally, the production cost becomes low by using a chitosan instead of expensive engineering-polymers [13].

$H_3PW_{12}O_{40}$ (12-phosphotungstic acid; PWA), one of the Keggin-type heteropolyacids, is considered to have a strong Brønsted acidity at the border between strong-acids and superstrong-acids [14,15]. Its primary structure is characterized by units in which a central phosphorous atom in a tetrahedral coordination is surrounded by 12 edge-sharing metal-oxygen octahedra (WO_6). The negative charge of this structure is neutralized in the acidic form by three protons. Therefore, PWA molecule exists the deprotonic form $[PW_{12}O_{40}]^{3-}$ in an aqueous solution. Since these PWA molecules have various properties, such as proton conducting [16,17], electrochromism [18], and oxidation–reduction [19], many investigations have occurred. Additionally, these PWA molecules are efficient catalysts for the selective oxidation of alkanes, aldehydes, and perfluorinated acids [20–25]. Especially, the epoxidation of allylic alcohols is important for the industrial catalysis. This scheme shows in Scheme 1. However, PWA molecules are high solubility in water and this property has been making it difficult to utilize as an industrial catalyst. Therefore, the networked supramolecular complex, that heteropolyacid was immobilized artificial polymers, has been reported for the triphase catalyst [26,27]. However, the utilization of artificial polymer has many weak points, such as cost or synthesis.

Hence, we prepared the water-insoluble heteropolyacid-conjugated chitosan matrix by the mixing with chitosan and heteropolyacid. This conjugate matrix was constructed by the cross-linking with the electrostatic interaction between the amino group in chitosan and negatively charged PWA molecules. So, we demonstrated the heteropolyacid-conjugated chitosan matrix to

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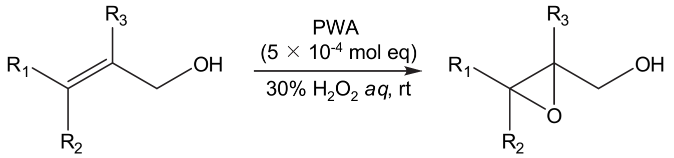


Scheme 1. Epoxidation of allylic alcohols with PWA. This catalytic reaction was carried out in the presence of 5×10^{-4} mol equiv of PWA at room temperature.

utilize for triphase catalyst as the epoxidation of allylic alcohols. As a result, this conjugate matrix suggests the highly catalytic activity and this activity was as same as that of pure PWA molecules. Furthermore, since this matrix did not dissolve in water, matrices could easily separate from the reaction solvent and recycle more than three times.

2. Experimental sections

2.1. Materials

Chitosan ($M_w = 1 \times 10^3$ to 3×10^4, 5×10^4, 1×10^5, 5×10^5, 1×10^7) and 12-phosphotungstic acid (PWA) were obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan. The degree of deacetylation in chitosan was ca. 80%. Cinnamyl alcohol, farnesol, geraniol, *trans*-2-octen-1-ol, *trans*-2-hexen-1-ol, 1-cyclohexyl-2-buten-1-ol, nerol, 3-methyl-2-buten-1-ol, 2-cyclohexen-1-ol, and crotyl alcohol (cis- and trans- mixture) for the substrate of triphase catalyst were purchased from Wako Pure Chemical Industries Ltd. or Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. The molecular structures and the properties in water of these materials show Table 1. These materials were used without further purification. The solvents were used the analytical grade in all the experiments described herein.

2.2. Preparation of PWA-conjugated chitosan matrices

Chitosan and PWA were dissolved in 5% acetic acid solution and water, respectively. PWA-conjugated chitosan matrices were prepared as follows; chitosan solution (50 μl, 0.01–50 mg/ml) and PWA solutions (50 μl, 0.5–200 mg/ml) were mixed on a glass plate. The mixing ratio (chitosan:PWA) was represented by the equation (1).

$$\text{Chitosan} : \text{PWA} = [\text{concentration of chitosan}] : [\text{concentration of PWA}] \tag{1}$$

The gelation of the chitosan and PWA solutions was detected by the construction of a water-insoluble gel. These PWA-conjugated chitosan matrices were rinsed with pure water (20 ml × 3 times) to remove the chitosan and PWA which were not gelled, and then stored in water. The immobilized amount of PWA in the conjugate matrix was determined by the following procedure: the conjugate matrix was hydrolyzed with 1 M HCl solution at 100 °C for 1 h [28]. At this reaction condition, polysaccharide, such as chitosan in conjugate matrix, was hydrolyzed to monosaccharide or oligosaccharide [28]. Therefore, PWA molecules liberate to an aqueous solution. The absorbance at 250 nm of the conjugate matrix-hydrolyzed solution was measured by a UV–Vis spectrophotometer U-2010 (Hitachi Co., Ltd., Tokyo, Japan) and the amount of PWA was estimated from the calibration curve.

2.3. Characterization of PWA-conjugated chitosan matrices

The stability in an aqueous solution of the PWA-conjugated chitosan matrix was confirmed by the following method: the conjugate matrices (1 mg) were incubated in ultra-pure water (20 ml) for various time intervals. The absorbance at 250 nm of the solution was measured, and the eluted amount of PWA from the conjugate matrix was estimated from the calibration curve. The thermal stability of the PWA-conjugated chitosan was analyzed by thermogravimetric – differential thermal analysis (TG-DTA) (DTG-60, Shimadzu Corp., Kyoto, Japan). The TG-DTA measurement was carried out at a heating rate of 10 °C min^{-1} under a dry-nitrogen flow. Sample weights of TG-DTA measurements were normalized at 5 mg.

2.4. Molecular structure of PWA-conjugated chitosan matrices

Pure chitosan matrix, PWA-conjugated chitosan matrices, and pure PWA materials were dried at room temperature overnight. The infrared (IR) absorption spectra of these materials were measured by KBr methods using a FT-IR 8200 Fourier transform infrared spectrometer (Shimadzu Corp., Kyoto, Japan). The IR spectrum was measured with the resolution of 4 cm^{-1}.

2.5. Catalytic activity test of PWA-conjugated chitosan matrices

The reaction condition in epoxidation of allylic alcohols was following [26,27]: the allylic alcohol (2.52 mmol), 30% hydrogen peroxide (5.05 mmol), pyridine (15.1 μmol; 0.378 ml, 0.04 M aqueous pyridine solution), and PWA-conjugated chitosan matrix (amount of PWA; 1.26 μmol) was mixed in glass vessel and stirred at room temperature. The reaction was measured by the reverse-phase high performance liquid chromatography (HPLC) using an Inertsil® ODS-P column (GL Science Inc., Tokyo, Japan) with a CH_3OH/water (80:20, 70:30, or 50:50 v/v). The detection of substrate and product was used a differential refractive index (RI) detector D-3300 (Hitachi Co., Ltd.). The reaction ratio of epoxidation was calculated by the area ratio of chromatograph. In this measurement, we also used pure PWA without chitosan for the control.

2.6. Recovering and reusability of PWA-conjugated chitosan matrices

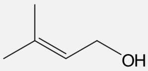
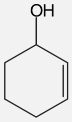
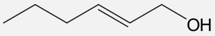
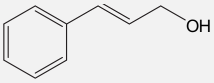
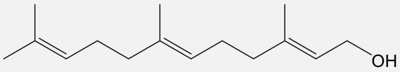
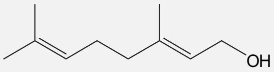
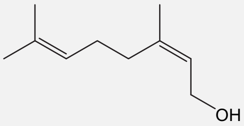
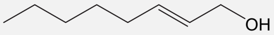
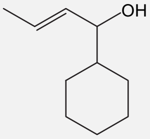
The reusability of PWA-conjugated chitosan matrix at the reaction of epoxidation was demonstrated as followed: the allylic alcohol, 30% hydrogen peroxide, aqueous pyridine solution, and PWA-conjugated chitosan matrix was mixed in glass vessel, reacted at room temperature, and then this reaction solution was removed by the pipette. The PWA-conjugated chitosan matrix was washed by the 0.04 M aqueous pyridine solution (2 ml × 3 times) in glass vessel. This matrix was re-mixed with the allylic alcohol, 30% hydrogen peroxide, and aqueous pyridine solution, and reacted at room temperature. This procedure has been repeated more than 3 times. In these measurements, we used the cinnamyl alcohol and farnesol for the allylic alcohol. The isolated yield of allylic alcohol was determined by the area ratio of HPLC chromatogram. On the other hand, the recovering values of catalyst-immobilized material were calculated from the weight of PWA-conjugated chitosan matrix before and after reaction.

3. Results and discussion

3.1. Preparation of PWA-conjugated chitosan matrix

The PWA-conjugated chitosan material was prepared by mixing the aqueous chitosan and the PWA solutions. The construction of the conjugate matrix was detected by the formation of a water-insoluble gel. Table 2 shows the screening for the construction of

Table 1
Molecular structures of various allylic alcohols and its isolated yield of epoxidation with the pure PWA and PWA-conjugated chitosan matrix (chitosan:PWA = 10:100).[a]

Substrate	Molecular structure	Reaction time at constant value	Isolated yield
		Pure PWA/PWA-conjugated chitosan	Pure PWA/PWA-conjugated chitosan
Crotyl alcohol[b] (cis- and trans- mixture)	$CH_3–CH{=}CH–CH_2–OH$	1 h 1 h	98% 99%
3-methyl-2-buten-1-ol[b]		2 h 2 h	92% 97%
2-cyclohexen-1-ol[b]		6 h 6 h	87% 84%
trans-2-hexen-1-ol[c]		3 h 3 h	99% 99%
cinnamyl alcohol[d]		6 h 6 h	97% 95%
farnesol[d]		8 h 4 h	99% 99%
geraniol[d]		48 h 48 h	98% 99%
nerol[d]		48 h 48 h	96% 93%
trans-2-octen-1-ol[d]		48 h 48 h	98% 95%
1-cyclohexyl-2-buten-1-ol[d]		168 h 168 h	96% 98%

[a] Reaction condition: allylic alcohol (2.52 mmol), 30% hydrogen peroxide (5.05 mmol), pyridine (15.1 μmol; 0.378 ml, 0.04 M aqueous pyridine solution), and PWA-conjugated chitosan matrix (amount of PWA; 1.26 μmol) was mixed and stirred at room temperature. The isolated yield of epoxidation was calculated by the area ratio of chromatograph.

[b] Water-soluble allylic alcohol.

[c] Slightly soluble in water.

[d] Water-insoluble allylic alcohol.

the matrices by the hybridization of chitosan ($M_w = 1 \times 10^5$) and the PWA solutions at various concentrations. When the highly concentrated solutions of chitosan ($\geq$ 5 mg/ml) and PWA ($\geq$ 25 mg/ml) were mixed, the water-insoluble PWA-conjugated chitosan matrices were immediately produced (see in ○ Table 2). Fig. 1 shows a photograph of the PWA-conjugated chitosan matrices (chitosan:PWA = 10:100) in aqueous solution. This PWA-conjugated chitosan matrix was an elastic material and was not broken by pinching with tweezers. The elasticity of the conjugate matrix decreased by the decrease of concentration of the chitosan and PWA solutions and produced a liquid with a high viscosity (see in △ Table 2). At the mixing with low concentrations of chitosan ($\leq$1 mg/ml) and PWA ($\leq$1 mg/ml), these phenomena, such as viscosity liquid, were not observed (see in × Table 2).

The construction of PWA-conjugated chitosan matrix was performed by the various chitosans with the differential molecular weight of 1×10^3 to 1×10^7 (data not shown). As a result, the chitosan with the high molecular weight ($\leq 5 \times 10^4$) produced the water-insoluble conjugate matrix. Additionally, the elasticity of the conjugate matrix increased with the increase of the molecular weight. However, the aqueous solution of chitosan with high molecular weight was high viscosity and the handling of this

Table 2
Construction of conjugate material by the hybridization of chitosan and PWA at various concentrations. (○), water-insoluble conjugate material; (△), liquid with high viscosity; (×), no construction.

		Concentration of chitosan (mg/ml)							
		50	25	10	5	3	1	0.5	0.01
Concentration of PWA (mg/ml)	200	○	○	○	○	△	×	×	×
	100	○	○	○	○	△	×	×	×
	50	○	○	○	○	△	×	×	×
	25	○	○	○	△	△	×	×	×
	10	△	△	△	×	×	×	×	×
	1	×	×	×	×	×	×	×	×
	0.5	×	×	×	×	×	×	×	×

solution was difficult. So, we prepared the water-insoluble PWA-conjugated matrices by the chitosan with the molecular weight of 1×10^5. On the other hand, at the low molecular weight (1×10^3 to 3×10^4), the water-insoluble conjugate matrix was not constructed.

3.2. *Stability of PWA-conjugated chitosan matrix in water*

We tested the water stability of PWA-conjugated chitosan matrix in aqueous solution. Fig. 2 (□), (○), and (△) shows the stability of PWA-conjugated chitosan matrix of chitosan:PWA = 10:50, 10:100, and 10:200, respectively. The amount of eluted PWA from the conjugate matrix was quantitated by absorption at 250 nm using UV spectrophotometer. The amount of eluted PWA increased with the incubation time and reached a constant value at 24 h. Additionally, the amount of eluted PWA increased with the increase of the mixing PWA (see (△) in Fig. 2). The PWA-conjugated chitosan matrix did not dissolve in an aqueous solution even after incubation in water for up to 1 month. The conjugate matrices were stored in ultra-pure water for more than one day to remove the water-soluble PWA and chitosan, and then used for the further experiments.

3.3. *Infrared spectra of PWA-conjugated chitosan matrix*

The infrared (IR) measurement of the PWA-conjugated chitosan matrix was demonstrated by KBr method. Fig. 3 shows the IR spectra of (a), pure chitosan without the conjugation of PWA; (b), chitosan:PWA = 10:1; (c), chitosan:PWA = 10:10; (d), chitosan:PWA = 10:25; (e), chitosan:PWA = 10:50; (f), chitosan:PWA = 10:100; (g), pure PWA without the conjugation of chitosan. The absorption band at $1595\ \mathrm{cm}^{-1}$, attributed to the antisymmetric vibration of the $-NH_3^+$ [29], was shifted to a lower wavenumber by the mixing of PWA (see the dashed line in Fig. 3). Similar results, such as the shift to lower wavenumber, have been reported at the chitosan–methandiphosphonic acid composite material with the electrostatic interaction [13]. Additionally, pure PWA shows absorption bands at $983\ \mathrm{cm}^{-1}$ and $896\ \mathrm{cm}^{-1}$, attributed to the stretching vibration of the terminal oxygen, W = O, and bridging oxygen, W–O–W, respectively [17,30–32]. These absorption bands shifted by $30\ \mathrm{cm}^{-1}$ and $8\ \mathrm{cm}^{-1}$ to lower and higher frequencies by the mixing of the chitosan, respectively. These shifts might be due to the interaction through the hydrogen bonding between the W=O or W–O–W groups in the PWA molecules and the $-NH_3^+$ in the chitosan. Therefore, in the PWA-conjugated chitosan matrix, PWA and $-NH_2$ in chitosan may act as acidic and basic molecules, respectively, and construct the conjugate matrix with the three-dimensional network through the electrostatic

Fig. 1. Photograph of PWA-conjugated chitosan matrix (chitosan:PWA = 10:100) in aqueous solution.

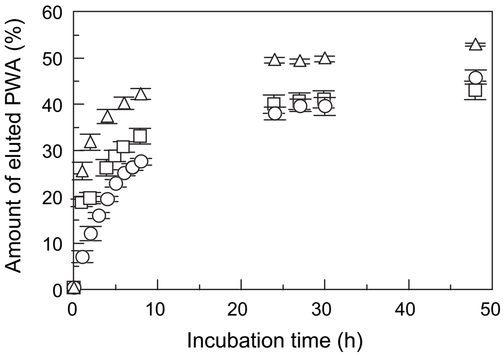


Fig. 2. Stability of PWA-conjugated chitosan matrices in water. (□), chitosan:PWA = 10:50; (○), chitosan:PWA = 10:100; (△), chitosan:PWA = 10:200. Each values in represents the mean of three separate determinations ± standard deviations (SD). Duplicate experiments gave similar results.

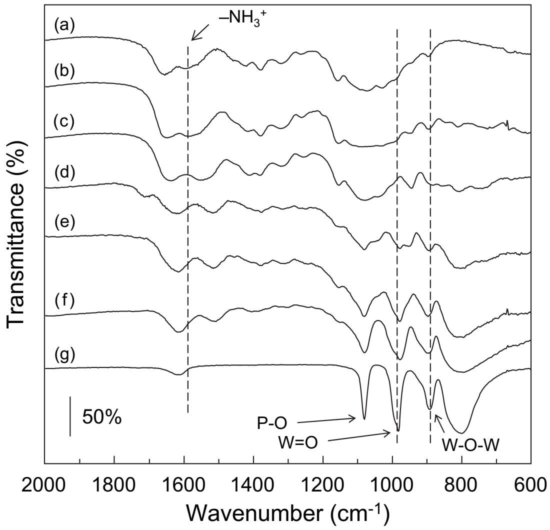


Fig. 3. IR spectra of PWA-conjugated chitosan matrix. (a), pure chitosan without the conjugation of PWA; (b), chitosan:PWA = 10:1 conjugated; (c), chitosan:PWA = 10:10 conjugated; (d), chitosan:PWA = 10:25 conjugated; (e), chitosan PWA = 10:50 conjugated; (f), chitosan:PWA = 10:100 conjugated; (g), pure PWA without the conjugation of chitosan. The IR spectrum was measured with the resolution of $4\ \mathrm{cm}^{-1}$.

cross-linking interaction. Fig. 4 shows the proposal model of PWA-conjugate chitosan with the three-dimensional network. In this model, the –NH$_3^+$ group in the chitosan interacts with the negatively charged PWA molecules by the electrostatic interaction. Therefore, PWA molecules play a role in a cross-linking point in PWA-conjugated chitosan matrix. Additionally, the water-insolubilization of the conjugated matrix is due to the construction of the three-dimensional structure. Similar phenomena, such as the water-insolubilization with the cross-linking point, have been reported at DNA-metal ion complex [33] and DNA-poly(allylamine) complex [34]. In contrast, a frequency shift of the central tetrahedron P–O band at 1081 cm^{-1} [17,30–32] was not observed. These phenomena have been also reported at the PWA-encapsulated self-assembled materials [17].

3.4. Thermal stability of PWA-conjugated chitosan matrix

Fig. 5(a) and (b) shows the thermogravimetric (TG) and differential thermal analyses (DTA) of (1) pure chitosan matrix, (2) PWA-conjugated chitosan matrix (chitosan:PWA = 10:100), and (3) pure PWA materials. The pure chitosan matrix showed the TG weight loss of ca. 10% below 200 °C (line (1) in Fig. 5(a)). This weight loss is due to the solvent evaporation from the matrix [13]. The pure PWA material indicated two endothermic peaks by the evaporation of hydrated water in PWA [35]. Surprisingly, these endothermic peaks almost disappeared by mixing with chitosan. These results suggested that the PWA-conjugated chitosan matrix formed an acid-base complex in the conjugate matrix through the electrostatic cross-linking between the amino group in chitosan and negative charge of PWA and thermally stabilized. These phenomena, such as the thermal stabilization by the acid-base complex, have been reported [13,17,36]. Additionally, the PWA-conjugated chitosan matrix showed a TG weight loss of 7% below 200 °C. This is due to the evaporation of solvent from the matrix. Therefore, these results suggest that the PWA-conjugated chitosan matrix can use for the catalyst in aqueous solution below 100 °C. On the other hand, pure chitosan and PWA-conjugated chitosan matrices indicated a high TG weight loss above 250 °C. This weight loss is due to the pyrolysis of chitosan [13].

3.5. Catalytic property of PWA-conjugated chitosan matrix

The epoxidation of allylic alcohols with the PWA-conjugated chitosan matrix was examined under triphase condition in aqueous H_2O_2 with a trace amount of pyridine at room temperature. After the incubation, since PWA-conjugated chitosan matrices did not dissolve in water or pyridine, matrices could easily separate from the reaction solvent. In this research, we used the PWA-conjugated matrix of chitosan:PWA = 10:100. The degree of epoxidation was estimated by the area ratio of HPLC chromatogram with the RI detector. Fig. 6(a) and (b) shows the chromatogram of cinnamyl alcohol in the absence and presence of pure PWA with the incubation time at 3 h, respectively. Additionally, Fig. 6(c) shows the chromatogram of cinnamyl alcohol in the presence of PWA-conjugated chitosan matrix with the incubation time at 3 hours. The peaks (A) and (B) in the chromatogram were related to the non-reacted cinnamyl alcohol and the epoxidized-cinnamyl alcohol, respectively. The peak (A) decreased with the increase of the incubation time. At the same time, the peak (B) increased with the incubation time. These results suggested that the PWA-conjugated chitosan matrices play a role in the catalysis as epoxidation of allylic alcohols.

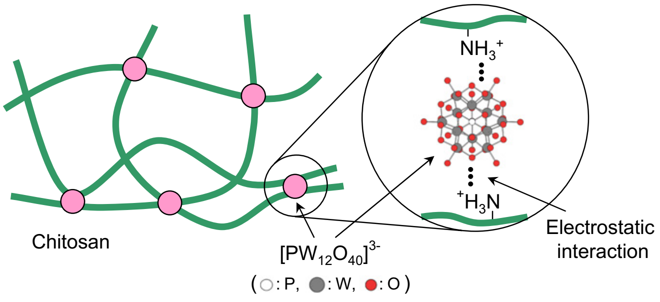


Fig. 4. Proposal model of PWA-conjugated chitosan matrix with three-dimensional network. The insert indicate the electrostatic interaction between PWA molecule and –NH$_3^+$ group of chitosan in the cross-linking point.

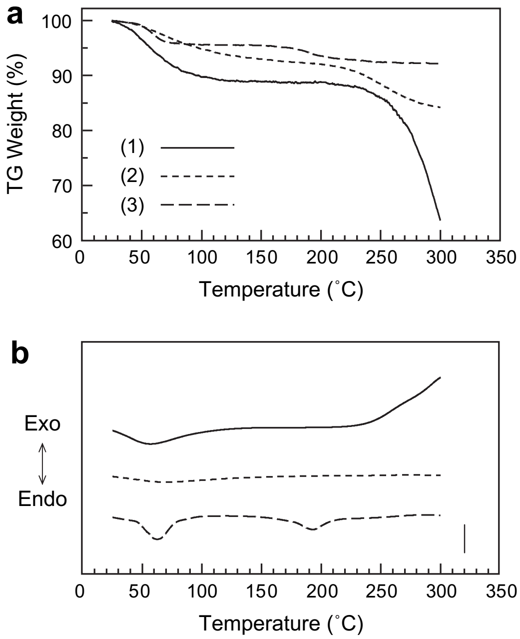


Fig. 5. TG (a) and DTA (b) curves of PWA-conjugated chitosan matrix with the heating rate of 10 °C min^{-1} under dry nitrogen. (1), pure chitosan matrix; (2), PWA-conjugated chitosan matrix (chitosan:PWA = 10:100); (3), pure PWA material. A scale bar in (b) indicates 100 μV.

Fig. 7 shows the isolated yield of epoxidation in cinnamyl alcohol, one of allylic alcohols, with the pure PWA and PWA-conjugated chitosan matrix. Additionally, the insert in Fig. 7 shows the molecular structure of the epoxidized-cinnamyl alcohol. In pure PWA, the isolated yield of epoxidation increased with the incubation time and reached a constant value at approximately 6 h (see ○ in Fig. 7). The similar phenomenon has obtained at the PWA-conjugated chitosan matrix (see ● in Fig. 7). Additionally, the epoxidation of pure PWA and PWA-conjugated chitosan matrix at the constant value were 97% and 95%, respectively. These results indicate that the PWA molecule in the conjugate matrix possesses the function of an epoxidizing reagent. In contrast, the cinnamyl alcohol in the absence of PWA or H_2O_2 did not produce the epoxidized-cinnamyl alcohol in spite of the long incubation (data not shown). Additionally, chitosan matrix without PWA molecule did not show the catalytic activity.

Next, we demonstrated the epoxidation of various allylic alcohols, such as geraniol, farnesol, *trans*-2-octen-1-ol, *trans*-2-hexen-1-ol, 1-cyclohexyl-2-buten-1-ol, nerol, 3-methyl-2-buten-1-ol, 2-cyclohexen-1-ol, and crotyl alcohol. Table 1 shows the reaction time at the constant value and the isolated yield of epoxidation. The isolated yield was estimated by the area ratio of HPLC chromatogram with the RI detector for various time intervals. The reaction

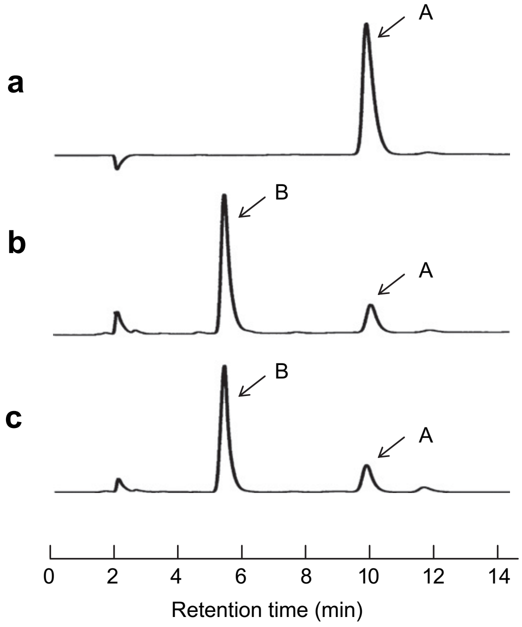


Fig. 6. Chromatogram of cinnamyl alcohol in the absence of pure PWA (a), the presence of pure PWA (b), and the presence of PWA-conjugated chitosan matrix (chitosan:PWA = 10:100) (c), respectively. The incubation time of (b) and (c) is 3 h. This chromatogram was measured by HPLC using an Inertsil® ODS-P column with a CH_3OH/water (50:50 v/v).

times at the constant value were 1–168 h. The reaction times of water-soluble allylic alcohols, such as crotyl alcohol, 3-methyl-2-buten-1-ol, and 2-cyclohexen-1-ol, were faster than that of water-insoluble allylic alcohols. This reason is following: water-soluble allylic alcohols can easily contact with water-soluble PWA. Therefore, PWA and PWA-conjugated chitosan matrix shows the highly catalytic activity for the water-soluble allylic alcohols. On the other hand, in water-insoluble allylic alcohols, the reaction time shortened with the increase of π electrons in allylic alcohols. This is due to the interaction between PWA and π electrons and these interactions, such as heteropolyacid and π electrons in substrate, have been reported [37]. Therefore, the allylic alcohols with many π electrons could approach to PWA molecules or PWA-conjugated chitosan matrices, react with the PWA, and then produced the epoxidized-allylic alcohols. In contrast, the reaction time of 1-cyclohexyl-2-buten-1-ol, which is water-insoluble secondary alcohol, was 168 h and the slowest in these allylic alcohols. This is due to the steric hindrance in substrate. These results suggested that PWA-conjugated chitosan matrix showed the catalytic activity to allylic alcohols. Additionally, this catalytic activity was as same as that of pure PWA. On the other hand, the epoxidation of these allylic alcohols is possible to produce an optically active epoxide. However, in our research, the chromatogram at the epoxidized-allylic alcohol showed single peak (see in Fig. 6(b) and (c)) and an optically active epoxide could not separate. Therefore, the isolated yield of epoxidation in Table 1 showed the mixed-value of optically active epoxide.

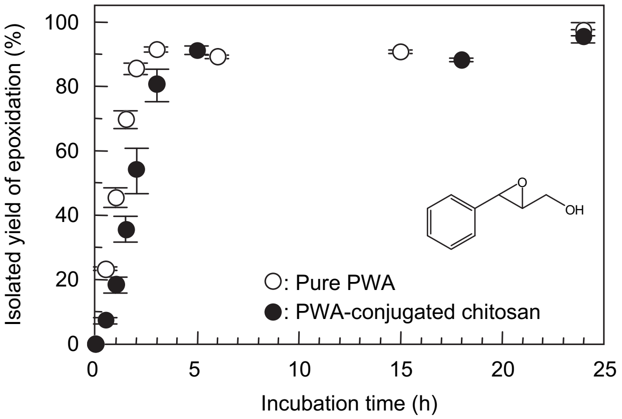


Fig. 7. The epoxidation of cinnamyl alcohol by the pure PWA (○) and PWA-conjugated chitosan matrix (●).The insert indicates the molecular structure of epoxidized cinnamyl alcohol. The isolated yield of epoxization was calculated by the area ratio of chromatograph for various time intervals. Each values in represents the mean of three separate determinations ± standard deviations (SD). Triplicate experiments gave similar results.

Table 3
Isolated yield of epoxidation with the recycling of PWA-conjugated chitosan matrix.

Allylic alcohol		Number of recycling (times)[a]		
		1	2	3
Cinnamyl alcohol	95%[b]	97%	96%	97%
Farnesol	99%[b]	98%	98%	98%

[a] Reaction condition: After each reaction, the PWA-conjugated chitosan matrix was washed by the 0.04 M aqueous pyridine solution in glass vessel and re-reacted with allylic alcohol. The epoxidation reactions were demonstrated at room temperature. The isolated yield of epoxidation was calculated by the area ratio of chromatograph.

[b] Initial yield of epoxidation.

3.6. Recovering and reusability of PWA-conjugated chitosan matrix

We measured the recovering of PWA-conjugated chitosan matrix with the epoxidation reaction of allylic alcohol. In this measurement, we used the farnesol for the one of the allylic alcohols. The recovering values were calculated from the weight of PWA-conjugated chitosan matrix before and after reaction. As a result, the recovering of matrix was 68%, 97%, and 98% at the recycling of 1, 2, and 3 times, respectively. Although the recovering of matrix at the first time is low value, the recovering at 2 and 3 times was high and constant value. The low value at the first time is due to the release of the fragments that existed in PWA-conjugated chitosan matrix. Therefore, after the release of fragments, the reaction at 2 and 3 times did not indicate the decrease of recovering value. These results suggested that the PWA-conjugated chitosan matrix in reaction solution can recover with the high recovering value.

Finally, we demonstrated the reusability of PWA-conjugated chitosan matrix. Reacted PWA-conjugated chitosan matrix was washed by the aqueous pyridine solution and re-reacted with allylic alcohols. Table 3 shows the isolated yield of epoxidation in cinnamyl alcohol and farnesol with the recycling process. In cinnamyl alcohol, the initial yield of epoxidation was 95%. Although the PWA-conjugated chitosan was recycled more than 3 times, the isolated yield of epoxidation in cinnamyl alcohol was maintained at more than 95% and did not appear to be decreasing. Similar results obtained at the farnesol. These results suggested that the PWA-conjugated chitosan matrix is used for the epoxidation catalyst of allylic alcohol with the reusability.

4. Conclusion

We prepared the water-insoluble PWA-conjugated chitosan matrix by mixing the aqueous PWA and chitosan solutions. This conjugate matrix constructed the three-dimensional structure with the cross-linking by the electrostatic interaction between the negatively charged-PWA and $-NH_3^+$ groups in chitosan. This conjugate matrix indicated the thermal stability at <100 °C. Additionally, the PWA-conjugated chitosan matrix had been maintained the property for triphase catalyst as epoxidation of allylic alcohols, such as cinnamyl alcohol, farnesol, and so on. Furthermore, PWA-conjugated chitosan matrix was used for the epoxidation catalyst of allylic alcohol with the reusability.

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