An efficient synthesis of α-acyloxyacrylate esters as candidate monomers for bio-based polymers by heteropolyacid-catalyzed acylation of pyruvate esters

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A series of α-acyloxyacrylate esters are candidate monomers for bio-based polymers, converted from biomass feedstock. Polymers from these monomers are useful materials for bio-based plastics showing high heat resistance and transparency. In this paper, a new efficient method for α-acyloxyacrylate ester synthesis with a strong inorganic acid, heteropolyacid, is presented. The reaction in the presence of the heteropolyacid catalyst was carried out in liquid phase under mild conditions and showed higher productivity than that of the conventional synthesis with a typical organic acid, *p*-toluenesulfonic acid. Among the various heteropolyacids examined, α-Keggin-type tungsten-based phosphotungstic acid, $H_3PW_{12}O_{40}$, showed the best performance, suggesting that the acid strength of the heteropolyacid is the crucial property for this reaction. We also found that pyruvate ester was consecutively converted into α-acyloxyacrylate ester *via* 2,2-diacyloxypropionate ester.

Introduction

Much interest has recently been shown in biorefinery, a process for producing useful chemicals and energies from biomass feedstock.[1] Because of its importance for the carbon neutral concept, reaction of biomass feedstock and its derivatives has been investigated by many researchers.[2] We have focused on the lactic acid platform and the conversion of lactic acid and its derivatives, as shown in Fig. 1. The main use of lactic acid is for the production of polylactic acid (PLA), which is a typical biodegradable polymer.[3] However, PLA has several problems in its properties, including heat resistance, thermal stability, transparency, and molding properties. The use of PLA is, therefore, limited and many polymer scientists are trying to improve its properties. We have been interested in producing another kind of "bio-based polymer", poly α-acyloxyacrylate ester,[4] by polymerization of an α-acyloxyacrylate ester monomer that is synthesized form lactic acid by esterification, oxidation and acylation.

α-Acyloxyacrylate esters have a structure similar to that of methacrylate esters, and polymers of α-acyloxyacrylate esters show higher thermal durability than that of poly(methyl methacrylate) (PMMA). PMMA is widely used as sheets, displays, water cisterns, optical fibres, and coating resins because of its high transparency and high durability. A series of α-acyloxyacrylate esters is synthesized from corresponding pyruvate esters by acylation with carboxylic anhydride and an acid catalyst. The pyruvate ester is produced by oxidative dehydrogenation of lactate ester,[5] which is the lactic acid derivative. There have been several reports on acylation of pyruvate esters with carboxylic anhydride, especially using ethyl pyruvate and acetic anhydride. In those studies, a strong organic acid, *p*-toluenesulfonic acid,[6] was used as a catalyst. Unfortunately, because of its low reactivity, a long reaction time and high temperature are needed, and the selectivity and yield of the product are not satisfactory. The development of an efficient procedure to convert pyruvate esters into α-acyloxyacrylate esters is therefore needed.

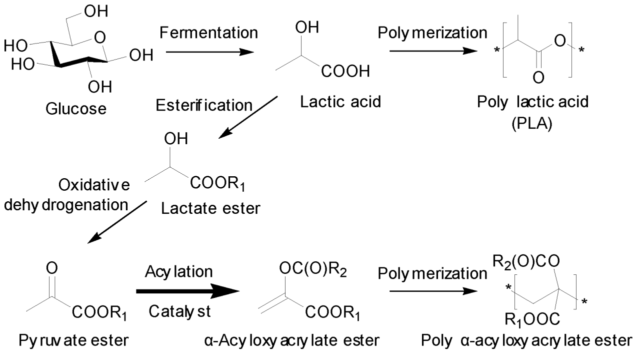

Fig. 1 Synthetic route from glucose to α-acyloxyacrylate ester.

Recently, we have shown that the acylation of pyruvate ester with carboxylic anhydride proceeded smoothly in the presence of a heteropolyacid (HPA) catalyst.[7] The HPAs were metal–oxygen clusters consisting of polyoxometalate anion and cation (H^+, Na^+, K^+, Cs^+, NH_4^+, Ca^{2+}, Cu^{2+}, *etc.*).[8] In the polyoxometalate

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anion structure, the central XO_a (X = P, Si, As, Ge, Te, B, Co, Fe, *etc.*, $a = 4$ or 6) is surrounded by octahedral MO_6 (M = W, Mo, V, Ru, Fe, Cu, Co, Ni, *etc.*). Their structures are categorized by the ratio of X/M in the polyoxoanion, such as Keggin-type ($[X_1M_{12}O_{40}]^{n-}$), Dawson-type ($[X_2M_{18}O_{62}]^{n-}$), Preyssler-type ($[NaX_5M_{30}O_{110}]^{n-}$) and Anderson-type ($[X_1M_6O_{24}]^{n-}$). Among them, Keggin-type HPAs (Fig. 2) possess excellent acid–redox bifunctional properties, which are both attractive for catalysis. Therefore, they have been widely utilized for various catalysis, hydration,[9] oxidation[10] and alkylation,[11] even in industrial use.

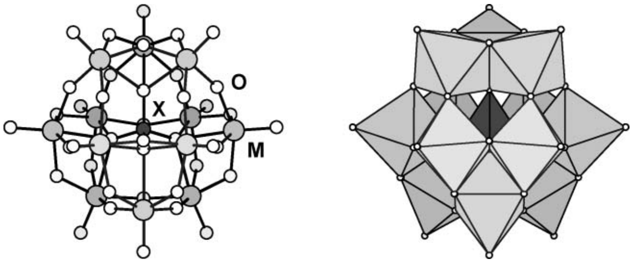
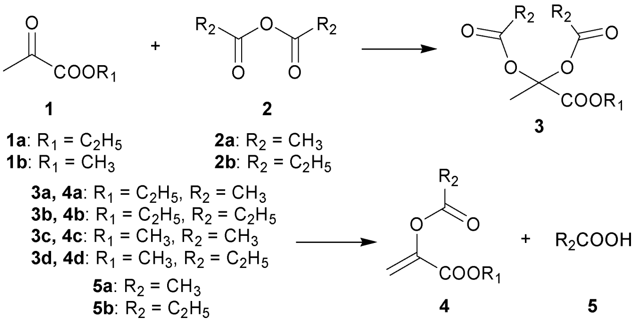


Fig. 2 Structure of α-Keggin-type HPA shown in ball and stick structure (left) and polyhedra structure (right).

In this paper, an efficient acylation of pyruvate esters catalyzed by HPAs in liquid phase is reported in detail, including effects of reaction conditions, reaction mechanism and reaction kinetics. We also found that α-acyloxyacrylate ester is consecutively generated *via* 2,2-diacyloxypropionate ester, a new acylal compound (Scheme 1).



Scheme 1 Acylation of pyruvate esters with carboxylic anhydrides.

Experimental

Materials

All chemicals were reagent grade and used as supplied. Chemicals hereafter described without a supplier's name were all purchased from Wako Pure Chemical Industries.

Preparation of the catalysts

Keggin-type heteropolyacids (HPAs), phosphotungstic acid ($H_3PW_{12}O_{40}$), silicotungstic acid ($H_4SiW_{12}O_{40}$), phosphomolybdic acid ($H_3PMo_{12}O_{40}$), and silicomolybdic acid ($H_4SiMo_{12}O_{40}$), were purchased from Nippon Inorganic Colour & Chemical Co. Ltd. Vanadium mono-substituted Keggin-type phosphomolybdic acid, $H_4PMo_{11}V_1O_{40}$, was prepared by refluxing a stoichiometric mixture of H_3PO_4 (Rasa Industries), MoO_3 (Taiyo Koko), and V_2O_5 (Kanto Chemical) in water at 363 K for 4 h. After filtration, the solution was evaporated in vacuum at 333 K by a rotary evaporator. The orange solid was dried at 343 K for 12 h. Formation of $H_4PMo_{11}V_1O_{40}$ was confirmed by ^{31}P-NMR (ECX-400, JEOL) in D_2O (−3.54 ppm *vs.* 85% H_3PO_4). Contents of crystal water in these HPAs were determined by TG-DTA (Thermo plus TG 8120, Rigaku) analysis as follows: $H_3PW_{12}O_{40}\cdot 22H_2O$, $H_4SiW_{12}O_{40}\cdot 16H_2O$, $H_3PMo_{12}O_{40}\cdot 14H_2O$, $H_4SiMo_{12}O_{40}\cdot 18H_2O$, and $H_4PMo_{11}V_1O_{40}\cdot 8H_2O$. Cs salts of $H_3PW_{12}O_{40}$, $Cs_xH_{3-x}PW_{12}O_{40}$, were prepared by adding a stoichiometric amount of an aqueous Cs_2CO_3 solution to a $H_3PW_{12}O_{40}$ solution. The produced white suspension was heated at 393 K for 24 h and a white solid was obtained. In the case of $Cs_3PW_{12}O_{40}$, the amount of crystal water was also determined as $Cs_3PW_{12}O_{40}\cdot 3H_2O$ by TG-DTA. H-Y (Si/Al = 5.5, JRC-Z-HY-5.5) and H-BEA (Si/Al = 150, JRC-Z-HB-150 (1)) were provided by Japan Reference Catalyst, Catalysis Society of Japan. MCM-41 was prepared from cethyltrimethylammonium bromide (CTAB, TOKYO Kasei, 15 mmol) with H_2O (300 g), tetraethyl orthosilicate (TEOS), and 28% NH_3 solution (initial molar ratio: CTAB/TEOS/NH_3 = 1/5.6/23) by hydrothermal synthesis at 393 K for 72 h and calcined at 813 K for 24 h. SiO_2 (CARiACT Q-10, 75–500 μm, Fuji Silysia Chemical) and cation-exchange-resin, AMBERLYST 15(H) (concentration of acid sites: 4.7 meq g^{-1}, MP Biomedicals Inc.), were purchased and used without any treatment. 20 wt% $H_3PW_{12}O_{40}/SiO_2$ was prepared by impregnation using an aqueous $H_3PW_{12}O_{40}$ solution and CARiACT Q-10 followed by drying at 393 K for 12 h.

Acylation of pyruvate ester with carboxylic anhydride in the presence of HPAs

A typical procedure for acylation using ethyl pyruvate (**1a**), acetic anhydride (**2a**) and $H_3PW_{12}O_{40}$ is as follows. A 10 ml test tube sealed with a cap (ST-16.5S, Nichiden-Rika Glass Co. Ltd.) was used for the reaction container. $H_3PW_{12}O_{40}$ (50 μmol) was dissolved in acetic acid (20 mmol). **1a** (2 mmol) and **2a** (20 mmol) were added to the $H_3PW_{12}O_{40}$ (7.5 mol% as proton *vs.* **1a**) solution. The test tube containing the reaction mixture was heated at 343 K in an aluminium metal bath (Koike Precision Instruments, Model MB-1H-UII). After reaction for 1 h, the test tube was cooled in an ice bath. $H_3PW_{12}O_{40}$ was removed as $Cs_3PW_{12}O_{40}$ by addition of Cs_2CO_3 followed by centrifugal separation. Quantitative analysis of the solution was carried out by gas chromatography with a flame ionization detector (GC-FID) equipped with a TC-WAX capillary column (GL Science) after *n*-butyl acetate had been added as an internal standard. Selectivity and yield of products were calculated on the basis of consumed amount and loaded amount of **1**, respectively.

Reaction using acetyl chloride (AcCl) as an acylation reagent was carried out in the presence of excess triethylamine. Acetic acid, propionic acid, acetonitrile, methanol, acetone, tetrahydrofuran (THF), *N*,*N*-dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) were investigated as solvents. The amounts of other catalysts, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_4PMo_{11}V_1O_{40}$, HNO_3, H_2SO_4, HCl, and *p*-TsOH·H_2O, were decided on the basis of their proton amount, the proton amount of each catalyst being 7.5 mol% of that of **1**. $AlCl_3$ (2.5 mol% *vs.* **1**) was also used as Lewis acid. Reaction temperatures were

363, 343, 323 and 295 K. The molar ratio of **2a** to **1a** (**2a**/**1a**) was investigated in the range of 0.1 to 25. The amount of the catalyst was examined in the range of 0 to 20 mol% *vs.* **1a**. The influence of additional H_2O was estimated in the range of 0 to *ca.* 8 wt% based on the sum of substrate, acylation reagent and solvent.

The reaction was monitored by using ^{1}H-NMR. In these conditions, a mixture of **1a** (2 mmol), acetic anhydride-d_6 (20 mmol), acetic acid-d_4 (20 mmol), and $H_3PW_{12}O_{40}$ (2.5 mol% *vs.* **1a**) was partly transferred into an NMR sample tube, and the ^{1}H-NMR signal was collected at ambient temperature after 4, 25 and 96 h.

Acylation of pyruvate ester with carboxylic anhydride over solid catalysts

20 wt% $H_3PW_{12}O_{40}/SiO_2$ (2.5 mol% as $H_3PW_{12}O_{40}$ *vs.* **1a**), H-Y (0.1 g), and H-BEA (0.1 g) zeolites were examined for the acylation of **1a** (2 mmol) with **2a** (20 mmol) in acetic acid (20 mmol) at 343 K for 1 h. In the case of using AMBERLYST 15(H) (3.4 g), **1a** (20 mmol) and **2a** (200 mmol) were reacted in acetic acid (200 mmol) at 343 K for 5 h. Because these reactions were heterogeneous, stirring was carried out with a magnetic stirrer.

Characterization of products and catalysts

α-Acyloxyacrylate esters (**4**) and 2,2-diacyloxypropionate esters (**3**) were identified by using ^{1}H- and ^{13}C-NMR (ECX-400, JEOL) and HR-MS (JMS-T100LP, JEOL) after appropriate purification. The purification and characterization of products were generally carried out as follows. After removal of the catalyst, the reaction mixture was condensed with a rotary evaporator. $NaHCO_3$ saturated aqueous solution was added to this condensed mixture. Then, diethyl ether was added to extract the products from the aqueous layer, and the ether layer was collected with a separation funnel. This operation was repeated several times. After drying the extracts with anhydrous Na_2SO_4 overnight, the solution was evaporated until an oily product was obtained. This oily product was purified by using column chromatography of SiO_2 (Kieselgel 60, Merck) with chloroform/hexane = 10/1 (v/v) as eluent, and analyzed by ^{1}H-, ^{13}C-NMR, and HR-MS. HR-MS measurements were carried out by the Centre for Instrumental Analysis, Hokkaido University.

Ethyl 2,2-diacetoxypropionate (3a). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27 (3H, t, J = 7.2 Hz, CH_3CH_2O); 1.94 (3H, s, CH_3–$C(OAc)_2COOC_2H_5$); 2.09 (6H, s, 2 × $CH_3C(O)O$); 4.23 (2H, q, J = 7.2 Hz, CH_3CH_2O). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3CH_2O); 21.3 (2 × $CH_3C(O)O$); 22.1 (CH_3–$C(OAc)_2C(O)OC_2H_5$); 62.5 (CH_3CH_2O); 98.4 (CH_3–$C(OAc)_2C(O)OC_2H_5$); 166.8 ($C(O)OC_2H_5$); 168.3 (2 × $CH_3C(O)O$). HRMS (ESI-TOF, NaI) calculated for $^{12}C_9{}^1H_{14}{}^{23}Na_1{}^{16}O_6$ ($[M+{}^{23}Na]^+$) 241.06881, found 241.06974.

Ethyl α-acetoxyacrylate (4a). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.2 Hz, CH_3CH_2O); 2.22 (3H, s, $CH_3C(O)O$); 4.25 (2H, q, J = 7.2 Hz, CH_3CH_2O); 5.47 (1H, d, J = 1.8 Hz, CH_2=C); 6.02 (1H, d, J = 1.8 Hz, CH_2=C). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.9 (CH_3CH_2O); 20.2 ($CH_3C(O)O$); 61.7 (CH_3CH_2O); 113.5 (CH_2=C); 144.8 (CH_2=C); 161.3 ($CH_3C(O)O$); 168.8 ($C(O)OC_2H_5$). HRMS (ESI-TOF, NaI) calculated for $^{12}C_7{}^1H_{10}{}^{23}Na_1{}^{16}O_4$ ($[M+{}^{23}Na]^+$) 181.04768, found 181.04690.

The analysis of HPAs was carried out by using FT-IR (FTIR Spectrometer PARAGON 1000, Perkin Elmer), XRD (Cu-Kα, RINT 2000, Rigaku), UV-vis (UV/VIS/NIR spectrophotometer V-570, JASCO), TG-DTA and ^{31}P-NMR.

Evaluation of polymer properties

Molecular weights (*Mw*) of poly(ethyl α-acetoxyacrylate) (PEAA) and PMMA were both approximately 100 000. *LACEA*® (H-100) was used as PLA. The value of %T was measured with reference to the method of JIS K 7105 published by the Japanese Industrial Standards Committee. The value of T_g was determined by differential scanning calorimetry (DSC 6220C, Seiko Instruments).

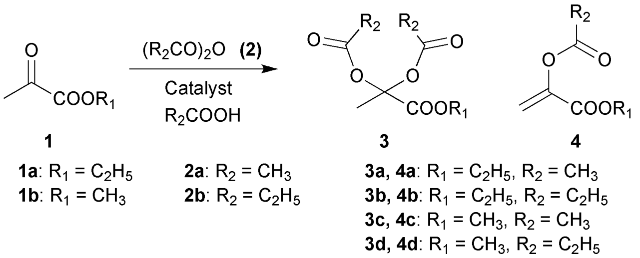
Results and discussion

Comparison of various homogeneous catalysts

Various homogeneous catalysts were examined for this acylation. As shown in Table 1, tungsten-based HPAs were more active and selective than molybdenum-based HPAs for the acylation between **1a** and **2a** (entries 1–5). All of the examined Keggin-type HPAs were soluble in the reaction mixture. However, small amounts of precipitate were observed during reaction, especially when Mo-based Keggin-type HPAs were used. $H_3PW_{12}O_{40}$ showed the best performance among the Keggin-type HPAs (entries 1–5). The acidity of the Keggin-type HPAs has been studied in detail, and the pK_n (n = 1–4) values of these HPAs in a polar solvent have been summarized in some reviews.[12] pK_1 values in acetic acid are almost the same: $H_3PW_{12}O_{40}$ (pK_1 = 4.77), $H_4SiW_{12}O_{40}$ (4.97), $H_3PMo_{12}O_{40}$ (4.70) $H_4PMo_{11}V_1O_{40}$ (4.68), $H_4SiMo_{12}O_{40}$ (4.78). There is a significant difference between the stability of Mo-based HPAs and that of W-based HPAs in reaction media. W-based HPAs were slightly reduced during the reaction and the colour of the reaction solution became slightly blue, but precipitation of the HPA salt occurred only when Cs_2CO_3 was added after the reaction. After reaction at 343 K for 1 h (entry 1), the $H_3PW_{12}O_{40}$ catalyst was precipitated as $Cs_3PW_{12}O_{40}$ by Cs_2CO_3 addition and analyzed by XRD and FT-IR. Its XRD pattern showed typical diffraction peaks for the cubic phase of $Cs_3PW_{12}O_{40}$, and its FT-IR peaks were characteristic of P–O (1080 cm^{-1}), W=O (985 cm^{-1}) and W–O–W (889, 880 cm^{-1}) in $[PW_{12}O_{40}]^{3-}$. These results mean that the Keggin structure of $H_3PW_{12}O_{40}$ is not essentially changed during reaction, despite the formation of slightly reduced species.

In contrast, the colour of the solution with Mo-based HPAs became deep blue after the reaction, and no precipitation occurred after addition of Cs_2CO_3. This result means that Mo-based HPAs, $H_3PMo_{12}O_{40}$, $H_3PMo_{11}V_1O_{40}$, and $H_4SiMo_{12}O_{40}$, were transformed into other species by hydrolysis and/or reduction. In addition, the mass balance of the reaction with Mo-based HPAs was rather low, and it was thought that **1a** was mainly consumed for side reactions. Because of their easiness for hydrolysis and reduction in solution, Mo-based HPAs do not catalyze this acylation despite their strong acidity.

Table 1 Acylation of **1** with **2** by various homogeneous catalysts[a]



		Substrate			Yield (%)			
Entry	Catalyst	1	2	Conversion (%)	3		4	
1	$H_3PW_{12}O_{40}$	**1a**	**2a**	68	**3a**	7	**4a**	61
2	$H_4SiW_{12}O_{40}$	**1a**	**2a**	65	**3a**	13	**4a**	52
3	$H_3PMo_{12}O_{40}$	**1a**	**2a**	32	**3a**	2	**4a**	6
4	$H_4PMo_{11}V_1O_{40}$	**1a**	**2a**	24	**3a**	0	**4a**	5
5	$H_4SiMo_{12}O_{40}$	**1a**	**2a**	27	**3a**	1	**4a**	4
6	$H_3PW_{12}O_{40}$	**1a**	**2b**	70	**3b**	8	**4b**	56
7	$H_3PW_{12}O_{40}$	**1b**	**2a**	85	**3c**	10	**4c**	64
8	$H_3PW_{12}O_{40}$	**1b**	**2b**	70	**3d**	8	**4d**	50
9	H_2SO_4	**1a**	**2a**	21	**3a**	12	**4a**	8
10	HCl	**1a**	**2a**	0	**3a**	0	**4a**	0
11	HNO_3	**1a**	**2a**	4	**3a**	0	**4a**	3
12	H_3PO_4	**1a**	**2a**	0	**3a**	0	**4a**	0
13	p-TsOH·H_2O	**1a**	**2a**	13	**3a**	3	**4a**	5
14	$AlCl_3$	**1a**	**2a**	22	**3a**	0	**4a**	2
15	None	**1a**	**2a**	0	**3a**	0	**4a**	0
16[b]	p-TsOH·H_2O	**1a**	**2a**	—	**3a**	—	**4a**	58
17[c]	p-TsOH·H_2O	**1b**	**2a**	—	**3a**	—	**4a**	37

[a] Reaction conditions: **1** (2 mmol), **2** (20 mmol), catalyst (entries 1–13, 7.5 mol% as H^+ *vs.* **1**, entry 14; 2.5 mol% *vs.* **1**), carboxylic acid (20 mmol), 343 K, 1 h. [b] See ref. 3 (393 K, 24 h). [c] See ref. 5a (reflux, 16 h).

Reaction with propionic anhydride (**2b**) proceeded smoothly to produce the corresponding α-acyloxyacrylate ester (**4b**) in a good yield (entry 6). When methyl pyruvate (**1b**) was used, the mass balance became low (entries 7 and 8). Decomposition of the methyl ester of pyruvate is easier than that of the ethyl ester, in which hydrolysis and decarboxylation are likely to occur.[13] Therefore, **1b** underwent decomposition during reaction and the yield of **4b** decreased.

Other mineral acid catalysts were also investigated (entries 9–12). Although p-TsOH·H_2O has been used as a catalyst in previous studies (entries 16, 17),[4,6] it was not a good catalyst under our reaction conditions (entry 13). Since our reaction conditions were milder than those used in the above-mentioned studies, for example, the temperature was lower and the reaction period was shorter, the activity of p-TsOH·H_2O is not sufficient for catalyzing the acylation. In addition, a significant difference between W-based HPAs and typical mineral acids is the softness of the anion moiety.[14] Anion sizes of HPAs, such as $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$ (*ca.* 1 nm), are much larger than those of SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-}, and p-TsO^-. This means that these HPA anions are much softer than typical mineral acids because of the large anion size and low surface charge density. This property will also work efficiently for the activation of cationic species during reaction.

$AlCl_3$ (entry 14), which is a Lewis acid, did not work as a catalyst.

From a viewpoint of catalyst reuse, separation of homogeneous HPA catalysts by precipitation as Cs-HPA salts such as $Cs_3PW_{12}O_{40}$ following by centrifugation is not the best way to recover catalysts. Immobilization of the $H_3PW_{12}O_{40}$ on supports is now being investigated in our group to achieve a greener procedure.

Comparison of various heterogeneous catalysts

Heterogeneous catalysts are attractive for industrial use because of their advantage in the separation process. Various solid catalysts were investigated as shown in Table 2. The use of supported catalyst, 20 wt% $H_3PW_{12}O_{40}/SiO_2$ (entry 1), resulted in a good yield of **4a**. In this case, partial catalyst leaching was observed. Improvement in catalyst preparation is therefore required for preventing catalyst leaching. Neither H-Y zeolite (entry 2) nor H-BEA zeolite (entry 3) worked as a good catalyst. H-Y did not catalyze the reaction at all, while H-BEA showed low activity. This difference is thought to be due to the influence of the pore structure.[15] MCM-41 (entry 4) and SiO_2 (entry 5) showed almost no activity. In contrast, cation-exchange-resin, AMBERLYST 15(H) (entry 6), moderately catalyzed the reaction. It has a sulfonic group, $-SO_3H$, on its polymer chain that works as a strong acid site.

Investigation of reaction conditions with $H_3PW_{12}O_{40}$

As mentioned above, $H_3PW_{12}O_{40}$ showed the highest performance for the acylation between **1** and **2**, owing to its excellent acid property. Therefore, various reaction conditions with $H_3PW_{12}O_{40}$ were evaluated in detail.

Table 2 Acylation of **1a** with **2a** by various heterogeneous catalysts[a]

Entry	Catalyst	Conversion (%)	Yield (%)	
			3a	**4a**
1	20 wt% $H_3PW_{12}O_{40}/SiO_2$	61	7	46
2	H-Y (5.5)[b]	0	0	0
3	H-BEA (150)[b]	25	5	20
4	MCM-41	0	0	0
5	SiO_2	17	0	1
6	AMBERLYST 15(H)	44	4	34

[a] Reaction conditions: **1a** (entries 1–5; 2 mmol, entry 6; 20 mmol), **2a** (entries 1–5; 20 mmol, entry 6; 200 mmol), catalyst (entry 1; 0.85 g, entries 2–5; 0.10 g, entry 6; 3.4 g), acetic acid (entries 1–5; 20 mmol, entry 6; 200 mmol), 343 K, 1 h. [b] Si/Al ratio

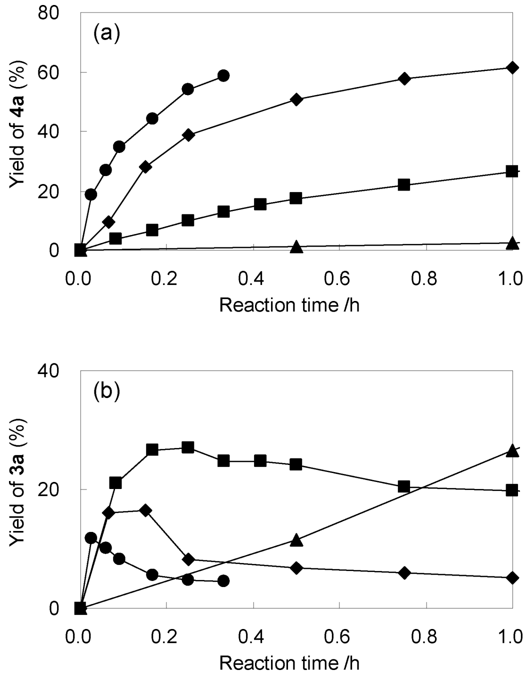


Fig. 3 Correlation between reaction time and product yield with $H_3PW_{12}O_{40}$ at various temperatures. (a) Yield of **4a**, (b) yield of **3a**, 363 K (●), 343 K (◆), 323 K (■), 295 K (▲). Reaction conditions were the same as those in entry 1 in Table 1.

Reactions were carried out at various temperatures, 295, 323, 343 and 363 K (Fig. 3). The yield of **4a** gradually increased at higher temperatures. In contrast, the yield of **3a** decreased. The correlation between the yields of **4a** and **3a** is associated with a consecutive reaction from **1a** to **4a** *via* **3a**. To clarify this point, we investigated the reaction order in the initial reaction period. It was found that this reaction is a first-order reaction with respect to both concentrations of **1a** and **2a**. This means that **3a** is first generated by reaction between **1a** and **2a**, and **3a** transforms consecutively into **4a**.

This behaviour in solution was also confirmed by ^{1}H-NMR in the reaction of **1a** and acetic anhydride-d_6 in acetic acid-d_4 with $H_3PW_{12}O_{40}$, as shown in Fig. 4. **1a** was gradually consumed, because the signal of the methyl group in **1a** at *ca.* 1.9 ppm (singlet) monotonically decreased. On the other hand, the signal of olefinic protons in **4a** at *ca.* 5.5 and 6.0 ppm (doublet) increased, corresponding to the results shown in Fig. 3(a). Hence, the signal of the methyl group in **3a** at *ca.* 2.4 ppm (singlet) increased after 4 h, but the signal was clearly decreased after 25 and 96 h. These results suggest that the formation of **4a** is a consecutive reaction from **1a** *via* **3a**. Syntheses of various acylal compounds have been examined by reaction between various aldehydes and carboxylic anhydrides.[16] However, to the best of our knowledge, this is the first report on 2,2-diacyloxypropionate esters.

The amount of $H_3PW_{12}O_{40}$ *vs.* **1a** was also investigated at 343 K for 1 h (Fig. 5). The yield of **4a** increased gradually with

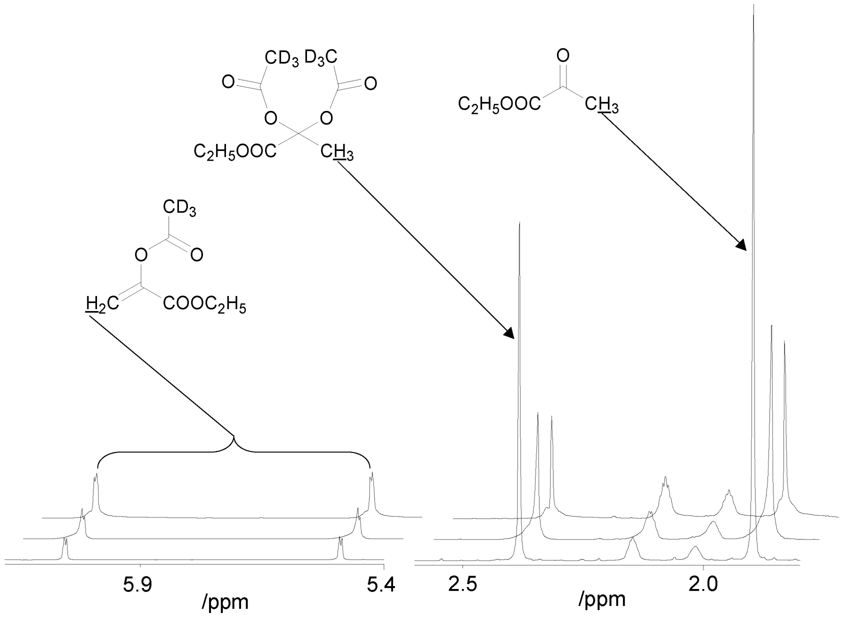


Fig. 4 ^{1}H-NMR (400 MHz) spectra of the reaction between **1a** and acetic anhydride-d_6 with $H_3PW_{12}O_{40}$ in acetic acid-d_4 at 295 K after 4 h (bottom), 25 h (middle), and 96 h (top).

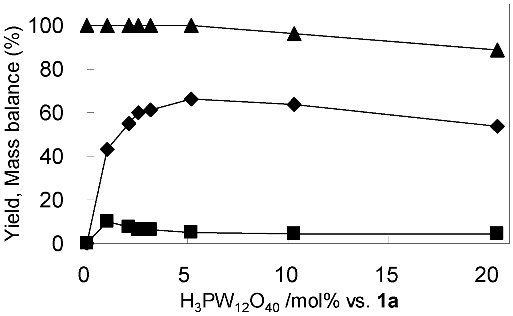


Fig. 5 Correlations between $H_3PW_{12}O_{40}$ amount, yield, and mass balance at 343 K for 1 h. Yields of **4a** (♦) and **3a** (■), mass balance (▲).

an increase in the amount of the catalyst, and a maximum yield was achieved at 5 mol% $H_3PW_{12}O_{40}$. When a small amount of $H_3PW_{12}O_{40}$ was used, the formation of **3a** was slightly increased. On the other hand, at more than 5 mol%, both the yield of **4a** and the mass balance gradually decreased, indicating that **4a** is consecutively decomposed into other compounds, such as ethanol, pyruvic acid and acetic acid. In addition, we detected the formation of ethanol and ethyl acetate. Ethanol was generated by hydrolysis of **1a**, and ethyl acetate was formed by the subsequent esterification between ethanol and **2a**. Pyruvic acid was also formed by hydrolysis of **1a**, and it often underwent decarboxylation to acetic acid. Formation of acetic acid during the reaction could not be detected because the solvent was acetic acid.

The effect of the molar ratio of acetic anhydride (**2a**) to **1a** was examined at 343 K for 1 h, as shown in Fig. 6. When no acylation reagent was used (0 equiv.), almost 80% of **1a** was transformed into ethanol, acetic acid and ethyl acetate by hydrolysis and decarboxylation. The yield of **4a** was maximum when the ratio of **2a** to **1a** was 10 equiv. The appropriate ratio of **2a** to **1a** was from 3 to 10 equiv. The use of a large amount of **2a** induced a decline of yield and mass balance that derived from side reaction or catalyst deactivation. On the other hand, when a small amount of **2a** was used, the yield was low. It is notable that when less than 0.5 equiv. of **2a** was used, no products, either **4a** or **3a**, were observed. In this case, 80% of **1a** was transformed into undesired products as mentioned above. This result suggests that a several-fold excess of carboxylic anhydride to pyruvate ester in molar amount is absolutely necessary for the effective acylation from pyruvate ester to α-acyloxyacrylate ester.

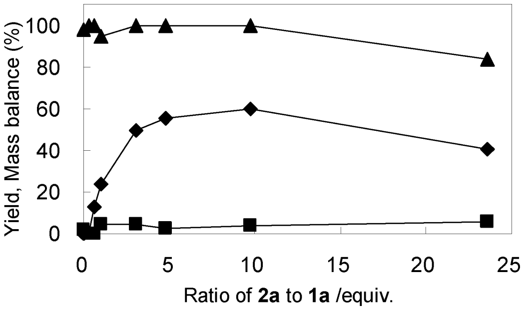


Fig. 6 Correlations between molar ratio of **2a** to **1a**, yield, and mass balance at 343 K for 1 h. Yields of **4a** (♦) and **3a** (■), mass balance (▲).

A different type of acylation reagent, acetyl chloride (AcCl), was also examined in combination with $H_3PW_{12}O_{40}$ catalyst and **1a** in acetic acid. The yields of **4a** (13%) and **3a** (9%) were very low, indicating that AcCl was not an appropriate acylation reagent.

The durability against H_2O of the reaction with $H_3PW_{12}O_{40}$ catalyst was tested. The effect of additional H_2O was evaluated at 343 K for 1 h. $H_3PW_{12}O_{40}$ itself has 22 molecules of crystal water. As shown in Fig. 7, *ca.* 2 wt% of additional H_2O (75 molecules with respect to the loaded $H_3PW_{12}O_{40}\cdot 22H_2O$) had almost no effect on **4a** yield. With an increase in the amount H_2O, the product yield gradually decreased. When 8 wt% H_2O was added, almost no desired product was formed, the hydrolysis of **1a** and **2a** being the dominant reaction. The reaction with $H_3PW_{12}O_{40}$ showed tolerance for H_2O in the range of less than 2 wt% H_2O, and it is a great advantage for the reaction without undesired hydrolysis of ester and anhydride.

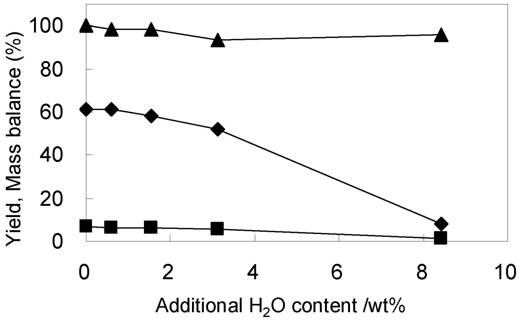


Fig. 7 Correlations between additional H_2O content, yield, and mass balance at 343 K for 1 h. Yields of **4a** (♦) and **3a** (■), mass balance (▲).

The effects of solvents were also investigated. HPAs were soluble in all solvents at the beginning of the reaction. As shown in Table 3, the best performance among the various solvents was achieved when acetic acid was used as the solvent. When propionic acid was used as the solvent, the catalytic performance of $H_3PW_{12}O_{40}$ was also high (Table 1, entry 6). When methanol was used, hydrolysis and decarboxylation mainly occurred, and methyl pyruvate (yield, 13%) was generated by transesterification of ethyl ester. In the case of THF, the formation of **4a** was observed with a low mass balance and many by-products were generated. Furthermore, in this case, almost all of the THF was consumed by oligomerization and acetylation of itself. Although small amounts of **4a** were formed when acetone,

Table 3 Acylation of **1a** with **2a** in various solvents[a]

			Yield (%)	
Entry	Solvent	Conversion (%)	**3a**	**4a**
1	Acetic acid	68	7	61
2	Acetonitrile	21	17	4
3	Methanol	65	0	0
4	Acetone	14	4	3
5	THF	96	0	56
6	DMF	24	0	10
7	DMSO	19	1	1

[a] Reaction conditions: **1a** (2 mmol), **2a** (20 mmol), $H_3PW_{12}O_{40}$ (7.5 mol% as H^+ *vs.* **1a**), solvent (20 mmol), 343 K, 1 h.

DMF and DMSO were used, none of them were appropriate as solvents. The use of carboxylic acid as a solvent in combination with $H_3PW_{12}O_{40}$ and carboxylic anhydride seems to be quite important. When no acetic acid was used in the reaction of **1a**, **2a** and $H_3PW_{12}O_{40}$, an exothermic phenomenon was also observed and many by-products were generated. In addition, the yield of **4a** was low without acetic acid (31%, 3 h) compared to that with acetic acid (38%, 2 h). From a thermodynamic point of view, it is thought that conditions without acetic acid are favourable for **4a** synthesis because an equivalent amount of acetic acid is generated by the formation of **4a**. Nevertheless, in our reaction conditions, the diluting effect by acetic acid as a solvent also works well not only for suppressing exothermic heat and undesired side reactions but also for enhancing the efficiency of the main reaction. These results imply that the combination of carboxylic acid as a solvent and heteropolyacid as a catalyst is appropriate for the acylation.

Reaction kinetics

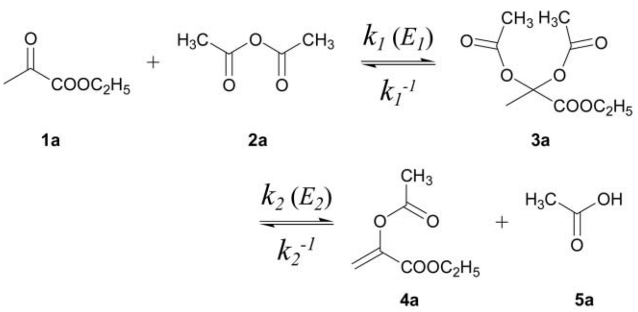
As mentioned above, the reaction order of the acylation was determined to be of first order with respect to both concentrations of **1** and **2**. Furthermore, it was found that the reaction proceeded consecutively from **1** and **2** to **4** *via* **3**. To clarify the reason for the good performance of $H_3PW_{12}O_{40}$ for this acylation, activation energies and rate constants for each reaction step were calculated. We assumed the equilibrium reaction pathway as that shown in Scheme 2. Moreover, we considered the reaction rate equations for **1a**, **3a**, and **4a**. Indeed, we have confirmed that **1a** was generated by a reaction using only **3a** as a substrate in acetic acid. On the basis of these assumptions, the correlation curves between reaction time and product yields with $H_3PW_{12}O_{40}$ (Fig. 3) and AMBERLYST 15(H) (Fig. 8) were fitted and the rate constants were compared. Activation energies for each step in the temperature range of 323–363 K and rate constants at 323 K are shown in Table 4. Apparent activation energies (E_a) were also determined by the Arrhenius method in the temperature range of 323–363 K. In this curve-fitting, the reaction curve at 295 K was excluded because the consecutive behaviour was not observed in this reaction period.

As shown in Table 4, the activation energy for the first step (E_1) is quite different between $H_3PW_{12}O_{40}$ and AMBERLYST 15(H), the value for the latter being almost two-times larger than that for the former. Remarkably, rate constants per mole of proton for $H_3PW_{12}O_{40}$ were several hundred-times higher than those for AMBERLYST 15(H). This result means that the activity of protons in $H_3PW_{12}O_{40}$ is much higher than that in AMBERLYST 15(H), reflecting the acid strength.

Table 4 Activation energies (363–323 K) and rate constants (323 K)[a]

Catalyst	$H_3PW_{12}O_{40}$	AMBERLYST 15(H)[b]
E_a/kJ mol^{-1}	31.6	43.3
E_1/kJ mol^{-1}	64.8	103.8
E_2/kJ mol^{-1}	89.8	95.2
k_1/dm^3 mol^{-1} s^{-1} (mol-H$^+$)$^{-1}$	1.1	1.3×10^{-3}
k_2/s^{-1} (mol-H$^+$)$^{-1}$	3.6	1.6×10^{-2}

[a] Reactions were carried out in the same conditions as those in entry 1 in Table 1 and entry 6 in Table 2 except for the reaction time. [b] Molar amount of protons in AMBERLYST 15(H) was calculated with its ion exchanging capacity, 4.7 meq g^{-1}.



$$\left\{\frac{C(\mathbf{1a})}{C_0(\mathbf{1a})}\right\}_{t_1} = \left\{\frac{C(\mathbf{1a})}{C_0(\mathbf{1a})}\right\}_t - k_1\left\{\frac{C(\mathbf{1a})}{C_0(\mathbf{1a})}\right\}_t\left\{\frac{C(\mathbf{2a})}{C_0(\mathbf{1a})}\right\}_t + k_1^{-1}\left\{\frac{C(\mathbf{3a})}{C_0(\mathbf{1a})}\right\}_t$$

$$\left\{\frac{C(\mathbf{3a})}{C_0(\mathbf{1a})}\right\}_{t_1} = \left\{\frac{C(\mathbf{3a})}{C_0(\mathbf{1a})}\right\}_t + k_1\left\{\frac{C(\mathbf{1a})}{C_0(\mathbf{1a})}\right\}_t\left\{\frac{C(\mathbf{2a})}{C_0(\mathbf{1a})}\right\}_t - (k_1^{-1}+k_2)\left\{\frac{C(\mathbf{3a})}{C_0(\mathbf{1a})}\right\}_t + k_2^{-1}\left\{\frac{C(\mathbf{4a})}{C_0(\mathbf{1a})}\right\}_t\left\{\frac{C(\mathbf{5a})}{C_0(\mathbf{1a})}\right\}_t$$

$$\left\{\frac{C(\mathbf{4a})}{C_0(\mathbf{1a})}\right\}_{t_1} = \left\{\frac{C(\mathbf{4a})}{C_0(\mathbf{1a})}\right\}_t + k_2\left\{\frac{C(\mathbf{3a})}{C_0(\mathbf{1a})}\right\}_t - k_2^{-1}\left\{\frac{C(\mathbf{4a})}{C_0(\mathbf{1a})}\right\}_t\left\{\frac{C(\mathbf{5a})}{C_0(\mathbf{1a})}\right\}_t$$

$C_0(\mathbf{1a})$: Initial concentration of **1a** [mol dm^{-3}]
$\{C(\mathrm{A})/C_0(\mathbf{1a})\}_t$: Concentration ratio of compound A at t
t_1: $t_1 = t + \Delta t$ [s]

Scheme 2 Assumed reaction pathway and equations for calculations.

On the other hand, the energy for the second step (E_2) was almost the same. In fact, the difference between the rate constants per mole of proton for the first step (k_1) was more significant than that for the second step (k_2). This result suggests that $H_3PW_{12}O_{40}$ can effectively catalyze the first reaction between

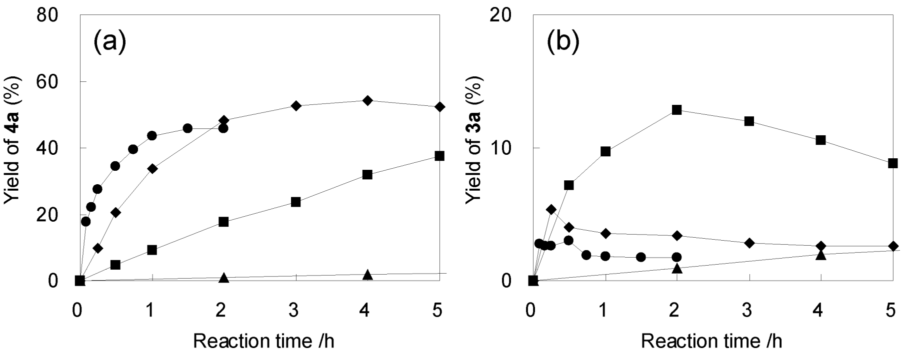


Fig. 8 Correlation between reaction time and yield with AMBERLYST 15(H) at various temperatures. (a) Yield of **4a**, (b) yield of **3a**, 363 K (●), 343 K (◆), 323 K (■), 295 K (▲). Reaction conditions were the same as those in entry 6 in Table 2.

pyruvate ester and carboxylic anhydride because of its quite strong acidity and softness.

Catalytic performance of $Cs_xH_{3-x}PW_{12}O_{40}$

Apart from supported HPAs on some carriers, HPAs can be used as heterogeneous catalysts by neutralization of protons with Cs.[17]

We prepared $Cs_xH_{3-x}PW_{12}O_{40}$ catalysts ($x = 0$, 1.0, 2.0, 2.5, 3.0) and examined their catalytic performance for acylation (Fig. 9). In this case, $H_3PW_{12}O_{40}$ ($x = 0$) was also dried at 393 K for 24 h to remove the crystal water. Due to this treatment, the solubility of $H_3PW_{12}O_{40}$ declined and the conversion was diminished from 68% (Table 1, entry 1) to 52% with almost the same selectivity. As the amount of Cs increased, the yield of **4a** gradually decreased. Hence, the yield of **3a** increased in the range of $x \geq 2$. This implies a simple drop in reaction rate or change in $H_3PW_{12}O_{40}$ property. Notably, $Cs_3PW_{12}O_{40}$ can catalyze the reaction in spite of no protons in its molecular formula after neutralization. The possibility of interaction between $[PW_{12}O_{40}]^{3-}$ anions and a small amount of protons dissociating from acetic acid is strongly suggested.

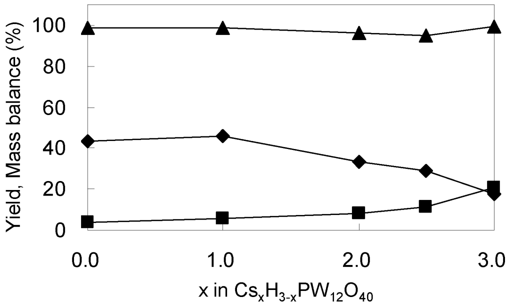


Fig. 9 Correlations between x in $Cs_xH_{3-x}PW_{12}O_{40}$, yield, and mass balance at 343 K for 1 h. Yields of **4a** (◆) and **3a** (■), mass balance (▲).

After a long-time reaction for 10 h at 343 K with the $Cs_3PW_{12}O_{40}$ catalyst, the yield of **4a** was increased to 34% and that of **3a** was decreased to 9%, meaning that $Cs_3PW_{12}O_{40}$ showed activity for at least 10 h and the consecutive reaction from **3a** to **4a** was gradually progressed. As a result of a leaching test with $Cs_3PW_{12}O_{40}$ in acetic acid, no $[PW_{12}O_{40}]^{3-}$ species was leached into the acetic acid solution. In this test, the UV-vis absorbance at 260 nm that derives from the $[PW_{12}O_{40}]^{3-}$ anion[18] of the decanted solution after stirring at 343 K for 1 h was almost the same as that of acetic acid solvent. This result strongly suggests that $Cs_3PW_{12}O_{40}$ can be separated after reaction by decantation, centrifugation and/or filtration, and be reused as a catalyst.

Table 5 Comparison of polymer properties

Polymer	PEAA	PMMA	PLA
Transmittance (%T)	93	93	Translucent[a]
T_g/K	406	378	333

[a] It was so low that the value of %T could not be measured.

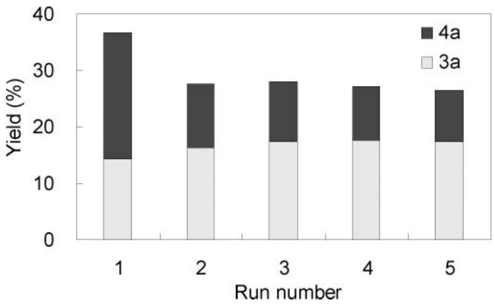


Fig. 10 Reusability of heterogeneous $Cs_3PW_{12}O_{40}$ in the reaction at 343 K for 1 h. Reaction conditions were the same as those in Fig. 9. $Cs_3PW_{12}O_{40}$ was used with no treatment between reactions in the second to fifth runs.

Reusability of the heterogeneous $Cs_3PW_{12}O_{40}$ catalyst, which was calcined at 573 K before the first reaction, was confirmed, as shown in Fig. 10. After each reaction at 343 K for 1 h with stirring, the catalyst was separated by centrifugation, and the reaction solution was analysed by GC. The separated catalyst was used for the next reaction without calcination. In the second run, a *ca.* 25% decrease in catalytic activity compared to that of the first run was observed. In fact, the colour of $Cs_3PW_{12}O_{40}$ was changed from white to light brown during the first run. This implies that $Cs_3PW_{12}O_{40}$ is partly reduced or solvated during reaction. In contrast, the total yield of **4a** and **3a** was almost the same in the second run or later. In these cases, there was almost no change in the colour of catalyst. However, it seemed that the ratio of **4a** formation was slightly diminished and that of **3a** formation was somewhat increased. These results mean that the catalyst activity is gradually declined during repeated reactions. Nonetheless, the reusability of $Cs_3PW_{12}O_{40}$ was clearly demonstrated, and this catalyst is considered to be the potential heterogeneous catalyst for this reaction. It is also quite meaningful to use $Cs_3PW_{12}O_{40}$, instead of $H_3PW_{12}O_{40}$ or $H_3PW_{12}O_{40}/SiO_2$, from the viewpoint of a greener catalyst separation.

Polymer properties

α-Acyloxyacrylate esters, **4**, are potential candidate monomers for bio-based polymers. We have also confirmed the properties of the homo-polymer of **4a**, poly(ethyl α-acetoxyacrylate) (PEAA). The optical transmittance and glass transition temperature (T_g) of PEAA were compared with those of PMMA and PLA, as shown in Table 5. PEAA showed higher heat resistance than PLA and PMMA and was as transparent as PMMA. Additionally, the thermal stability of PEAA and PMMA was measured by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The 5% weight loss temperatures of these polymers were in the range of 553 to 563 K, which means that their thermal degradation properties are comparable. The fact that **4** can also be co-polymerized with various monomers by radical polymerization is an advantage for its practical use.[19]

Conclusions

We have developed a HPA-catalyzed acylation for α-acyloxyacrylate ester synthesis from pyruvate ester and carboxylic anhydride in carboxylic acid under mild conditions, that is, at lower temperature and in a shorter reaction period and with a smaller amount of catalyst than that used in previous methods. The important requirements for the catalyst are acid strength, stability and probably softness of the anion in carboxylic acid solvents. These requirements are well met by HPAs, particularly $H_3PW_{12}O_{40}$, its reaction rate being much higher than that of a cation exchange resin. Furthermore, we have identified the intermediate species, a *gem*-diacetate compound, for this reaction.

Since pyruvate esters can be obtained from lactic acid, one of the most important glucose fermentation products, the facile and efficient transformation of pyruvate ester to a useful polymer component will open up new possibilities for lactic acid platform utility.

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