Heteropolyacid Catalyzed Acylation of Pyruvate Esters to α-Acyloxyacrylate Esters as Candidate Monomers for Bio-based Polymers

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Biorefinery, which is a process for producing various useful chemicals and energies from biomass feedstock, have been paid much attention for years.1) Among various key compounds for biorefinery, lactic acid derivatives are one of the most important substrates. In this research, acylation of pyruvate esters, which are derived from lactic acid by esterification and oxidative dehydrogenation, are investigated in detail.2) α-Acyloxyacrylate esters are synthesized by this acylation, which are candidate monomers for bio-based polymers. Furthermore, this reaction is well catalyzed by Keggin-type heteropolyacids (HPAs), owing to their strong acidity.

α-Acyloxyacrylate ester (4) was synthesized from pyruvate ester (1) and carboxylic anhydride (2), and 2,2-diacyloxypropionate ester (3) was also generated as an intermediate (Scheme 1). As shown in Figure 1, tungsten-based Keggin-type HPAs, H3PW12O40 and H4SiW12O40, demonstrated much higher catalytic performance than other acid catalysts at 343 K for 1 h (R1: C2H5, R2: CH3). Other mineral acids did not work as effective catalysts because of their rather weak acid strength than W-based HPAs. In contrast, the reason for low performance of molybdenum-based HPAs was different from that of other mineral acids. Since Mo-based HPAs are less stable than W-based HPAs in solution and toward reduction, they were decomposed or deeply reduced during reaction.

However p-toluenesulfonic acid (p-TsOH) has been used as an organic acid for this reaction, reaction conditions were so severe, high temperature (393 K) and long reaction period (16 h).3) Our mild reaction condition has significant superiority to previous researches. Polymer properties were also examined (Table 1), and poly ethyl α-acetoxyacrylate (PEAA) showed high transparency and heat resistance compared to PMMA and PLA.

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