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Solid acid catalyzed esterification of dicyclopentadiene with organic acids to bio-based functional monomers†

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Here, we report the synthesis of new functional monomers of dicyclopentadiene (DCPD) by esterification with carboxylic acids that can be derived from biomass. We demonstrate that the esterification of DCPD proceeds *via* a reaction intermediate, that is, cydecanol (DCPD-OH), and propose an esterification mechanism over solid acid catalysts.

Dicyclopentadiene (DCPD) is one of the interesting cyclic olefins for polymer chemistry.[1] DCPD is mostly used in the form of cross-linked DCPD (poly-DCPD), exhibiting excellent impact strength and chemical resistance.[2] Yet the lack of chemical functionality of poly-DCPD has restricted its broader application. For example, poly-DCPD cannot be applied as a paint source without oxidizing the surface,[3] due to its hydrophobicity and disagreeable odor.[4]

A functionalized DCPD polymer can be obtained by sequential reactions of (i) functionalization of the DCPD monomer and then (ii) polymerization.[4–10] For example, Wang *et al.* reported the direct addition of aliphatic acid with DCPD using sulfamic acid as a catalyst.[10] Saha *et al.* reported a method for the derivatization of DCPD to obtain alcohol, esters, and ethers.[4] For example, treatment of DCPD with SeO_2 in a 1,4-dioxane/water medium gave *endo*-α-1-hydroxydicyclopentadiene in the presence of triethylamine, while ether derivatives were obtained by nucleophilic substitution of alkyl halides in the presence of sodium hydride in dry dimethylfuran.[4]

Considering the limited amounts of crude oil and the environmental impact of petrochemical processing, a shift in the chemical industry to a sustainable and environmentally friendly solution is necessary.[11–15] Thus, reacting petroleum derived olefins with biomass derived acids is an interesting option,[16,17] which can help achieve sustainability thresholds.[18]

Here, we report the functionalization of DCPD with carboxylic acids, which can be derived from renewable feedstocks such as biomass.[19] It is known that homogeneous catalysts such as sulfuric acid and hydrochloric acid can catalyze esterification of carboxylic acids with olefins.[20,21] However, there are drawbacks to homogeneous acids such as corrosion of equipment and difficult separation of target products from the reaction mixture.[22,23] These limitations can be resolved by the employment of heterogeneous catalysts,[24,25] providing a corrosion-free atmosphere, easy separation and effective recovery of the catalysts.[26] Cationic ion-exchange resins, one of the industrial heterogeneous acid catalysts, are versatile catalysts, particularly with their macroreticular pore structures. Amongst them, Amberlyst resins are strongly acidic catalysts with surface sulfonic groups that can be utilized for esterifications.[27,28] In terms of scale up, Amberlyst has some advantages as it is commercially available in large quantities and is relatively cheap. Its properties are well understood and it is used in commercial processes already.

We used heterogeneous Amberlyst resin catalysts for liquid phase esterification of DCPD with levulinic acid (LA), which is obtained from biomass[29–32] (Fig. 1a). After 4 h of reaction, the DCPD-LA ester was obtained and its structure was analyzed by ^{1}H nuclear magnetic resonance spectroscopy (NMR) and gas chromatography coupled with mass spectrometry (GC-MS) (Fig. 1b, S1 and S2, ESI†). After esterification, the disappearance of the proton of the carboxylic acid group in levulinic acid (δ_{1H} 11.1 ppm) and the double bond in the norbornene ring of DCPD (5.3–6.0 ppm) are observed (Fig. 1b). Among the possible isomers of DCPD-LA esters, the simulated ^{1}H NMR spectra elucidated that the double bond in the norbornene side reacted to form DCPD-LA ester during the esterification between DCPD and LA, in line with the experimental results (Fig. S2, ESI†). It has been reported that steric repulsion of substituted bicyclic structures in DCPD is the main reason for the difference in reactivity between the two double bonds of DCPD.[9,33,34] Because of its more strained structure, the double bond in the norbornene ring in DCPD is more reactive than the bond in the

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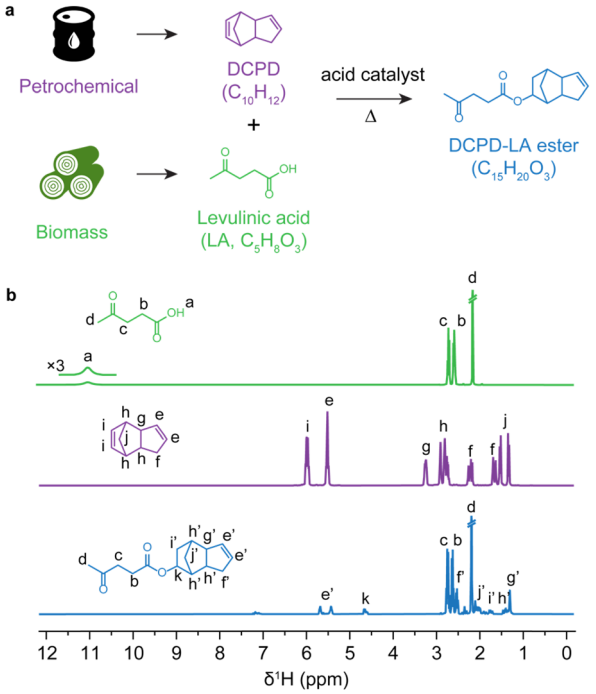


Fig. 1 (a) Scheme of the esterification between DCPD and LA. (b) ^{1}H NMR spectrum of DCPD, LA, and the DCPD-LA ester after purification using column chromatography.

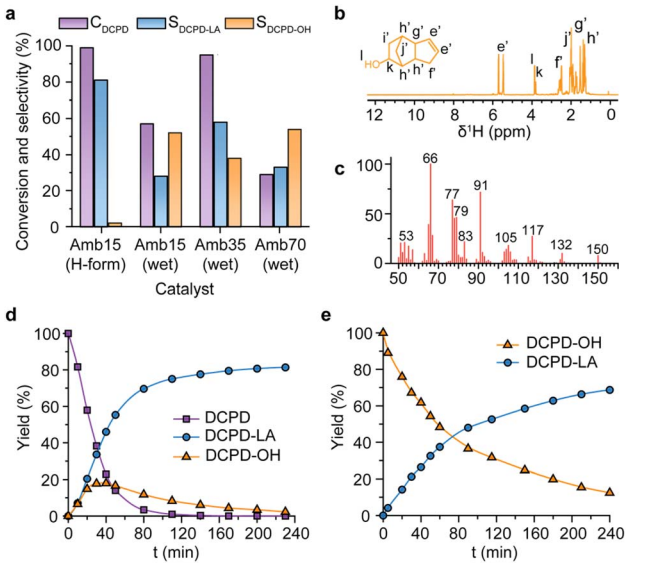


Fig. 2 (a) Esterification results between DCPD and LA over different Amberlyst resin catalysts. Reaction conditions: 80 °C, mole ratio (DCPD : LA) = 1 : 1, catalyst loading = 20 g-dry resin L^{-1}. The structure of DCPD-OH analyzed by (b) ^{1}H NMR and (c) GC-MS, after column chromatography. (d) The time course of the esterification of DCPD with LA over Amberlyst-15 (hydrogen form) at 80 °C. (e) The time course of the esterification of DCPD-OH and LA over Amberlyst-15 (hydrogen form) at 80 °C.

cyclopentene ring.[33,34] The GC-MS analysis also indicated the formation of DCPD-LA ester, showing a molecular mass of 248 g mol^{-1} with the corresponding fragmentation MS patterns (Fig. S1, ESI†).

As the physicochemical properties of Amberlyst resin catalysts could play crucial roles in acid catalyzed esterification,[35] four different types of Amberlyst resin catalysts were tested for the DCPD esterification with LA. The properties of the Amberlyst resins such as the acidity, the surface area, and the moisture content are summarized in Table S1, ESI.† Fig. 2a shows the results of the DCPD esterification with LA over the Amberlyst resin catalysts. Amberlyst-15 (hydrogen form) showed the highest yield of DCPD-LA ester (80%). However, the wet resin catalysts showed lower DCPD conversion (Fig. 2a). For example, in the case of Amberlyst-15 (wet form), which only differs in the water content compared to Amberlyst-15 (hydrogen form) (Table S1, ESI†), much lower DCPD conversion and DCPD-LA ester selectivity were observed (57% and 28% for C_{DCPD} and $S_{DCPD-LA}$, respectively). Due to the presence of water in their macroreticular pore system, the rate of esterification can be slowed down, and even the reverse reaction of the esterification, that is, the hydrolysis of the ester to the alcohol, can be promoted.[36] Meanwhile, among the wet resin catalysts, the higher acid site concentration leads to higher DCPD conversion and DCPD-LA selectivity, suggesting the importance of the acid amount for the esterification (Fig. 2a, Table S1, ESI††).

Interestingly, the formation of cydecanol (DCPD-OH) was observed during the esterification of DCPD with LA (Fig. 2b and c). During the esterification, DCPD-OH formation was mostly observed for the wet resin catalysts, but Amberlyst-15 (hydrogen form) also produced DCPD-OH. For example, Fig. 2d illustrates the time course of the esterification between DCPD and LA with Amberlyst-15 (hydrogen form). DCPD was consumed completely after 2 h, while the DCPD-LA ester was formed gradually to the maximum yield throughout 4 h of reaction. The formation of DCPD-OH reached maximum at 40 min (18% yield) and then gradually decreased, suggesting that the esterification between DCPD and LA proceeds *via* a reaction intermediate, that is, DCPD-OH. The kinetic analysis also suggested that the esterification between DCPD and LA is a consecutive reaction of two elementary steps, that is, the hydration of DCPD to form DCPD-OH, followed by the esterification of DCPD-OH and LA (Fig. S3 and S4, ESI†). We deliberately synthesized DCPD-OH (~95% purity after column chromatography) and performed the esterification of DCPD-OH with LA under identical reaction conditions to DCPD (Fig. 2e). The consumption of DCPD-OH and the simultaneous formation of DCPD-LA ester were observed, which clearly suggests that DCPD-OH acts as an intermediate during the esterification between DCPD and LA.

Based on the results, we propose the reaction mechanism for the esterification of DCPD and carboxylic acids (Fig. 3). In the presence of cation-exchange resin, which acts as a proton donor, the addition of a proton to the DCPD molecule can form a dicyclopentadienyl carbonium ion as a transition state, especially in the double bond in the norbornene ring of DCPD.[37] The carbonium ion simultaneously reacts with the lone pair of the oxygen atom of the H_2O to form DCPD-OH. Then, the esterification between DCPD-OH and the protonated carboxylic

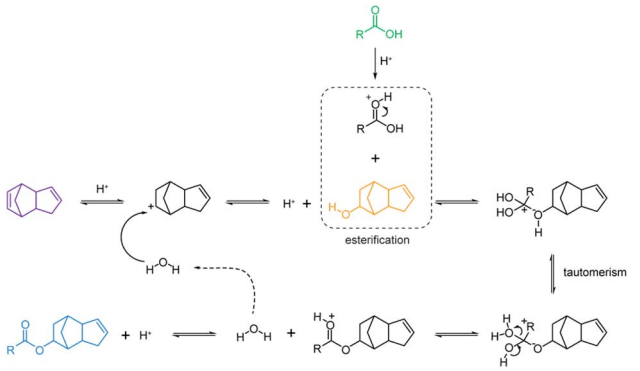


Fig. 3 Proposed mechanism of the esterification between DCPD and carboxylic acids.

acid takes place according to the Fischer esterification reaction.[38–40] Under acidic conditions, the addition of a proton to the carbonyl oxygen can lead to a more reactive electrophile carbon. Subsequently, the nucleophilic substitution of the alcohol (1,2-addition by the alcohol) on the electrophile carbon gives a tetrahedral intermediate and one of these hydroxyl groups is eliminated as a water molecule after a proton shift (tautomerism). The protonated ester would be subsequently deprotonated, yielding the ester of DCPD and acids.

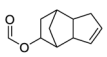
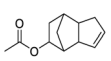
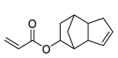
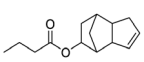
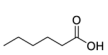
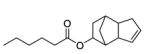
It is interesting to note how water is supplied for the hydration step during the esterification. For example, Amberlyst-15 (hydrogen form) only contains less than 1.6% of moisture, which can only give 12% yield of DCPD-OH theoretically, and the amount of water is not sufficient for the observed 80% yield of the DCPD-LA ester (Fig. 2a). We thus believe that the water formed during the esterification is again utilized for the hydration of DCPD. Moreover, we expect the effective removal of water to form DCPD-OH in the system drives the chemical equilibrium towards the completion of the esterification reaction.[41]

To compare the reactivity of other acids which can be potentially derived from biomass, we further carried out the esterification of DCPD with different carboxylic acids, such as formic acid,[42] acetic acid,[43] acrylic acid,[44] butyric acid[45] and hexanoic acid[46] (Table 1). The formation of each ester was verified by GC-MS (Fig. S5–S9†) and ^{1}H NMR (Fig. S10–S14†). DCPD was fully consumed with shorter chain carboxylic acids (formic, acetic and acrylic acids), while the DCPD conversion was lower for butyric and hexanoic acids. We expect two contributions to the observed lower product yield for longer chain carboxylic acids. The inductive effect could result in an increase in the electron-releasing ability of the acid with a longer alkyl chain.[47] Although the inductive effect facilitates the protonation of the carbonyl oxygen, it also lowers the electrophilicity of the carbonyl carbon, resulting in a more energy-hindered nucleophilic attack by the alcohol[36] (DCPD-OH in our case). Furthermore, the steric hindrance can also increase with the molecular size, inducing electronic repulsion between nonbonded atoms of reacting molecules. This repulsive hindrance lowers electron density in the intermolecular region and disturbs bonding interactions. Therefore, as the alkyl chain in the carboxylic acid increases, its steric effect can increase as well.[36]

To compare with other resins, we tested Dowex 50WX8 for the reaction under identical conditions. However, the conversion was low. We think that the different structures (gel-type Dowex and macroreticular-type Amberlyst) and the surface textures after coming into contact with water (or other solvents) give different reactivities.[48] Kuzminska *et al.* suggested using get-type resins in a polar medium in order to induce their swelling and to provide good accessibility to active sites.[48] For our system, we used a non-polar solvent (toluene). The test indicates that not all resins will give the same reactivity for this reaction.

To test the possible leaching of sulfonic acid groups, we carried out a leaching test using Amberlyst-15. After 20 min of reaction, the catalyst was removed quickly by filtration, and the reaction was continued in the absence of the catalyst. No further conversion of DCPD was observed after removal of the catalyst from the reaction mixture (at 20 min), indicating that the active species of the resin catalyst were not leached out (Fig. S15†). We believe that leaching is avoided because the reaction temperature (80 °C) is much lower than the maximum operating temperature of Amberlyst-15 (120 °C) and the reaction is performed in the non-polar solvent, toluene.

Table 1 Synthesis of various DCPD esters using carboxylic acids that can be derived from biomass[a]

Acid	Chemical structure of acid	Product structure	DCPD conversion (%)	Product yield (%)
Formic acid			>99	86
Acetic acid			>99	78
Acrylic acid			>99	62
Butyric acid			97	35
Hexanoic acid			72	25

[a] Reaction conditions: 80 °C, mole ratio (DCPD : carboxylic acid) = 1 : 1, catalyst loading = 20 g-dry resin L^{-1}.

We noted a small increase in the mass of the catalyst after the reaction, suggesting that the pores may contain the reaction solvent, reactants or products. Therefore, the reactivation and regeneration of the catalyst are necessary before the recycling test. For this, we carefully washed the resin catalyst with minimum amounts of water, ethanol and acetone and dried at 112 °C. A couple of recycling tests were then carried out using this procedure which gave similar results, indicating the restoration of the activity.

In summary, we report the direct esterification of DCPD with acids that can be derived from biomass, using Amberlyst resin catalysts. During the esterification, we found that DCPD-OH was formed as a key reaction intermediate and the proposed reaction mechanism includes the acid catalyzed formation of a dicyclopentadienyl carbonium ion to form DCPD-OH by the lone pair of the oxygen atom of H_2O. Finally, conventional Fischer esterification between DCPD-OH and the protonated carboxylic acids can yield DCPD-esters.

Author contributions

N. R. S. conceptualized the work, acquired the funding and administered the project. S. C. performed preliminary experiments to validate the concept. M. D. conducted catalytic tests and formal analysis. H. W. conducted additional experiments for the revision. M. D. wrote the original draft, and S. C. and N. R. S. reviewed and edited the draft. All the authors discussed the experiments, analysed the data and contributed to the writing of the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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