Catalyzed Dioctyl Phthalate Formation Using a Nanostructured Solid Acid Resin

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Introduction

Polymeric solid acid resins have become increasingly important as catalysts in many industrial reactions because they offer several advantages over homogeneous (i.e., liquid) acids, such as easier product separation and facile catalyst recovery.[1] Solid catalysts also permit processing options that are not possible with homogeneous acid catalysts (e.g., fixed bed reactors), and they can even result in improved reaction selectivities compared to homogeneous catalysts.[2] Currently, there are two main types of commercially available solid acid resins: (1) cross-linked polystyrene sulfonic acid resins (e.g., Amberlyst^{TM}, DOWEX), and (2) perfluorinated sulfonic acid resins (e.g., Nafion®). Both of these types of resin materials are amorphous in nature and are either macroporous, as in the case of the polystyrene sulfonic acid resins, or relatively nonporous, as in the case of the perfluorinated sulfonic acid resins. These catalysts have been applied in a number of important industrial organic reactions, such as etherification of olefins, dehydration of alcohols, alkylation of phenol substrates, condensation reactions, olefin hydrations, and esterifications.[2]

One particular acid-catalyzed process of importance is the formation of dioctyl phthalate (DOP) from phthalic anhydride (PA) and two equivalents of 2-ethyl-1-hexanol in a sequential diesterification process (Figure 1). DOP is widely used as an all-purpose plasticizer for polymers, such as poly(vinyl chloride), and the annual market of DOP in the U.S. is approximately $350 million (386,000 short tons).[3] The first part of the process is the reaction of PA with one equivalent of the alcohol to give the mono-octyl phthalate (MOP) ester intermediate in an exothermic, autocatalytic, ring-opening addition reaction. The first reaction is fast and normally carried out at about 130-150°C without the need for an acid catalyst. The MOP intermediate subsequently reacts with another equivalent of the alcohol to form the DOP product. The water formed as a by-product in this step is usually removed to force the reaction to the diester.[4,5] This second esterification reaction is slow and considered the rate-determining step for the overall DOP process. Acid catalysts (e.g., mineral acids and Lewis acids) are used to lower the activation energy in the second step. Organic titanates are often used as acid catalysts in industrial DOP synthesis, but the residual titanates are very difficult to remove completely from the final product.[6] Consequently, there has been a great deal of interest in using a solid acid resin, such as Amberlyst^{TM}, to catalyze the DOP process because solid acid resins have been used to catalyze a related reaction, the esterification of maleic anhydride with ethanol to produce diethyl maleate.[7] Unfortunately, no detailed information has been reported in the literature on this topic.

Our research group recently developed a nanostructured sulfonic acid resin (resin **1**) based on lyotropic liquid crystals (LLCs) that is chemically similar to Amberlyst^{TM}-15 but has a very uniform porous nanostructure analogous to MCM-41 mesoporous sieves (Figure 2).[8] Preliminary studies with this nano-

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structured acid resin in an esterification test reaction involving benzyl alcohol and 1-hexanoic acid showed that it affords purer ester product with higher yield than commercial Amberlyst$^{\text{TM}}$-15 at 75°C.[8] In this report, we describe the use of nanostructured resin **1** as a heterogeneous acid catalyst for DOP formation at 95°C and compare its activity and selectivity to amorphous Amberlyst$^{\text{TM}}$-15.

Experimental

Amberlyst$^{\text{TM}}$-15 was purchased from Fluka, Inc. Amberlyst$^{\text{TM}}$-15 is a cross-linked polystyrene resin in the form of beads with an acid site concentration of ≥4.7 equiv./kg, a surface area of 53 m^2/g, an average pore diameter of 30 nm, and a dry to phenol swelling of 38%.[9] LLC resin **1** was prepared as described in the literature.[8] The structure of resin **1** was confirmed by powder X-ray diffraction and chemical analysis, as described previously.[8] The solid acid resins were powdered and sieved to a consistent particle size range of 38-53 μm. MOP was obtained from TCI America and used as received. All the other reagents and solvents were purchased from Aldrich, and were further dried before use. The esterification test reactions were carried out in an argon-filled 25 mL Schlenk flask with a stoichiometric ratio of MOP and 2-ethyl-1-hexanol, or PA and 2-ethyl-1-hexanol, in dry *p*-xylene. The initial concentrations of PA and MOP in the reactions were 0.1 M. The solid acid catalyst loading was 5 mole % relative to the reactants, based on the number of accessible H$^+$ sites in the resins as determined previously by aqueous titration.[8] To confirm that MOP and resin **1** have a similar number of accessible acid sites to MOP in *p*-xylene, additional titration experiments were performed in *p*-xylene with an organic amine base (ethyl-1-piperidinepropionate) that is similar in size to MOP. The data from these experiments showed that during the course of the 30 h catalysis test reactions, Amberlyst$^{\text{TM}}$-15 and resin **1** both have similar acid site accessibility in *p*-xylene to organic molecules comparable in size to MOP (up to ca. 60-70% of the theoretical acid sites).

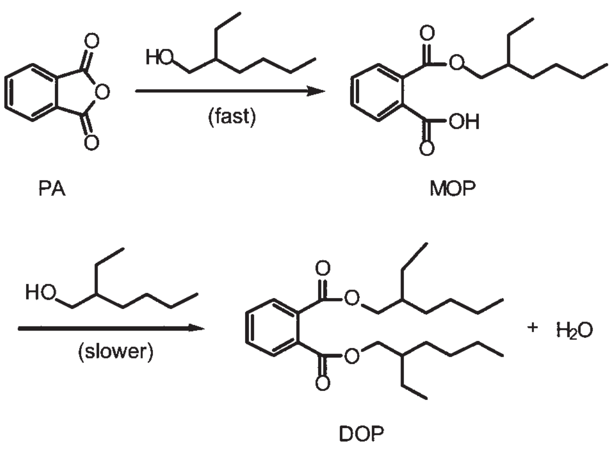

Figure 1. Reaction scheme for the formation of DOP from PA and 2-ethyl-1-hexanol.

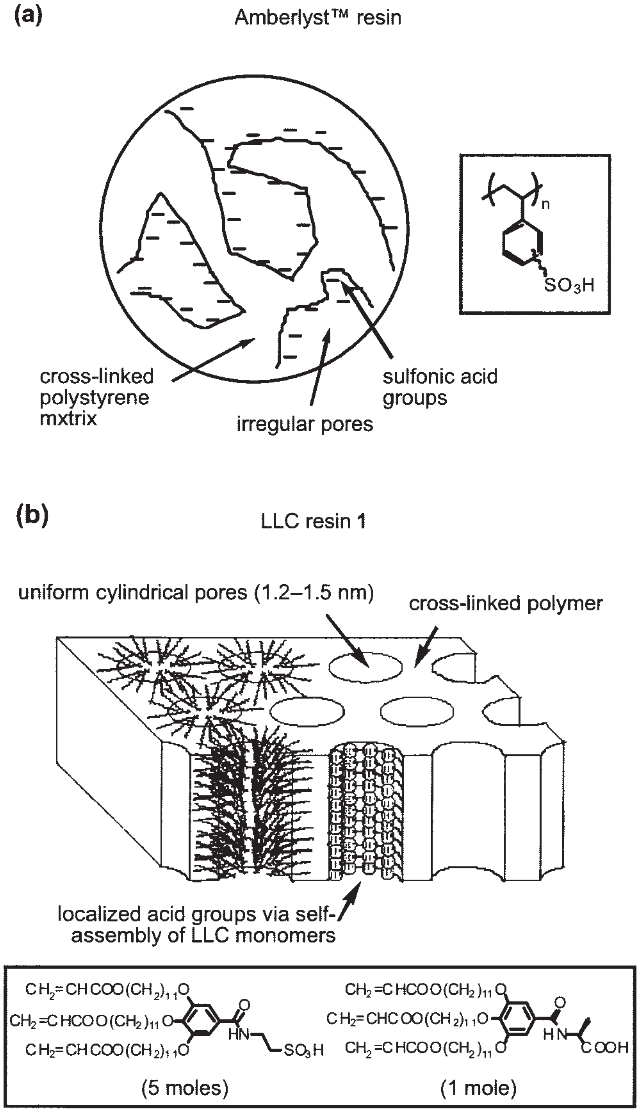

Figure 2. Representations of the structure of (a) Amberlyst$^{\text{TM}}$ and (b) LLC resin 1.

For the esterification reactions, a certain amount of *n*-dodecane was added to each reaction mixture to serve as an internal standard for quantitative GC analysis. The reactions were initiated by heating with stirring in a 95°C temperature-regulated oil bath. The progress of the reactions was monitored by withdrawing samples of the supernatant under Ar flush via syringe at intermittent time intervals. The samples were diluted 20 times in *N,O*–bis(trimethylsilyl)acetamide (a stabilizer for MOP during GC analysis as recommended by TCI America), and then analyzed using a Hewlett-Packard HP5890 gas chromatograph (GC) equipped with a flame ionization detector and an Ultra 2 capillary column. The GC was set with an injector temperature of 200°C and a temperature profile as follows: initial temperature: 180°C (0 min); temperature ramp rate: 6°C/min; final temperature: 300°C (15 min). The GC response factors for the individual reactants and products were determined via GC analysis of standard solutions of the compounds containing *n*-dodecane internal standard.

Results

Due to the nature of its preparation, Amberlyst$^{\text{TM}}$ resin has a very non-uniform structure and morphology. For example, it

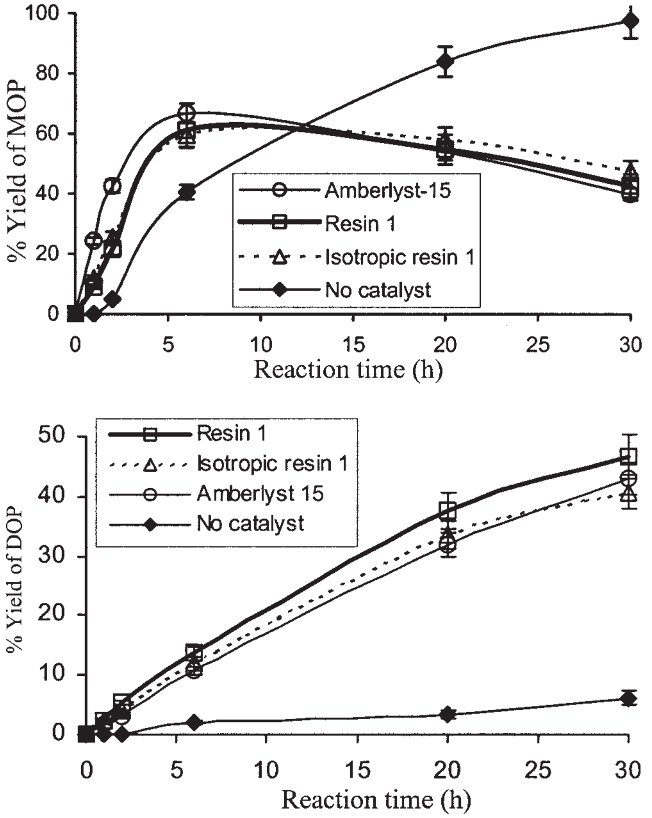

Figure 3. (a) MOP yield vs. time plots and (b) DOP yield vs. time plots for reactions containing one equivalent of PA and two equivalents of 2-ethyl-1-hexanol in *p*-xylene at 95°C.

The data points presented are the mean values over three independent runs, and the error bars represent the standard deviation in the values.

is possible to introduce more than one sulfonic acid group onto one aromatic ring in the polystyrene chain, which could increase the local acidity.[10] The pores in Amberlyst$^{\text{TM}}$ are also not uniformly distributed in size or proximity, and this non-uniform morphology can also lead to large variations in local acidity, leading to multiple reaction pathways and products during acid catalysis. In contrast, LLC resin **1** is a very structurally uniform cross-linked copolymer of two acidic LLC monomers that forms by amphiphilic self-assembly. One monomer containing a sulfonic acid head group acts as the strong acid catalyst, while the other monomer containing a weakly acidic amino acid group directs the self-assembly process to form the inverted hexagonal phase shown in Figure 2.[11] This self-assembly process localizes the acid groups exclusively inside monodisperse cylindrical nanochannels that are ca. 1.2-1.5 nm in diameter, and this structure is fixed upon in situ cross-linking (Figure 2). Consequently, resin **1** should provide a more uniform local acid microenvironment and open cavity structure than Amberlyst$^{\text{TM}}$ resins, which could lead to faster reaction and/or purer product.

In order to test this supposition, laboratory-scale DOP formation test reactions were conducted by reacting one equivalent of PA with two equivalents of 2-ethyl-1-hexanol in the absence of acid catalyst and with added Amberlyst$^{\text{TM}}$-15 and resin **1**. These test reactions were performed in *p*-xylene solution at 95°C, conditions that allow for facile reaction sampling and simultaneous determination of MOP and DOP formation by GC. The yield profiles of MOP and DOP vs. time for these test reactions are shown in Figures 3a and 3b, respectively. Without acid catalyst, MOP initially forms very slowly under these reaction conditions. However, once some MOP is generated, it quickly accumulates over a short period of time, which is consistent with an autocatalytic reaction for the first esterification process. Unfortunately, very little DOP is formed in the absence of added acid catalyst (Figure 3b), which is consistent with the second esterification reaction being much slower (i.e., having a significantly higher activation energy) than the first esterification event. With 5 mole % added Amberlyst$^{\text{TM}}$-15 or resin **1** as catalyst, it takes very little time for MOP to form in appreciable amounts in the test reactions. The initial rate of MOP formation with Amberlyst$^{\text{TM}}$-15 (i.e., the initial slope of the profile) is higher than that with resin **1**. However, as can be seen in Figure 3b, resin **1** gives a slightly higher overall total DOP yield and initial DOP formation rate for the entire reaction up to 30 h. These results suggest that Amberlyst$^{\text{TM}}$-15 is a better catalyst for the first esterification process that forms MOP, but resin **1** is a better catalyst for the rate-determining second esterification process that converts MOP to DOP, since it affords an overall faster rate of DOP production.

In order to test this idea, a second series of experiments were performed that focused only on the effect of the acid resins on the slower, second esterification process that forms DOP from the MOP intermediate. Using commercially available MOP and one equivalent of 2-ethyl-1-hexanol as the starting materials in these reactions (0.1 M each in dry *p*-xylene), it was found that very little DOP is produced from MOP in the absence of acid catalyst (7% conversion after 30 h at 95°C), and the initial rate was 0.021 h^{-1}, as determined by the integral analysis method for an irreversible bimolecular-type second-order reaction.[12] Specifically, this was determined by evaluating the slope of the inverse of the MOP concentration vs. time, where the slope of the straight line regression equals the rate constant.[12] The yield data are shown in Figure 4. For this analysis, the assumption is made that the reverse reaction is not significant at the start of the reaction. When Amberlyst$^{\text{TM}}$-15 or resin **1** are present, the rate is greatly increased. However, resin

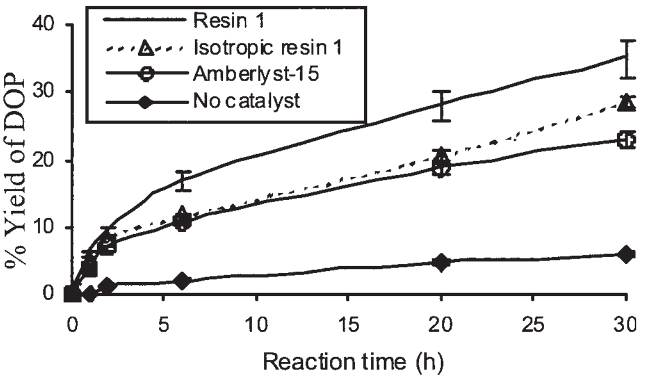

Figure 4. DOP yield vs. time plots for the reaction of one equivalent of MOP with one equivalent of 2-ethyl-1-hexanol in *p*-xylene at 95°C.

1 was found to give approximately 35-40% higher yield of DOP from MOP compared to Amberlyst^{TM}-15 after the first 5 h of the reaction (Figure 4). The average initial rate[12] observed for resin **1** is 0.519 h^{-1} while that for Amberlyst^{TM}-15 is 0.376 h^{-1}, corresponding to a 38% increase in rate. These results confirm that resin **1** is a much better catalyst for the rate-determining second esterification reaction, resulting in faster overall DOP production, even though Amberlyst^{TM}-15 is a better catalyst for initial MOP formation.

Control experiments were also performed using an isotropic analog of resin **1** (that is, same composition but without the nanostructure) in order to ascertain the role of catalyst nanostructure on the catalytic enhancement observed for **1** in the overall DOP formation process and in the second esterification step. When the isotropic sample of **1** was tested in the full DOP reaction, it gave a lower overall yield of DOP compared to ordered resin **1** (Figure 3b), but it showed very little difference compared to resin **1** in the MOP-forming step (Figure 3a). These results are consistent with the nanostructured LLC resin having a very prominent enhancement effect on the second esterification process but very little effect on the first esterification reaction. When the isotropic analog of resin **1** was tested in the MOP to DOP conversion reaction, it afforded a significantly lower yield and a lower initial rate of DOP production from MOP than nanostructured resin **1** (0.470 h^{-1} vs. 0.519 h^{-1}) (Figure 4). Thus, the nanostructured catalyst accounted for a 10% increase in initial rate compared to an identical but non-ordered catalyst. The isotropic analog of **1** was almost identical to amorphous Amberlyst^{TM}-15 in its ability to catalyze this slower esterification process. Prior temperature-programmed desorption studies indicated that Amberlyst^{TM}-15 and resin **1** have similar effective acidities.[8] Consequently, the higher overall reaction rate and product yield observed for resin **1** in the second esterification reaction cannot be attributed to acidity differences between the two acid resins. It is apparent that a major part of the higher catalytic activity exhibited by LLC resin **1** in the second part of the DOP formation process is due to its regular nanostructure and the more uniform local acid microenvironment it presents.

Lastly, control experiments were performed to confirm that the reactivity differences observed between resin **1** and Amberlyst^{TM}-15 were not the result of mass transfer limitations. Amberlyst^{TM}-15 was found to generate a lower reaction rate than the nanostructured LLC acid resin **1** when catalyst particle sizes of 38-53 μm were used in both cases. To confirm that mass transfer limitations were not the cause of these rate differences, additional experiments were performed with larger 54-108 μm Amberlyst^{TM}-15 particles. The rate of reaction of one equivalent of PA with two equivalents of 2-ethyl-1-hexanol was statistically identical for the smaller (38-53 μm) and larger (54-108 μm) particle sizes, indicating that mass transfer limitations are not in effect in our test reactions.

Conclusions

Two heterogeneous sulfonic acid resins, Amberlyst^{TM}-15 and LLC resin **1**, were tested in the acid-catalyzed synthesis of DOP from PA and 2-ethyl-1-hexanol. It was found that nanostructured resin **1** gave a slightly higher overall yield of DOP for this diesterification reaction than amorphous Amberlyst-15. Experiments focusing on the slower second esterification process revealed that resin **1** is a much better catalyst for the formation of DOP from MOP than Amberlyst^{TM}-15, resulting in a 38% increase in the rate of DOP production from MOP. Control experiments using isotropic samples of resin **1** indicated that the nanostructure of resin **1** plays a significant role in its higher catalytic activity in the second step. Optimizing the reaction conditions and the catalyst composition for this reaction is currently underway. We are also in the process of designing new LLC monomers with different acidic head groups, so that we can tailor the resin acidities to other reactions.

Acknowledgments

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