Rasta Resin-TBD as a Reusable Catalyst for Transesterification Reactions

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Abstract: Rasta resin-TBD has been synthesized and used to catalyze a wide range of transesterification reactions, including biodiesel synthesis and ring-opening polymerizations. It was found to be a more efficient heterogeneous catalyst than a related polystyrene-based analogue based on the Merrifield resin architecture involving divinylbenzene cross-linking. In the reactions studied rasta resin-TBD was separated from the desired products simply by filtration, and it could be regenerated and reused numerous times without significant loss of catalytic activity.

Key words: polymer-supported catalyst, transesterification, rasta resin, organocatalysis, biodiesel

In recent years biodiesel has been studied extensively as a renewable energy source due to the rising costs and unsustainability of fossil-based fuels.[1] Common components of biodiesel are fatty acid methyl esters (FAME), which are usually produced by catalytic transesterification reactions of vegetable oils with methanol.[2] Although FAME production has been industrialized, research is still being conducted with the aim of obtaining pure product more efficiently and economically. In this regard, solid-supported catalysts have received attention as these can be removed from reaction mixtures simply by filtration. While numerous solid-supported acid and base catalysts have been reported, most of these heterogeneous materials suffer from slow reaction rates or catalyst leaching.[3] Thus, the development of highly efficient, easily separable and reusable solid-supported catalysts for transesterification of vegetable oils under mild conditions is still of great interest.

We have been studying the use of various organic polymers to facilitate organic chemistry[4] and have reported the use of heterogeneous JandaJel as a core for the rasta resin (RR) architecture (Figure 1) in the synthesis of RR-supported reagents and catalysts.[5] In the search for a suitable RR-bound transesterification catalyst for biodiesel synthesis, we were interested in examining a supported 1,5,7-triazabicyclo[4.4.0]dec-5-ene (RR-TBD, **1**) catalyst.[6] Numerous examples of polymer-supported TBD have been reported, and these materials have been studied as recyclable catalysts.[7] In fact, the synthesis and catalytic activity of a RR-TBD catalyst, **2**, have been described by Vaccaro and co-workers (Scheme 1).[8] Polymer **2** was syn-

thesized by treating commercially available RR-chloride **3** with TBD (**4**), and was demonstrated to be a reusable catalyst in processes such as Michael addition reactions of dimethylmalonate (**5**) or nitroalkanes **6** to α,β-unsaturated ketones **7** to afford adducts **8** in good yields using solvent-free conditions (Scheme 2, a). Additionally ring-opening reactions of phenyl glycidyl ether (**9**) were also catalyzed by **2** using pro-nucleophiles **10** to form products **11** in high yields (Scheme 2, b).
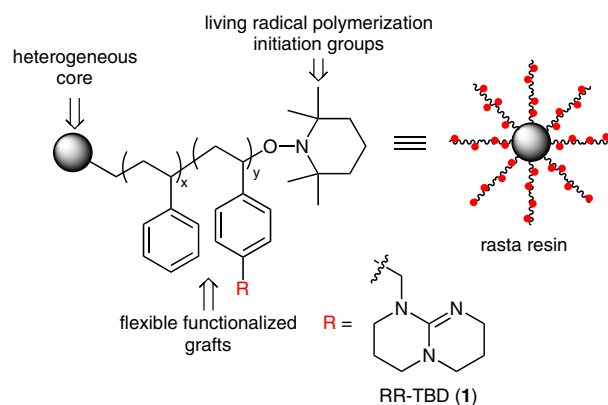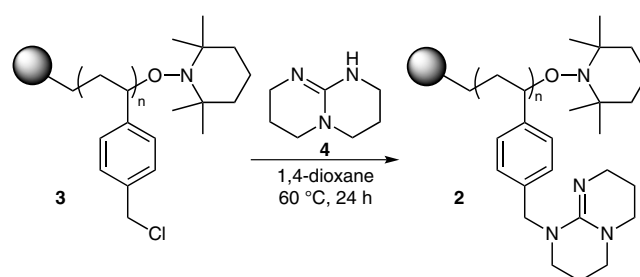

**Figure 1** Rasta resin-TBD (RR-TBD, **1**)

Scheme 1 Synthesis of **2**

The synthesis of catalyst **1** is outlined in Scheme 3. RR-benzyl chloride (**12**) was synthesized by radical copolymerization of heterogeneous JandaJel core **13**, styrene (**14**), and 4-vinylbenzyl chloride (**15**).[9] It should be noted that **14** was incorporated in the synthesis of **1** in order to increase the flexibility of the polymeric grafts. Since the TBD groups are larger than the styrene groups to which they are attached in **1**, it seems safe to assume that a fully or highly loaded functionalized polymer would be rather inflexible due to steric crowding. On the other hand, in-
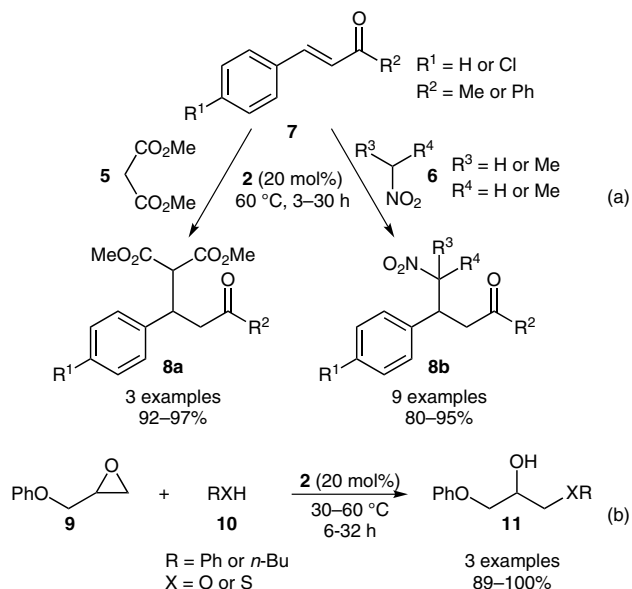
**Scheme 2** Michael addition and ring-opening reactions catalyzed by **2**

cluding a lot of **14** to space out the TBD groups would lead to low loading, and therefore require a lot of catalyst polymer to be used compared to the amount of substrate. Thus, a compromise was made and we used a 5:1 ratio of **14**:**15** to prepare our catalyst, since this ratio worked well in our previous studies of related polymers.[5] Resin **12** was then treated with deprotonated TBD (**16**) in THF to afford **1** in nearly quantitative yield. The loading of **1** was determined by elemental analysis to be 1.25 mmol/g.
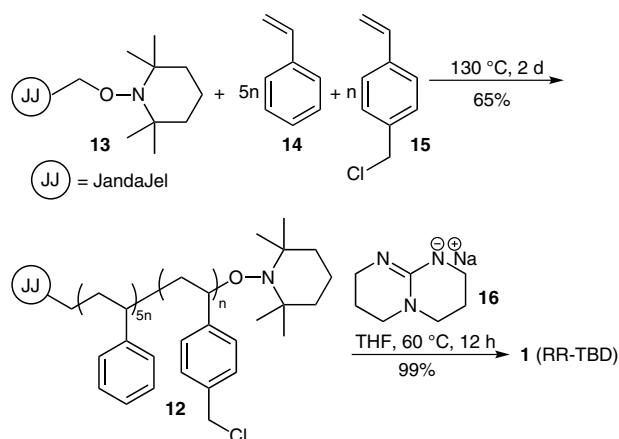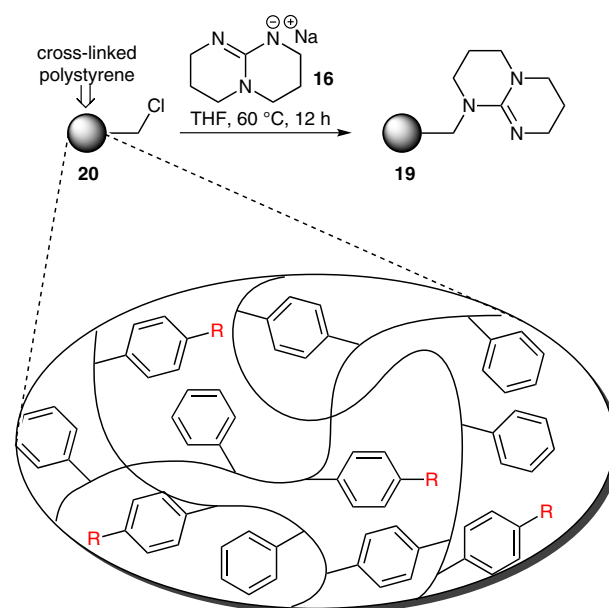

Scheme 3 Synthesis of **1**

We next set out to examine the performance of **1** as a catalyst for the transesterification of sunflower oil **17** with MeOH as shown in Scheme 4. In this reaction, **17** was vigorously stirred with MeOH and **1** at room temperature for 24 hours.[10] The reaction mixture was then filtered, and the filtrate was analyzed by ^{1}H NMR spectroscopy to determine the conversion of **17** into **18**. Using these conditions, **1** successfully catalyzed the reaction to afford **18** quantitatively. The reaction was also carried out on a 5-gram

scale with **18** purified by filtration and aqueous washing, and isolated in 96% yield.
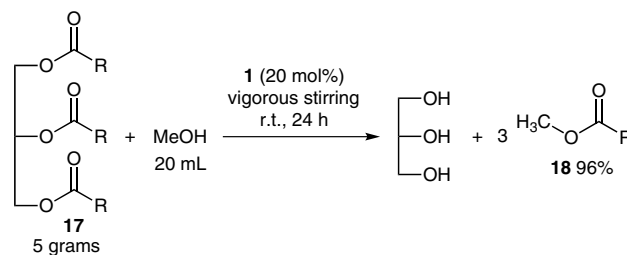
Scheme 4 Transesterification of **17** catalyzed by **1**

For comparison, a macroporous cross-linked polystyrene-supported TBD (PS-TBD, **19**) was synthesized from a commercially available Merrifield resin (**20**) and **16** using conditions similar to those used for the synthesis of **1** (Scheme 5). Unlike the TBD groups located on the flexible grafts of **1**, the TBD groups of **19** are located in the relatively rigid heterogeneous core, which makes them less accessible to substrates. Thus, when **19** was used to catalyze the reaction of **17** with MeOH, only less than 5% conversion to **18** was observed (Table 1, Run 0). This result illustrates the advantage of using rasta resin as a catalyst support over traditionally used Merrifield resin.

Scheme 5 Synthesis of **20**

To examine the recoverability and reusability of **1**, it was collected by filtration after the reaction was complete and reused directly for another reaction cycle. Unfortunately only 90% conversion was observed in the second run, and we presume this was due to a trace amount of free carboxylic acids present in the sunflower oil that deactivated the catalyst. Therefore, recovered **1** was regenerated by suspending it in a mixture of aqueous sodium hydroxide in methanol for 24 hours and then reused in transesterifica-

tion reactions of **17**. Gratifyingly, regenerated **1** showed identical catalytic activity compared to that of freshly prepared **1**. Using this recycling strategy, **1** could be effectively used in at least eight runs (Table 1).[11] The slight decrease in catalytic activity observed after run four was attributed to the loss of small quantities of **1** during each of the recycling processes.

Table 1 Transesterification of **17**

Run	Catalyst recovery (%)	Conversion (%)[a]
0	99	<5[b]
1	99	99
2	99	99
3	98	99
4	99	98
5	98	96
6	99	95
7	97	94
8	98	93

[a] Reaction conditions: **17** (0.50 g), MeOH (2.0 mL), and **1** (20 mol%) vigorously stirred at r.t. for 24 h.
[b] Compound **19** was used as the catalyst.

After the success of the using **1** as a recyclable catalyst for FAME synthesis, we explored its versatility in other transesterification reactions. For example, since TBD and its derivatives have shown great catalytic activity in ring-opening polymerization processes,[12] we envisioned that **1** could serve as a catalyst in these reactions too. As shown in Scheme 6, a catalytic amount of **1** was able to polymerize lactide at room temperature using butan-1-ol as the initiator to give polylactide **21**. In addition, **1** together with thiourea **22** also polymerized δ-valerolactone to give poly(δ-valerolactone) **23** with essentially complete conversion. The recovered **1** from these two polymerizations was found to have slightly decreased catalytic activity, as only 90% conversion was observed in subsequent reaction cycles. This is again probably due to a trace amount of hydrolyzed lactide or δ-valerolactone present in the reaction mixture, which neutralized the catalyst.

We next studied the catalytic activity of **1** in transesterification reactions involving various alcohols **24** and vinyl acetate (**25**).[13] The reaction mixtures were heated in THF at 60 °C for 24 hours, and we envisioned that after completion of the reactions **1** could be removed by filtration while the solvent, acetaldehyde by-product, and excess **25** in the filtrate could be removed under reduced pressure to easily afford pure desired products **26**. As shown in Table 2, benzyl alcohol, phenol, and primary alcohols (entries 1–4) were successfully converted into the corresponding acetates in high yields using the standard conditions.[14] In these cases, the products obtained after filtration and con-
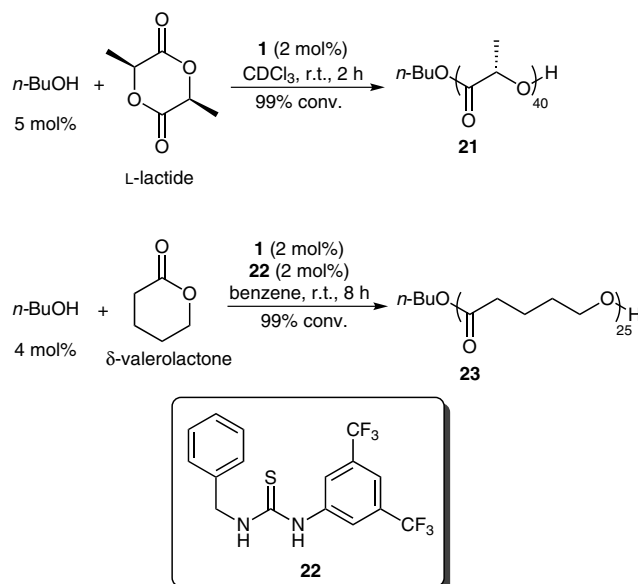
Scheme 6 Ring-opening polymerizations catalyzed by **1**

centration were essentially pure according to ^{1}H NMR and ^{13}C NMR spectroscopy, and recovered **1** showed essentially the same catalytic activity (entry 1). Interestingly, a reaction of **24a** with **25** catalyzed by **19** was incomplete under identical reaction conditions, with the desired product isolated in 60% yield (entry 1). When secondary and tertiary alcohols were used as substrates the reactions proceeded sluggishly or not at all, probably due to steric hindrance of the alcohols (entries 5–8).

Transesterification reactions of dimethyl carbonate (**27**) with alcohols have been reported as a safer method to produce organic carbonates compared to processes involving phosgene,[15] and recently, TBD was reported to be an effective catalyst in reactions for synthesizing unsymmetrical carbonates and polycarbonates.[16] Therefore, we were interested in determining if **1** can serve as a catalyst in these reactions as well. As shown in Scheme 7, *n*-butyl methyl carbonate (**28**) was successfully synthesized from **27** and butan-1-ol with 10 mol% **1** as the catalyst.
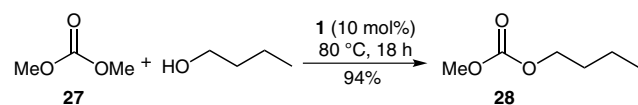
Scheme 7 Synthesis of **28** catalyzed by **1**

In conclusion, we have applied the rasta resin architecture as a support for a recyclable, heterogeneous TBD catalyst (**1**), and used it to catalyze transesterification reactions to afford FAME **18**, polylactide **21**, poly(δ-valerolactone) **23**, acetates **26**, and carbonate **28**. Catalyst **1** could be regenerated and reused at least seven times in transesterification reactions of **17** without significant loss of activity. Direct comparison of **1** with Merrifield resin analogue **19** indicated that the rasta resin architecture allowed **1** to be more efficient as a catalyst. This is probably due to the po-

Table 2 Reactions of Various Alcohols with Vinyl Acetate[a]

Entry	Substrate	Product	Isolated yield (%)
1	**24a**	**26a**	98 (97)[b] (60)[c]
2	**24b**	**26b**	97
3	**24c**	**26c**	91
4	**24d**	**26d**	98
5	**24e**	**26e**	55
6	**24f**	**26f**	17
7	**24g**	**26g**	0
8	**24h**	**26h**	0

[a] Reaction conditions: alcohol **24** (1.0 mmol), **25** (1.2 mmol), **1** (0.10 mmol), and THF (1.0 mL) heated at 60 ºC for 24 h.
[b] Result using recovered **1**.
[c] Result using **19** (0.10 mmol) as the catalyst.

sitioning of the TBD groups of **1** on flexible grafts that are more accessible to dissolved substrate molecules than the TBD groups of **19**, which are located in the interior of the heterogeneous polymer.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(11) **General Procedure for the Transesterification of 17**: Sunflower oil **17** (0.500 g, 0.59 mmol), MeOH (2.0 mL), and **1** (0.095 g, 0.24 mmol) were added to a 7-mL vial equipped

with a magnetic stirrer. The reaction mixture was vigorously stirred at r.t. (20–22 °C) for 24 h. The reaction mixture was then poured onto a Büchner funnel and the filtrate was concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy. The integrated area of methoxy groups in the FAME **18** (3.67 ppm, singlet) and that of the methylene protons adjacent to the carbonyl groups present in the triglycerides (2.29 ppm, triplet) of **17** were used to calculate conversion. The beads collected on Büchner funnel were washed with hexanes (10 mL) and then dried under vacuum. Recovered **1** (0.095 g), MeOH (2 mL), and aq 0.5 M NaOH (2 mL) were added to a 7-mL vial equipped with a magnetic stirrer. The mixture was stirred slowly for 24 h and then poured onto a Büchner funnel. The beads collected on funnel were washed with H_2O (10 mL), MeOH (10 mL), THF (5 mL), Et_2O (5 mL), hexanes (5 mL) and then dried to constant weight under vacuum.

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(14) **General Procedure for the Reaction of Various Alcohols with Vinyl Acetate**: Alcohol **24** (1.0 mmol), vinyl acetate (**25**; 0.103 g, 1.20 mmol), **1** (0.080 g, 0.10 mmol), and THF (1.0 mL) were added to a 3-mL vial. The vial was immersed in an oil bath regulated at 60 °C for 16 h. The reaction mixture was then cooled to r.t. and filtered. The beads collected on funnel were further washed with THF (5 mL) and the combined filtrate was concentrated under reduced pressure. The residue of concentrated filtrate afforded essentially pure products as analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy for the substrates in Table 2 (entries 1–4). In cases when the reactions were incomplete under the given conditions, the products were purified using silica gel column chromatography with hexane as the eluent.

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