Highly selective pressure-dependent (transfer) hydrogenative depolymerization of polybutylene succinate

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Highly selective pressure-dependent (transfer) hydrogenative depolymerization of polybutylene succinate

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Ru-MACHO®-BH is an effective catalyst for controlled depolymerization of polybutylene succinate. Under low pressure hydrogen the catalyst produces *gamma*-butyrolactone *via* a novel transfer hydrogenation wherein dehydrogenation and hydrogenation deconstruct the polymer chain. Simply increasing the hydrogen pressure selectively generates 1,4-butanediol.

Chemical recycling pathways have increased dramatically in the last decade as the environmental impact of plastic waste becomes increasingly apparent.[1] Currently, most recycled post-consumer plastic waste undergoes incineration or a mechanical recycling process, the latter of which degrades the mechanical properties of the recovered material, thus limiting its utility.[2] Chemical recycling processes are a promising approach because the resulting small molecules can be purified prior to repolymerization to prepare new materials of equal quality or for use in other applications (e.g. solvents, chemical building blocks, etc.). Chemical recycling to monomer can create a closed loop in which the materials can be repeatedly reused and represents an idealized circular system.[3] However, with roughly two-thirds of post-consumer plastics currently being landfilled or escaping to the environment, chemical recycling that produces value-added products will also be needed to make better use of plastic waste streams. Such a pathway carries significant environmental benefits because portions of the inherent value of the plastic could be recovered for other applications by treating waste plastic as a chemical feedstock. Reductive depolymerization to produce value-added products from plastic waste is one such route that has experienced recent rapid growth.[4]

Hydrogen gas has been the primary reductant used for reductive depolymerizations of polyesters, polycarbonates, or polyamides, predominantly producing diols and diamines, accordingly.[5] While these typically require forcing conditions or costly catalysts, they have very high atom economy. Marks and coworkers have also recently developed polyester hydrogenation systems leading to dicarboxylic acid and alkane[6a]
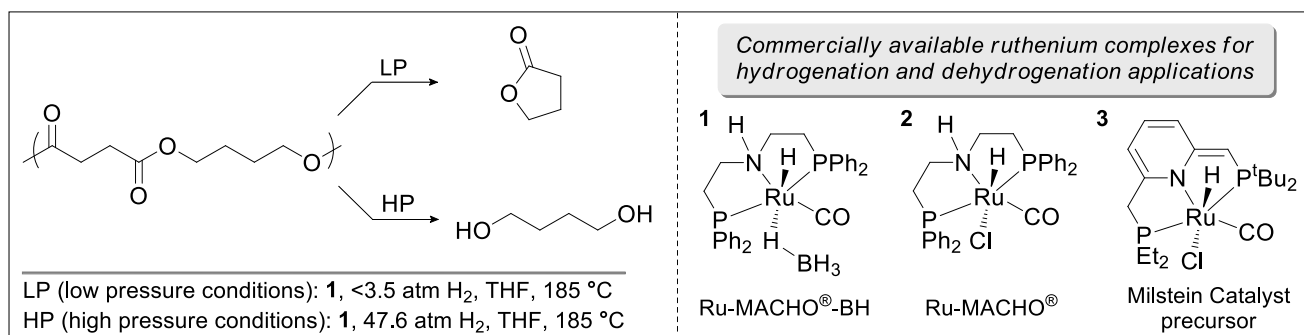
or alkene[6b] products. de Vries and coworkers demonstrated transfer hydrogenation of a low molecular weight aliphatic polyester using ethanol as the hydrogen source.[7] Other approaches use hydrosilanes under comparatively mild conditions.[8] More recently, elegant techniques for the depolymerization of polyesters and polycarbonates using hydroboranes as the reductant have been reported as well.[9] In most of these polyester systems, diols, or the corresponding silylated or borylated products, are obtained. The ability to create a wider variety of chemical products from plastic waste would be advantageous for diverting greater amounts of materials from entering landfills after only one use.

Polybutylene succinate (PBS) is a commercially available biodegradable material, which can also be biorenewable, with the potential to be used in a wide range of applications.[10] Compared to polyethylene terephthalate, relatively few studies have investigated routes for chemical recycling of PBS.[1b] Although PBS is biodegradable, converting it to useful molecules for other applications would carry environmental benefits. To date, PBS depolymerization efforts include hydrogenation to tetrahydrofuran,[11] transesterification,[12] hydrolysis,[13] melt processing,[14] or enzymatic degradation.[15] Recent heterogeneous catalytic hydrogenation[16] and reductive depolymerization with pinacolborane[9a,b] yielded the corresponding diols and diboranes. Hydrogenation of PBS using ruthenium catalysts would be expected to produce solely 1,4-butanediol (BDO) based on the products obtained from previous polyester hydrogenations.[5,16] However, BDO is also readily dehydrogenated to *gamma*-butyrolactone (GBL) in the presence of ruthenium catalysts, presumably due to stability of the five-membered lactone product.[17] Furthermore, while GBL formation from BDO is endothermic, the Gibbs free energy of the reaction becomes favorable at elevated temperatures.[18] We therefore hypothesized that a ruthenium complex capable of catalyzing hydrogenation and dehydrogenation reactions at elevated temperatures could selectively generate either GBL or BDO from PBS through fine tuning of reaction conditions

LP (low pressure conditions): **1**, <3.5 atm H$_2$, THF, 185 °C
HP (high pressure conditions): **1**, 47.6 atm H$_2$, THF, 185 °C

Commercially available ruthenium complexes for hydrogenation and dehydrogenation applications

Ru-MACHO®-BH   Ru-MACHO®   Milstein Catalyst precursor

Scheme 1. Reaction sequence for selective depolymerization of PBS to lactone or diol using complexes **1**-**3**.

(Scheme 1). Both GBL and BDO are industrially important molecules,[19] therefore routes to produce these from PBS would enable a new chemical recycling pathway for this polyester. Ruthenium-pincer complexes seemed an ideal choice because they are able to perform dehydrogenation reactions even while under an overpressure of hydrogen gas,[20] and have demonstrated remarkable versatility in a variety of catalytic transformations since their inception.[21]

We initially screened commercially available ruthenium complexes (**1**-**3**, Scheme 1) using conditions developed in our previous work with aliphatic polyesters.[5k] Under 13.6 atm initial H$_2$ pressure, heating **1** with PBS to 150 °C for 24 h led to complete depolymerization producing a 25:75 mixture of GBL:BDO as determined by GC, whereas **2** and **3** activated with *tert*-butoxide contained residual polymeric solids in the reaction mixture, indicating an incomplete reaction (Table S1 and Fig. S1). We therefore worked to optimize conditions for **1** to selectively generate GBL or BDO, which had the added advantage of not needing KO^{t}Bu to activate the catalysts.

To select for GBL, we anticipated that a minimum amount of hydrogen would be needed to initiate the depolymerization. Table 1 displays screening conditions for targeting GBL. A molar ratio between carbonyl:Ru of 100:1, 160 °C, 3.4 atm initial H$_2$ pressure, and 1 mL tetrahydrofuran (THF) produced 93% GBL (Table 1, entry 1). Increasing the temperature to 185 °C yielded 99.0% GBL in 94% isolated yield following simple rotary evaporation of the solution found outside of the glass sleeve in the reactor (Table 1, entry 2). Decreasing catalyst loading to 200:1 or 150:1 carbonyl:Ru led to a small reduction in GBL selectivity but a significant drop in percent yield (Table 1, entries 3 and 4). Reducing the H$_2$ pressure below 3.4 atm maintained high GBL selectivity, however, percent yield greatly decreased below 1.4 atm (Table 1, entries 5-9). An initial pressure of 0 atm gauge H$_2$ yielded only 51% in 20 h, but extending the reaction time to 48 h produced GBL in 99.5% selectivity with 96% isolated yield. Interestingly, the hydrogen pressure following the reaction was slightly lower than the initial pressure; we attribute this to the formation of GBL, which is a liquid that can dissolve hydrogen gas, whereas the starting PBS solid cannot. Depolymerization to GBL does not consume hydrogen, but rather may involve a transfer hydrogenation within the polymer system. Presumably, when the BDO portion of the polymer repeat unit cyclizes to GBL, the hydrogen generated from that process can transfer to the succinate

portion of the repeat unit, enabling two equivalents of GBL to form per PBS repeat unit.

To better understand this process, we performed the reaction sealed under nitrogen in the absence of hydrogen. Surprisingly, **1** was still active for depolymerizing PBS to GBL, albeit at a significantly slower rate, as only 18% yield of GBL was obtained after 72 h. Increasing the catalyst loading and extending reaction time to 6 days generated GBL exclusively in 70% isolated yield (Table 1, entry 10). No reaction occurs in the absence of **1**, even when PBS is exposed to hydrogen gas (Table 1, entry 11). Because depolymerization occurs even in the absence of hydrogen gas, **1** is likely catalyzing a transfer hydrogenation. Given that the presence of hydrogen greatly increases the rate of reaction (Table 1, entries 2 vs 5 vs 10), we suspect that molecular hydrogen is involved, but we cannot rule out that the absence or presence of hydrogen gas alters the mechanism. Further studies will be needed to fully elucidate this mechanism.

Table 1. Optimization conditions for targeting GBL from depolymerization of PBS^a

Entry	Cat., (mol%)	T (°C)	P (atm)	Solvent	% GBL^b	% yield^c
1	**1**, 1.0	160	3.4	THF	93.0	91
2	**1**, 1.0	185	3.4	THF	99.0	94
3	**1**, 0.5	185	3.4	THF	90.1	40
4	**1**, 0.75	185	3.4	THF	94.8	45
5^d	**1**, 1.0	185	0.0	THF	99.5	96
6	**1**, 1.0	185	0.7	THF	98.0	59
7	**1**, 1.0	185	1.4	THF	99.0	95
8	**1**, 1.0	185	2.0	THF	98.0	88
9	**1**, 1.0	185	2.7	THF	98.0	95
10^e	**1**, 2.0	185	n.a.	THF	>99.9	70
11^f	n.a.	185	3.4	THF	0	0
12	**1**, 1.0	185	3.4	me-THF	97.1	93
13^g	**1**, 1.0	185	3.4	THF	95.7	93
14^h	**1**, 1.0	185	3.4	n.a.	99.0	77
15	**2**, 1.0	185	3.4	THF	97.1	83
16	**3**, 1.0	185	3.4	THF	85.5	51

^{a} Reaction conditions: 1.0 g PBS, Ru is mol % relative to carbonyl, 1.0 mL solvent, 20 h, P = gauge pressure. ^{b} Determined by ratio between GBL and BDO/2 signals in quantitative ^{13}C NMR. ^{c} Determined by isolated mass incorporating the ratio between GBL and BDO in the product. ^{d} 48 h reaction time. ^{e} Reaction under 0 atm gauge nitrogen. ^{f} No catalyst. ^{g} 0.5 mL THF. ^{h} No solvent

We selected tetrahydrofuran (THF) as the primary reaction solvent for screening purposes because both BDO and GBL are miscible with THF, whereas the BDO phase separates from anisole or toluene, complicating characterizations. Furthermore, the low boiling point of THF facilitates product
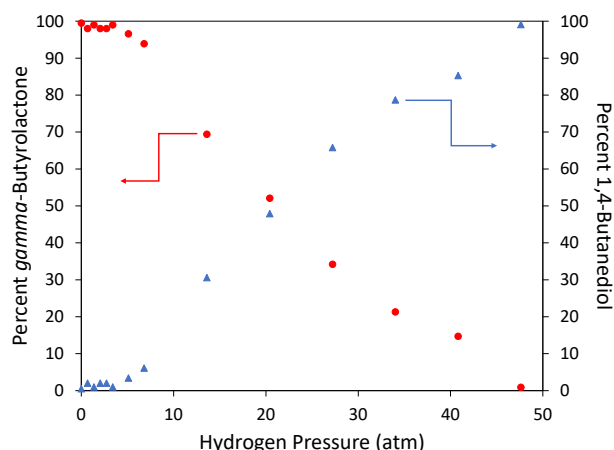
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Figure. 1 Effect of hydrogen pressure on GBL (•) and BDO (▲) selectivities observed in PBS depolymerization reactions.

isolation because both GBL and BDO have significantly higher boiling points than THF. We also found that methyl-tetrahydrofuran (me-THF), a greener reaction solvent,[22] worked very well, generating GBL in 97.1% selectivity and 93% yield (Table 1, entry 12). The reaction even proceeds in the absence of solvent to produce GBL in 99.0% selectivity and 77% isolated yield (Table 1, entry 14). Applying low pressure conditions with catalysts **2** and **3** led to GBL in lower selectivity and yield (Table 1, entries 15-16).

Increasing hydrogen pressure steadily increased selectivity for BDO (Table S2, entries 17-24). Figure 1 shows the pressure dependence on percent selectivity of GBL and BDO. An initial pressure of 47.6 atm H_2 furnished BDO in 99.0% selectivity and 95% yield in as little as one hour. Interestingly, the reaction proceeds significantly faster at high pressure than low pressure, as indicated by a drop in pressure of 4.0 atm that occurs between 10-15 minutes during heating. At high pressures, me-THF was also found to be an effective solvent for hydrogenation to BDO (98.8% selectivity, 91% yield).

After demonstrating that **1** selectively depolymerized PBS to GBL or BDO, we explored whether the large entropic gain generated by a depolymerization could overcome the enthalpic barrier of forming lactone rings with more ring strain than GBL. Thus, we sought to target *epsilon*-caprolactone (ECL) or *delta*-valerolactone (DVL) by applying low pressure conditions for GBL selectivity to the corresponding polyesters (Scheme 2). The polymers were synthesized from the appropriate diols and

dicarboxylic acids *via* step-growth polymerization catalyzed by *para*-toluenesulfonic acid (*p*-TsOH), and Dean-Stark reflux was employed to remove the water generated by the polycondensation reaction. As our initial PBS depolymerizations were performed on commercially produced PBS, we also synthesized PBS following this procedure to ensure that any incomplete depolymerizations were not caused by impurities or byproducts stemming from our polycondensation.

When exposed to the conditions for GBL selectivity, the PBS analogue prepared from succinic acid and BDO produced GBL as the primary product (Fig. S28), indicating that the simple step-growth procedure used does not impede the depolymerization reaction. Unfortunately, we were not able to obtain DVL from poly(1,5-pentylene glutarate) or ECL from poly(1,6-hexylene adipate) when they were exposed to 3.4 atm hydrogen. Instead, a mixture of oligomers were the likely products (Figs. S29 and S30). We also found that when the reactors were charged with either the corresponding diol or the lactone and pressured to 3.4 atm hydrogen, the product mixtures matched those stemming from the polymers (Figs. S28-S30), indicating that even if DVL or ECL form in a depolymerization reaction, they can undergo ring opening polymerization (ROP) under the reaction conditions used. However, the carbonyl region indicates that it is not a clean ROP, presumably because of regiochemical shifts stemming from ruthenium catalyzed dehydrogenative polymerization to produce a mixture of head to head, tail to tail, and tail to head ester repeat units as previously observed.[17a] We are currently working to alter reaction conditions to select for the corresponding lactones for these polyesters. Increasing the H_2 pressure to 47.6 atm furnished the expected diols for all three synthesized polyesters (Figs S31-S33).

This system is a novel approach for cleanly generating two separate products from PBS by simply adjusting the H_2 pressure. To the best of our knowledge, this is the first example of a chemical depolymerization wherein transfer hydrogenation occurs within the polymer. We are currently working to understand this mechanism. Further optimization and application of this methodology to other polyesters with new catalysts is worth pursuing to better increase the utility of waste polymers as a feedstock to generate a wider variety of useful small molecules. We are continuing to alter conditions to target other lactones such as GVL and ECL.
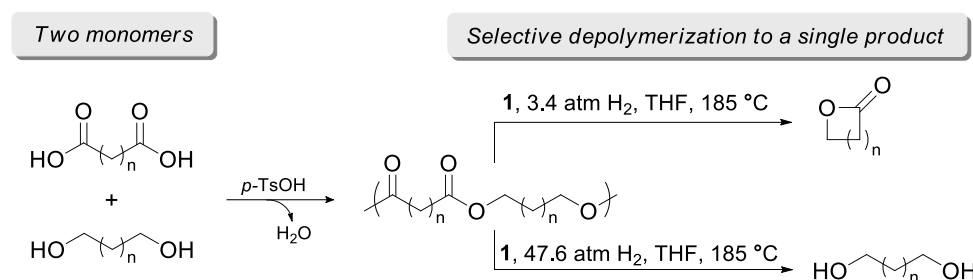
Scheme 2. General scheme for potentially broadening hydrogenative depolymerization to additional aliphatic polyesters derived from diacid and diols.

Conflicts of interest

There are no conflicts to declare.

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