

Article

Hydrogenative Depolymerization of Polyesters Catalyzed by a PN^3 -Ruthenium Complex Using Both H_2 and EtOH as Hydrogen Sources

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ABSTRACT: Selective hydrogenative depolymerization of polyesters to diols is regarded as a promising strategy for plastics upcycling. However, many catalysts documented in literature still involve harsh reaction conditions, such as high temperature and high H_2 pressure. In this work, we present a PN^3 -ruthenium complex catalyzed polyesters upcycling into various highly value-added diols under mild reaction conditions using H_2 as a hydrogen source. It is worth noting that PLA depolymerizes into 1,2-propanediol under 1 MPa hydrogen pressure at ambient temperature within 2 h; the conditions are much milder than those of previous reports. Aromatic polyester PET degradation needs harsher reaction conditions (80 °C, 4 MPa, 3 h). The different reaction conditions enable direct separation of the degradation products of PLA and PET mixture via sequential depolymerization, as well as mixing them with polyolefins (PE, PP, PS). More strikingly, this catalyst is also effective for the catalytic hydrogenation of polyesters in the presence of ethanol to afford various diols, avoiding the use of harsh reaction conditions and an expensive autoclave.

Keywords: Polyesters; Hydrogenative depolymerization; Upcycling; PN^3 -Ru complex; Diols



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1. Introduction

Plastic has become an indispensable type of polymer material in human life due to its advantages, such as easy manufacturing, low cost, good barrier properties, chemical and temperature resistance [1]. The wide use of plastic products has led to their annual production proliferating, as well as the accumulation of a large amount of plastic waste, which poses a deadly threat to life systems [2–4]. Over the past 50 years, more than 8 billion tons of plastic waste have accumulated, and it is expected that 12 billion tons by 2050 [1,5]. Plastics degrade very slowly in the natural environment conditions, and the released microplastic fragments and toxic chemicals can cause a threat to public health [6–8]. Therefore, it is urgent to develop effective methods to address the negative impact of plastic pollution on human society and the natural environment [9].

Polyester is an important member of the plastic family. Compared with polyolefins, their backbones contain the labile ester linkages, which provide the possibility for degradation and recycling [10,11]. Some polyesters can even degrade in natural environments [3]. However, the production of biodegradable polyester is very low, and the value of the waste polyesters cannot be restored by this method [12–15]. Therefore, developing green and efficient methods to achieve the controlled recycling of waste polyesters has gradually become a hot topic in both academia and industry [9,16,17].

Traditional methods for polyester degradation, including hydrolysis [18], glycolysis [19,20], alcoholysis [21] and aminolysis [22] generally require the usage of a great deal of solvents, degradation agents, and high reaction pressure. The separation of degradation products from the oligomeric byproducts is often very laborious [23,24]. In recent years,

hydrogenative depolymerization has emerged as an excellent alternative method for waste polyesters degradation to produce diols, which cannot be obtained through traditional recycling processes [16,17]. Hydrogenative depolymerization using hydrogen gas as a reducing agent is an atom-economic, green, and sustainable chemical conversion pathway, as H_2 can be obtained from renewable resources and does not produce stoichiometric waste during the depolymerization process [16]. The typical catalysts for polyester hydrogenative depolymerization are summarized in Figure 1.

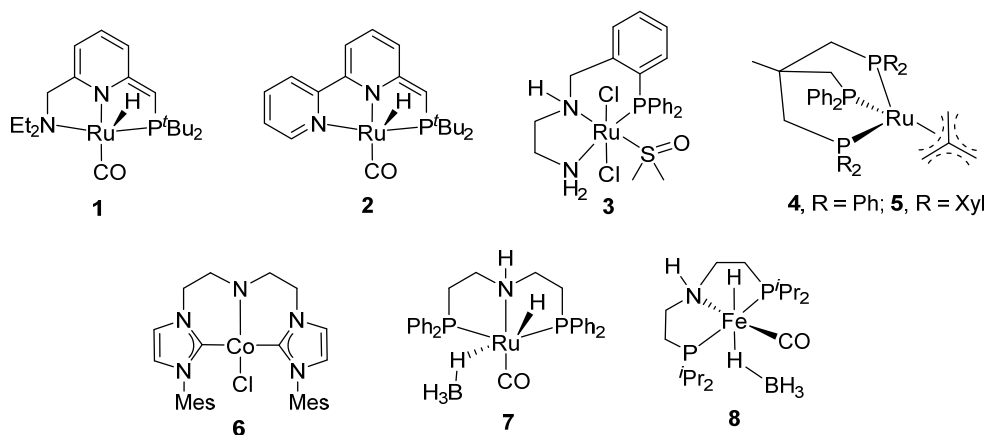


Figure 1. Typical catalysts for polyester hydrogenative depolymerization.

In Robertson and coworkers' seminal report, they used the versatile Milstein catalysts **1** and **2** to implement the hydrogenative depolymerization of polyesters [25]. Poly(1,10-decanediol) [26] obtained from the dehydrogenative polymerization of 1,10-decanediol was successfully reduced to the corresponding diol in 80% isolated yield under 13.6 atm of hydrogen pressure at 120 °C in the presence of **1**. Unfortunately, **1** was unable to depolymerize PLA and fully depolymerize PET even under the elevated temperature (160 °C) and H_2 pressure (54.4 atm) conditions. However, PET, ϵ -CL and polycarbonates could be completely depolymerized into various diols using **2** as a catalyst, probably due to the less sterically bulky dipyrindyl backbone [16]. Interestingly, the hydrogenative depolymerization of poly(*R*-3-hydroxybutyric acid) and poly(3-hydroxypropionic acid) catalyzed by **2** produced only butyric acid and propionic acid. Recently, they used the commercially available Ru-MACHO-BH **7** to catalyze polybutylene succinate depolymerization, and both γ -butyrolactone and 1,4-butanediol were obtained through tuning the hydrogen pressure [27].

Clarke et al. demonstrated the hydrogenation of PET flakes in the presence of **3** and KO^tBu under 50 bar of H_2 and 110 °C, affording 1,4-benzenedimethanol (BDM) and ethylene glycol (EG) in 53% isolated yield [28]. In 2018, the Klankermayer group investigated the hydrogenative depolymerization of several types of waste polyesters into the corresponding diols catalyzed by **4** and **5** under the activation of bis(trifluoromethanesulfonyl)imide (HNTf₂). **4**/HNTf₂ can catalyze PLA and PCL samples to give 1,2-propanediol and 1,6-hexanediol in 99% yields under 10 MPa of H_2 at 140 °C for 16 h. But this system was low efficient for PET degradation, probably arising from the formation of ether byproducts. Replacing the phenyl group in **4** with 3,5-dimethylphenyl, the catalytic counterpart **5**/HNTf₂ was competent for PET and PBT depolymerization into the relevant diols [29].

In 2019, Liu et al. reported on the hydrogenative depolymerization of PCL. By *in-situ* mixing of complex **6** and KO^tBu, the yield of 1,6-hexanediol was as high as 97% after 16 h of reaction at 30 bar H_2 and 100 °C. This is the first example of a base metal non-phosphine complex catalyzing the hydrogenation of polyester to diols, and the authors have conducted in-depth research on the hydrogenation mechanism [30].

Recently, Xie and coworkers developed a novel transesterification/hydrogenation relay strategy and designed a new class of quinaldine-based ruthenium-pincer catalysts with high compatibility with protic solvents, which enables highly efficient hydrogenative polyesters depolymerization in CH₃OH. With this protocol, a broad range of commercially available or post-consumer PET sources, and other types of polyester plastics were degraded in excellent yields under very mild conditions [31].

Although the study on dehydrogenative depolymerization of polyesters using H_2 as the hydrogen source has made significant progress, it usually involves the use of an expensive high-pressure reactor. To avoid this, de Vries and coworkers reported on the use of the Fe-ⁱPrⁿMACHO-BH complex **8** in the base-free transfer hydrogenation of polyesters into diols with EtOH as a hydrogen source. Under the optimal conditions, 1,6-hexanediol was obtained in 87% isolated

yield through depolymerizing Dynacol 7360. This study opened the possibility to recycle polyesters by deconstructing them to their monomers using a completely new, easy, and green strategy [32].

Research in our group is predominantly concerned with waste polyester recycling and preparation of new polymeric materials by utilizing a series of phosphorus-nitrogen pincer complexes [33–35]. Herein, we demonstrate an air- and moisture-stable ruthenium PN^3 -pincer complex, which exhibits excellent activity for the hydrogenation of esters to alcohols [36], catalyzing polyesters upcycling to respective diols under mild conditions by using both H_2 and EtOH as hydrogen sources.

2. Materials and Methods

All experiments (if not mentioned otherwise) with metal complexes were carried out under an atmosphere of dry nitrogen in a glovebox or using standard Schlenk techniques. All glassware was rigorously dried. All solvents were distilled from sodium benzophenone ketyl before use. All other chemicals were commercially available and used as received. $\text{PN}^3\text{-Ru}$ complex was prepared according to the literature procedure [36]. NMR spectra were recorded at 400 MHz (^1H) and 101 MHz (^{13}C) using a Bruker Avance-400 NMR spectrometer. ^1H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents (7.26 ppm, CDCl_3 ; DMSO- d_6 , 2.50 ppm), and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents (CDCl_3 , 77.16 ppm; DMSO- d_6 , 39.52 ppm). The data of quantitative ^{13}C NMR spectra were acquired with more than 50 mg of depolymerization products solubilized in 0.5 mL of deuterated solvent. All spectra were measured at 25 °C using a 90° pulse (zgig), inverse-gated decoupling, at least 2000 scans, and a delay of 8 s for samples run without relaxation reagent.

2.1. Typical Procedure for Hydrogenative Depolymerization of Polyester with H_2

In the glovebox, $\text{PN}^3\text{-Ru}$ complex (24.0 mg, 0.05 mmol), KO'Bu (44.9 mg, 0.40 mmol), and solvent (2.0 mL) were added to a glass vial, and the mixture was stirred for 5 min at room temperature to activate the catalyst precursor. Then the mixture was transferred to a high-pressure stainless steel autoclave, equipped with a stir bar, and subsequently polyester (2.0 mmol, referring to its repetition unit) was added. Once the autoclave was sealed and pressurized with hydrogen, the reaction mixture was stirred for several hours at the set temperature. Afterwards, the reaction was cooled in an ice bath, and the pressure was carefully released. The crude reaction mixture was analyzed by ^1H and quantitative ^{13}C NMR spectroscopy.

2.2. Hydrogenative Depolymerization of the Mixture of PLA and PET

In the glovebox, $\text{PN}^3\text{-Ru}$ complex (24.0 mg, 0.05 mmol), KO'Bu (44.9 mg, 0.40 mmol), and solvent (2.0 mL) were added to a glass vial, and the mixture was stirred for 5 min at room temperature to activate the catalyst precursor. Then the mixture was transferred to a high-pressure stainless steel autoclave, equipped with a stir bar, and subsequently the mixture of PLA and PET (1.0 mmol, 1.0 mmol, respectively, referring to its repetition unit) was added. The autoclave was sealed and pressurized with hydrogen (1 MPa), and the reaction mixture was stirred for 2 h at room temperature. Afterwards, the reaction was cooled in an ice bath, and the pressure was carefully released. The crude reaction mixture was filtered, washed with a little toluene, and the filtrate was analyzed by ^1H and quantitative ^{13}C NMR spectroscopy. Then the residual solid, and another dosage of activated catalyst were added to another autoclave again, filled with 4MPa H_2 and reacted at 80 °C for 3 h. The crude reaction mixture was also analyzed by ^1H and quantitative ^{13}C NMR spectroscopy.

2.3. Typical Procedure for Hydrogenative Depolymerization of Polyester with Ethanol

In the glovebox, $\text{PN}^3\text{-Ru}$ complex (24.0 mg, 0.05 mmol), KO'Bu (44.9 mg, 0.40 mmol), polyester (2.0 mmol, referring to its repetition unit), and ethanol (2.0 mL) were added to a Schlenk flask with a stir bar, and subsequently the flask was sealed and stirred for several hours at the set temperature. Afterwards, the reaction was cooled in an ice bath. The crude reaction mixture was analyzed by ^1H and quantitative ^{13}C NMR spectroscopy.

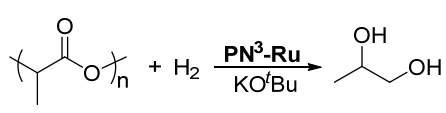
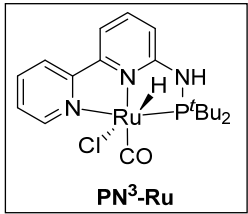
3. Results and Discussion

3.1. Hydrogenative Depolymerization of PLA

In Robertson's seminal work, polyesters' depolymerization needed a high temperature (>120 °C) and high pressure of hydrogen for a long reaction time [25]. Therefore, we started our experiment on PLA degradation in toluene under 4 MPa H_2 pressure at 120 °C using 2.5 mol% of $\text{PN}^3\text{-Ru}$ and 20 mol% KO'Bu as activator. After 48 h, the polymer was

converted to 1,2-propanediol (PG) quantitatively. As shown in Figure 2A, the signals at 3.90, 3.60 and 3.40 ppm in the ^1H NMR spectrum of the reaction mixture after the reaction completion are attributed to the methine and methylene protons of PG, and the methyl protons resonate at 1.15 ppm. Correspondingly, the three carbons of PG could be found in the quantitative ^{13}C NMR spectrum (Figure 2B) at 68.3, 67.9 and 18.9 ppm with the integral ratio of 1:1:1. No PLA residual was found in both the ^1H and ^{13}C NMR spectra. Reducing the reaction time to 6 h, PLA was still completely converted. Further optimizing the reaction conditions, we found that PG was generated in more than 99% yield under 1 MPa H_2 pressure at room temperature for 2 h. Declining the hydrogen pressure to 0.5 MPa or shortening the reaction time to 1 h led to the incomplete conversion (Figures S2 and S3). In the absence of H_2 , no product was detected. A slight decrease in the yield (96%) was observed when reducing the catalyst loading to 2.0 mol%, and the tendency further increased when reducing the catalyst loading to 1.25 mol%. Interestingly, decreasing the feeding ratio of **PN³-Ru**: KO^tBu to 1:4, the yield of PG dramatically declined to 74%, and nearly no product was observed under the ratio of 1:1. As shown in Table 1, an excess of base is needed, indicating the role of KO^tBu include not only activating the pre-catalyst, but also scavenging the trace moisture from the reaction system. This is consistent with the reports in the literature [37–39]. When KO^tBu was replaced by K_2CO_3 (Table 1, Entry 21), there was also no product observed under the ratio of **PN³-Ru**: K_2CO_3 to 1:8.

Table 1. Hydrogenative depolymerization of PLA with **PN³-Ru** complex ^a.

  PN³-Ru					
Entry	solv. (mL)	P _{H2} (MPa)	t (h)	T (°C)	Yield (%) ^b
1	Toluene	4	48	120	>99
2	Toluene	4	6	120	>99
3	Toluene	3	6	120	>99
4	Toluene	2	6	120	>99
5	Toluene	1	6	120	>99
6	Toluene	1	6	100	>99
7	Toluene	1	6	80	>99
8	Toluene	1	6	60	>99
9	Toluene	1	6	r.t.	>99
10	Toluene	1	3	r.t.	>99
11	Toluene	1	2	r.t.	>99
12	Toluene	1	1	r.t.	86
13	Toluene	0.5	2	r.t.	83
14 ^c	Toluene	-	2	r.t.	N.R. ^d
15 ^e	Toluene	1	2	r.t.	96
16 ^f	Toluene	1	2	r.t.	46
17 ^g	Toluene	1	2	r.t.	74
18 ^h	Toluene	1	2	r.t.	Trace
19 ⁱ	Toluene	1	2	r.t.	N.R.
20 ^j	Toluene	1	2	r.t.	N.R.
21 ^k	Toluene	1	2	r.t.	N.R.
22	1,4-Dioxane	1	2	r.t.	>99
23	Anisole	1	2	r.t.	>99
24	THF	1	2	r.t.	>99
25 ^l	Toluene	1	2	r.t.	>99

^a Condition: **PN³-Ru** (0.05 mmol), KO^tBu (0.40 mmol), solvent (2.0 mL), PLA (2.0 mmol, calculated on the repetition unit). **PN³-Ru** was activated with KO^tBu for 5 min before transferring to an autoclave containing PLA. ^b yield was determined by ^1H and quantitative ^{13}C NMR spectra. ^c N_2 (1 MPa). ^d N.R. stands for No Reaction. ^e $[\text{PLA}]:[\text{PN}^3\text{-Ru}]:[\text{KO}^t\text{Bu}] = 50:1:8$. ^f $[\text{PLA}]:[\text{PN}^3\text{-Ru}]:[\text{KO}^t\text{Bu}] =$

80:1:8. ^g [PLA]:[PN³-Ru]:[KO'Bu] = 40:1:4. ^h [PLA]:[PN³-Ru]:[KO'Bu] = 40:1:1. ⁱ [PLA]:[PN³-Ru]:[KO'Bu] = 40:1:0. ^j [PLA]:[PN³-Ru]:[KO'Bu] = 40:0:8. ^k KO'Bu was placed by K₂CO₃. ^l PN³-Ru (0.25 mmol), KO'Bu (2.0 mmol), solvent (8.0 mL), PLA (1.44 g, 20.0 mmol, calculated on the repetition unit), PN³-Ru activated with KO'Bu for 5 min before transferring to an autoclave containing PLA.

Moreover, the PN³-Ru complex or KO'Bu could not catalyze individually the hydrogenative depolymerization. Switching the solvent to 1,4-dioxane, anisole, and THF, the reaction proceeded smoothly in a quantitative yield. These results disclosed that the PN³-Ru catalytic system is very efficient for PLA depolymerization into PG. For a larger-scale experiment (PLA, 1.44 g), the PG was also successfully obtained in a 99% yield (Table 1, Entry 25), demonstrating that the catalytic system has a promising prospect for industrial application.

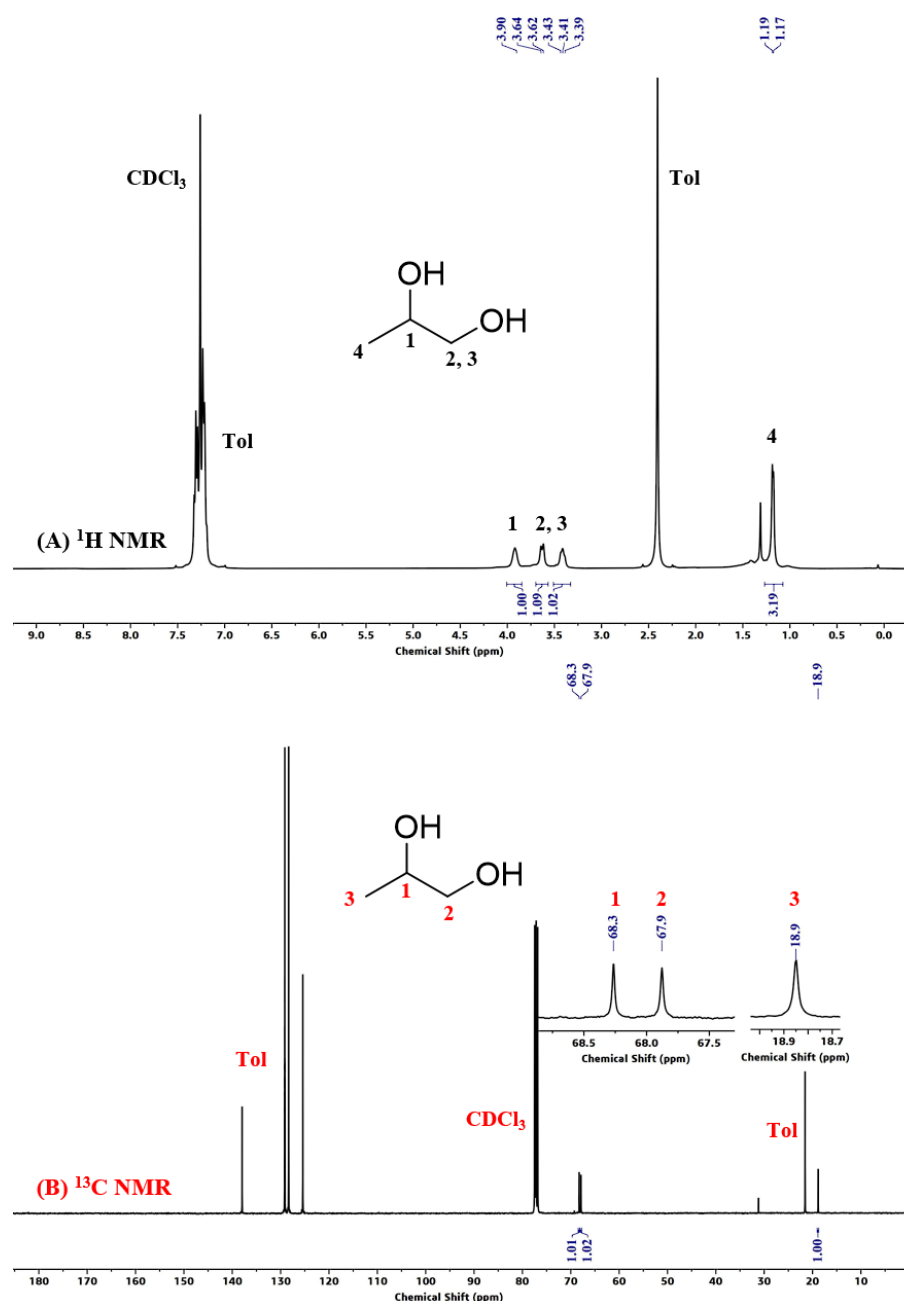


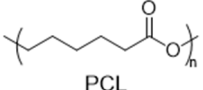
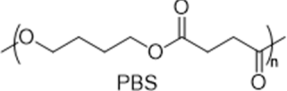
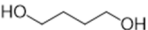
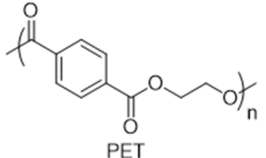
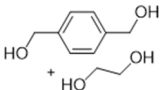
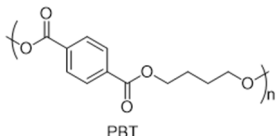
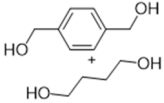
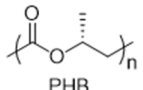
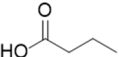
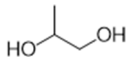
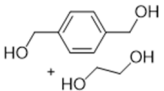
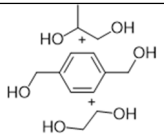
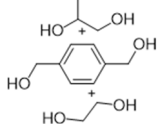
Figure 2. ¹H (A) and ¹³C (B) NMR spectra of crude reaction mixtures of PLA depolymerization (Table 1, Entry 1).

3.2. Hydrogenative Depolymerization of Other Polyesters

With this active catalytic system in hand, we set out to investigate the hydrogenative depolymerization of other polyesters. As shown in Table 2, under the optimal conditions, the aliphatic polyester PCL could be converted to 1,6-hexanediol in a little longer time (Table 2, Entry 1). However, depolymerization of PBS needed higher H₂ pressure (4 MPa), higher temperature (80 °C) and a longer reaction time (3 h) to achieve complete conversion (Table 2, Entry 2). Under the same conditions as PBS, aromatic polyesters PET and PBT could also be degraded to the respective diols in

more than 99% yields (Table 2, Entries 4 and 5). Similar to Robertson's report [25] PHB depolymerized to butyric acid in 50% yield rather than 1,3-butanediol, probably arising from the formation of a transient six-membered ring and which subsequently generates crotonyl chain-end via β -elimination. The crotonyl chain-end is relatively stable because of the conjugation effect of the carbon-carbon double bond and the ester bond, and further transforms into crotonic acid, which is finally hydrogenated into butyric acid by the ruthenium complex (Figure S33). Based on these results, we further investigated the upcycling of the post-consumer PLA and PET products. The PLA sucker and PET bottle were cut into flakes and directly subjected to the autoclaves without any further pretreatment (Figure 3). Under the identical reaction conditions, the corresponding diols were generated nearly quantitatively, indicating the tolerance of the catalyst for additives and impurities in the consumer products.

Table 2. Hydrogenative depolymerization of various polyesters with $\text{PN}^3\text{-Ru}$ complex ^a.

Entry	Polyester	P_{H_2} (MPa)	t (h)	T (°C)	Product(s)	Yield (%) ^b
1	 PCL	1	3	r.t.		>99
2	 PBS	4	3	80		>99
3	 PET	4	3	80		>99
4	 PBT	4	3	80		>99
5	 PHB	4	6	120		50
6	post-consumer PLA	1	2	r.t.		>99
7	post-consumer PET	4	3	80		95
8	PLA, PET	-	-	-		99
9	PLA, PET, PP, PS, PE	-	-	-		99

^a Condition: $\text{PN}^3\text{-Ru}$ (0.05 mmol), KO^tBu (0.40 mmol), Toluene (2.0 mL), polyesters (2.0 mmol, calculated on the repetition unit). $\text{PN}^3\text{-Ru}$ was activated with KO^tBu for 5 min before transferring to an autoclave containing polyester. ^b yield was determined by ^1H and quantitative ^{13}C NMR spectra.

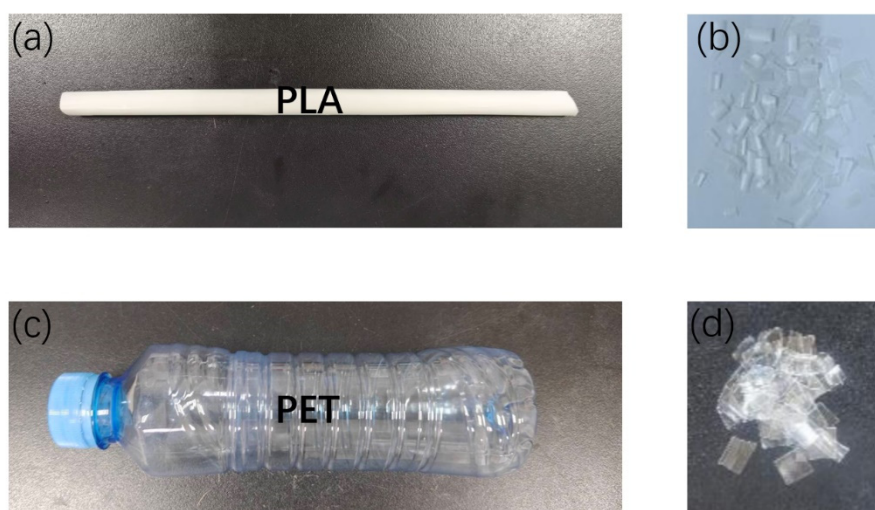


Figure 3. (a) Post-consumer PLA sulker. (b) fragment of (a). (c) Post-consumer PET bottle. (d) fragment of (c).

In view of the different degradation temperatures and H_2 pressure of PLA and PET, we then started to separate their hydrogenation products. Firstly, 1.0 mmol PET and 1.0 mmol PLA were mixed and reacted at room temperature under 1 MPa H_2 for 2 h (Table, Entry 8), and the autoclave was subsequently transferred to a glovebox. The NMR-monitoring experiment disclosed the full conversion of PLA, with marginal PET decomposition being detected under such temperature and pressure. After filtering and washing the residual solid with toluene (to remove the produced PG and the catalyst), another dosage of catalyst and toluene combined with the filter residue were added to another autoclave, again filled with 4 MPa H_2 and reacted at 80 °C for 3 h. Finally, full conversion of PET to 1,4-benzenedimethanol and ethylene glycol was achieved. To imitate the realistic post-consumer plastics which usually contain complicated compositions, we further mixed equimolar amounts of PE, PP, PS, PLA and PET and carried out the reaction using the same procedure as that of PLA and PET. High yields of PG, BDM and EG were obtained, leaving polyolefins as untouched residues, as shown in Figure 4. Consequently, our catalytic system shows great promise toward the end-of-life polyesters degradation and recycling.

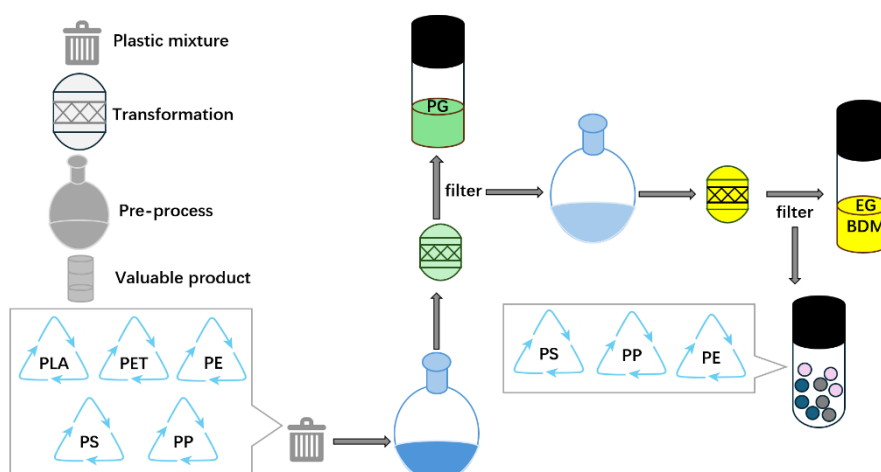


Figure 4. Degradation and separation of mixed plastics under different conditions.

3.3. Hydrogenative Depolymerization of Polyesters with Alcohol

As described above, the PN^3-Ru complex is an excellent catalyst for a variety of aliphatic and aromatic polyesters deconstruction using H_2 as a hydrogen source. Nevertheless, high pressures are usually required for catalytic hydrogenation, which results in the use of expensive autoclaves as well. Therefore, exploring safe and cost-effective alternatives to replace H_2 as a hydrogen source is crucial in polyester depolymerization. Transfer hydrogenation (TH) is an attractive alternative to classical catalytic hydrogenation, in which isopropanol is the most widely used reagent. For this reason, we first chose isopropanol as a hydrogen source to conduct the TH of PLA. As shown in the 1H NMR

spectrum of Figure S21 (Table 3, entry 1), PLA absolutely converted into isopropyl lactate catalyzed by **PN³-Ru/KO^tBu** in the presence of 20 equivalent of isopropanol at room temperature for 2 h, the signals at 4.99, 4.16, 1.33 and 1.20 ppm are attributable to the methine and methyl protons respectively, no any diol signals was observed, suggesting the catalyst is also an effective catalyst for alcoholysis of polyesters. Maintaining otherwise conditions unchanged, elevating the reaction temperature to 80 °C, a set of signals attributed to PG in the ¹H NMR spectrum of the reaction mixture could be found, with an NMR yield of 5%. In the meantime, a signal at 2.17 ppm corresponding to acetone could also be observed, meaning that the catalytic system is also an efficient catalyst for TH. Further elevating the temperature to 100 °C, the yield of 1,2-propanediol reached 43%. Switching isopropanol to ethanol and maintaining the other conditions unchanged, PG and ethyl lactate were produced in 7% and 93% yields (Table 3, Entry 4, Figure 5a), respectively, at ambient temperature, which rose to 23% and 77% at 80 °C (Table 3, Entry 5, Figure 5b). When elevating the temperature to 100 °C, all PLA was converted to PG, accompanied by ethanol oxidation to form ethyl acetate production (Table 3, Entry 6, Figure 5c). As shown in the quantitative ¹³C NMR spectrum, the peaks at 68.0, 67.6 and 18.5 ppm are attributed to the carbons of PG, and the characteristic signal of carbonyl carbon in ethyl acetate resonates at 171.6 ppm; no other byproduct was observed. These results indicated that ethanol is an ideal hydrogen source for TH of PLA in our catalytic system. For the catalytic transfer hydrogenation reaction, isopropanol usually shows better performance than ethanol. However, our catalytic system involves both transesterification and transfer hydrogenation processes. This could be confirmed by the products of isopropyl lactate, acetone, ethyl lactate and ethyl acetate. The transesterification efficiency of isopropanol is much slower than that of ethanol, thus leading to poor reaction [32,40]. When changing the solvent to methanol, the alcoholysis of PLA to afford methyl lactate in 99% yield was achieved at room temperature within 2 h, and no PG was produced under these conditions. Moreover, the yield of PG was negligible as the reaction temperature elevated to 80 °C and even 100 °C, maybe originating from the catalyst poisoning through forming a less reactive carbonyl complex [32].

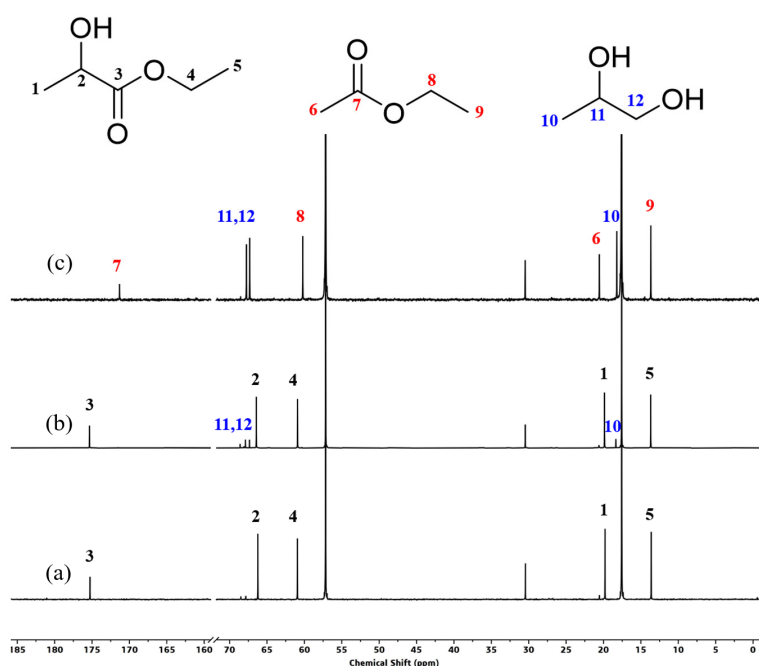


Figure 5. ¹³C NMR spectra of PLA depolymerization with EtOH: (a) (Table 3, Entry 4), (b) (Table 3, Entry 5), (c) (Table 3, Entry 6).

Table 3. Hydrogenative depolymerization of polyesters with alcohol ^a.

Entry	Polyester	Alcohol	t (h)	T(°C)	Conv. (%)	Ester(%)	Diol (%)
1	PLA	ⁱ PrOH	2	r.t.	>99	>99	0
2		ⁱ PrOH	2	80	>99	95	5
3		ⁱ PrOH	2	100	>99	57	43
4		EtOH	2	r.t.	>99	93	7
5		EtOH	2	80	>99	77	23
6		EtOH	2	100	>99	0	>99
7		MeOH	2	r.t.	>99	>99	0

8		MeOH	2	80	>99	97	3
9		MeOH	2	100	>99	88	12
10	PCL	EtOH	8	100	>99	4	96
11		EtOH	8	100	>99	60	40
12 ^b	PET	EtOH	8	100	>99	0	>99

^a Conditions: **PN³-Ru** (0.05 mmol), KO^tBu (0.40 mmol), Toluene (2.0 mL), polyester (0.5 mmol, calculated on the repetition unit), alcohol (20 equiv.), conversion and yield determined by NMR spectroscopy. ^b 96 equiv of EtOH with respect to PET.

Therefore, we chose ethanol as a hydrogen source to catalyze other commercial polyesters via TH in the presence of **PN³-Ru** catalyst. The aliphatic polyester PCL could completely convert into 1,6-hexanediol in 96% yield. For the widely used aromatic polyester PET, BDM and EG were obtained in 40% yields when using 20 eq EtOH as a hydrogen source. Increasing EtOH to 96 eq, the yield of BDM was improved to 96%.

4. Conclusions

The bipyridine-based ruthenium pincer complex exhibited high efficiency for hydrogenative depolymerization of various polyesters into diols under mild conditions. Under the optical conditions, the waste PLA sucker and PET bottle were successfully converted into 1,2-propanediol and 1,4-benzenedimethanol/EG. Through tuning the reaction temperature and H₂ pressure, highly pure products of PLA and PET mixture were obtained, which is extended to separate more complicated PLA, PET, PE, PP, and PS mixture, thus indicating the potential practical application value. More strikingly, this catalyst is also capable of catalytic transfer hydrogenation of polyesters into diols in excellent yields by using EtOH as a hydrogen source. This avoids the use of expensive and dangerous hydrogen gas, as well as the harsh reaction conditions. Further investigation of more effective catalytic systems for polyesters depolymerization and direct use of the degradation products for new material preparation is ongoing in our laboratories.

Supplementary Materials

The following supporting information can be found at: <https://www.sciepublish.com/article/pii/762>, Table S1. The Manufacturer and Purity of Required Chemical Reagent; Figure S1. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry11); Figure S2. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry12); Figure S3. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry13); Figure S4. Quantitative ¹³C NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 15); Figure S5. Quantitative ¹³C NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 16); Figure S6. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 17); Figure S7. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 18); Figure S8. Quantitative ¹³C NMR spectrum (CDCl₃, 25 °C) of PLA depolymerization. (Table 1, Entry 19); Figure S9. Quantitative ¹³C NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 20); Figure S10. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 21); Figure S11. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 22); Figure S12. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 23); Figure S13. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 24); Figure S14. ¹H NMR spectrum (CDCl₃) of PLA depolymerization (Table 1, Entry 25); Figure S15. ¹H NMR spectrum (CDCl₃) of PCL depolymerization (Table 2, Entry 1); Figure S16. ¹H NMR spectrum (CDCl₃) of PBS depolymerization (Table 2, Entry 2); Figure S17. ¹H NMR spectrum (CDCl₃) of PET depolymerization (Table 2, Entry 3); Figure S18. ¹H NMR spectrum (CDCl₃) of PBT depolymerization (Table 2, Entry 4); Figure S19. ¹H NMR spectrum (CDCl₃) of PHB depolymerization (Table 2, Entry 5); Figure S20. ¹H NMR spectrum (CDCl₃) of PLA, PET depolymerization (Table 2, Entry 8); Figure S21. ¹H NMR spectrum (CDCl₃) (Table 3, Entry 1); Figure S22. ¹H NMR spectrum (CDCl₃) (Table 3, Entry 2); Figure S23. Quantitative ¹³C NMR spectrum (CDCl₃) (Table 3, Entry 2); Figure S24. ¹H NMR spectrum (CDCl₃) (Table 3, Entry 3); Figure S25. Quantitative ¹³C NMR spectrum (CDCl₃, 25 °C). (Table 3, Entry 4); Figure S26. Quantitative ¹³C NMR spectrum (CDCl₃, 25 °C). (Table 3, Entry 5); Figure S27. Quantitative ¹³C NMR spectrum (CDCl₃) (Table 3, Entry 6); Figure S28. ¹H NMR spectrum (CDCl₃) (Table 3, Entry 7); Figure S29. ¹H NMR spectrum (CDCl₃) (Table 3, Entry 8); Figure S30. Quantitative ¹³C NMR spectrum (CDCl₃) (Table 3, Entry 9); Figure S31. Quantitative ¹³C NMR spectrum (CDCl₃) (Table 3, Entry 10); Figure S32. ¹H NMR spectrum (CDCl₃) (Table 3, Entry 12); Figure S33. The possible pathway for converting PHB to butyric acid through Ru catalyst under H₂.

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Author Contributions

Experimental designing, data collection and analysis, writing manuscript, R.W. and Y.R.; supervision, W.Y., Z.J. and C.Y.; formal analysis, R.W. and L.C.; investigation, Y.P.; editing, Y.R. and C.Y.; conceptualization, C.Y. All authors have read and agreed to the published version of the manuscript.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

Data will be made available on request.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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