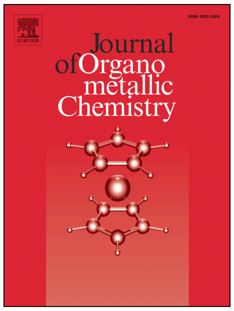

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Metal-catalysed Poly(Ethylene) Terephthalate and Polyurethane degradations by glycolysis

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Abstract

The recovery of Polyol from PolyUretane (PU) and Bis(2-HydroxyEthyl) Terephthalate (BHET) from Poly(Ethylene) Terephthalate (PET) from plastic waste by transesterification reactions was achieved, by using a wide scope of simple air-stable metal salts, Lewis acids, mixtures of commercially available phosphine/phosphite ligands with metal salts and low-valent [Ni(COD)$_2$] as catalytic precursors, in the presence of ethyleneglycol as a transesterification agent. A kinetic study with cobalt chloride led to the conclusion that the PET degradation with metal salts behaves as a consecutive reaction with an induction period. The use of σ-donor or σ-donor/π-acceptor bidentate phosphine ligands, such as dcype and dppe, along with CoCl$_2$ or [Ni(COD)$_2$] improved the PET degradation process. For both rigid and flexible PU, FeCl$_3$ was the most active catalyst precursor.

Keywords: glycolysis, polyurethane, polyethylene terephthalate, degradation, catalysis.

Introduction

Poly (Urethane) (PU) and Poly (Ethylene Terephthalate) (PET) are polymeric materials widely used in a variety of applications. Their properties have made them very useful and largely produced, making PU and PET-recycling an important task to be addressed. Besides solving pollution problems, their chemical degradation is an attractive field because it can recover the monomers to be re-used for the manufacture of products with the same quality as the original, like new PET bottles, along with the reduction of waste production.[1-4]

Glycolysis is a simple method for PET and PU chemical degradation with advantages such as mild reaction conditions, low-volatility of solvents and their products, the final product Bis(2-hydroxyethy) Terephthalate (BHET) and the recovered polyol, can be easily recovered and then mixed with virgin raw materials.[5-9] Many catalysts have been developed for PET degradation by glycolysis in recent years, for instance metal acetates,[11,12,13] oxides,[14,15] carbonates and sulfates,[16,17,18] titanium phosphate,[13] zeolites,[19] ionic liquids (ILs)[7,20-22] and MOFs.[23] For catalysts used in PU degradation include alkanolamines, metal hydroxide, alkoxides, acetates and octoates,[9] mostly for flexible PU foam glycolysis. Also relevant recent examples for PET degradation using organocatalysed protocols have been disclosed with good yields and recyclability of the catalysts.[29]
Even when these catalysts are effective in the PET and PU glycolysis, they also present drawbacks and are limited by disadvantages in their technical scope. Thus, their chemical recycling is still far from being a real solution. Consequently, more efforts to develop new

catalysts and improve the chemical degradation processes to make them more profitable are needed.

Herein, we describe the improved PU and PET degradation by transesterification reactions for polyol and Bis (2-HydroxyEthyl) Terephthalate (BHET) recovery using a wide scope of air-stable metal-salts and Lewis acids with ethyleneglycol as a low-cost transesterification agent. We also describe the use of phosphine/phosphite ligands with air stable transition metal salts and [Ni(COD)$_2$] for the first time in this type of applications, as well as the use of triethylborane to carry out the glycolysis process in good isolated yields.

Results and Discussion

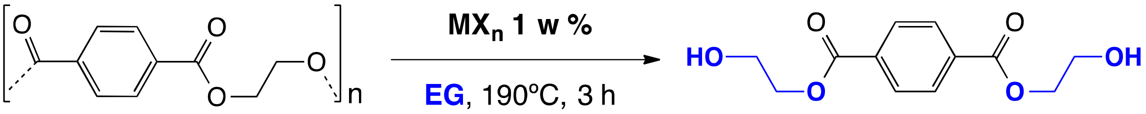
1. PET Degradation

1.1. Metal Salts and Lewis Acids

A wide range of metal salts and Lewis acids were used to carry out the PET degradation using the conditions shown in **Table 1**. In all cases (entries 2-16), the monomer bis (2-hydroxyethyl) terephthalate was obtained. A blank experiment showed that the degradation of PET without a catalytic precursor wasn´t observed (entry 1), not even PET solubility was achieved at 190^{o}C.

The highest yields were obtained with $ZrCl_4$ (69%, entry 15), $CoCl_2{\cdot}6H_2O$ (67%, entry 13) and BEt_3 (56%, entry 16). To note, once full conversion of PET was reached, the reaction mixture became a single homogeneous phase, with yields of BHET higher than 55%, which indicates that soluble intermediates (oligomers), continue reacting to produce BHET.

Table 1. PET degradation with metal salts and Lewis acids



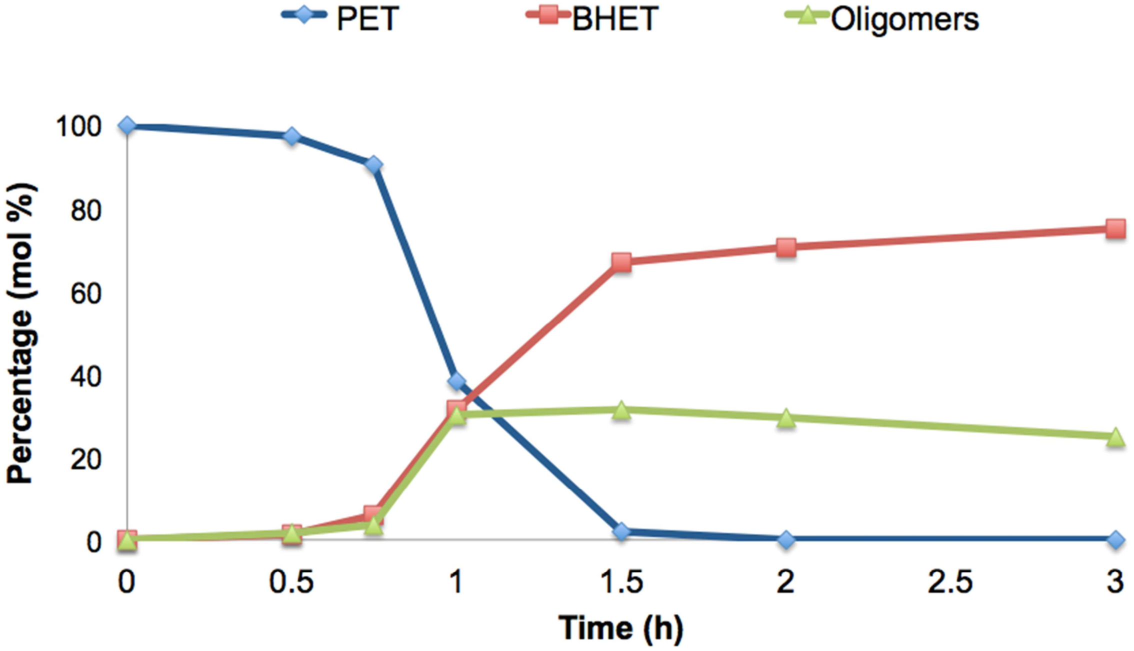
Entry	Catalytic Precursor	PET Conversion (%)	Yield of BHET (%)	TON
1	---	0	0	---
2	$Ni(NO_3)_2{\cdot}6H_2O$	13	4	3
3	$FeSO_4{\cdot}7H_2O$	44	12	9
4	$CuSO_4{\cdot}2H_2O$	49	17	15
5	$CuCl_2{\cdot}2H_2O$	53	19	12
6	$Zn(OAc)_2{\cdot}2H_2O$	55	23	22
7	$FeCl_3{\cdot}6H_2O$	57	42	31
8	$AlCl_3$	59	44	29
9	$ZnCl_2$	60	45	29
10	$MnCl_2{\cdot}4H_2O$	62	48	31
11	$NiSO_4{\cdot}7H_2O$	100	55	42
12	$NiCl_2{\cdot}6H_2O$	100	55	38
13	$ZnSO_4{\cdot}7H_2O$	100	57	48
14	$CoCl_2{\cdot}6H_2O$	100	65	46
15	$ZrCl_4$	100	69	80
16[a]	BEt_3	100	56	37

*All reactions were carried out in a Parr reactor (25 mL) and heated at 190°C per 3 hours, with 1 g of PET, 10 mL of ethylene glycol and 1 weight % of catalytic precursor. [a] Prepared inside a glovebox (<1 ppm H_2O and O_2) and heated in a Schlenk Flask with a reflux condenser, connected to an inert-gas/vacuum double manifold.

The activity trend found for metal chlorides $Co^{2+} > Mn^{2+} > Zn^{2+}$ was different from that reported for the acetates by Ghaemy and Mossaddegh[24], $Zn^{2+} > Mn^{2+} > Co^{2+}$ using ethylene glycol. Likewise, with metal sulphates, the obtained trend was the following: $Zn^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+}$. No clear relation between cation and anion has been established to explain the improved yield of BHET, but probably is related to the cation interaction with polyester, thus, related to its hardness, charge density and anion softness. The combination of all these properties may allow an interaction with the carbonyl groups in the polyester chains in PET that favour its degradation. Furthermore, the recyclability of metal salts/ethylene glycol system was studied, having very good results in terms of yield after more than one cycle (see **SI** section **S18**).

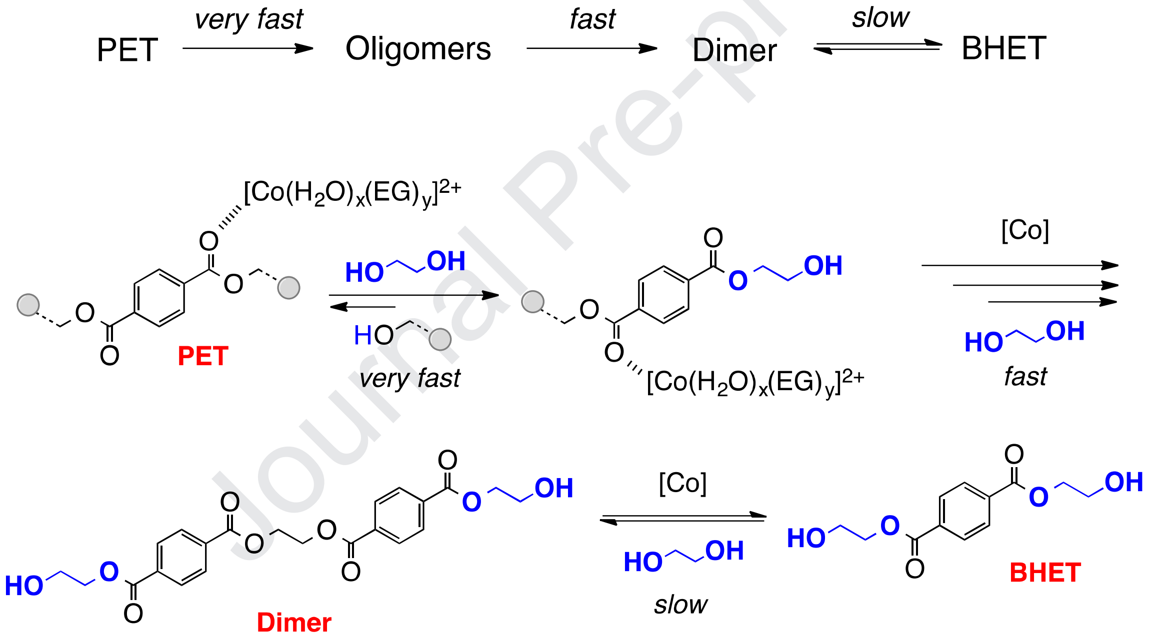
The PET degradation kinetics was studied using $CoCl_2{\cdot}6H_2O$ as a catalyst precursor at 200°C. A consecutive reaction behaviour with an initial induction period was identified in **Scheme 1**, which was also confirmed with a PET pseudo-first order plot (S10). The induction period was required to allow the metal-carbonyl interaction at the ester group with the small amount of soluble PET. This Lewis acid type interaction allowed for a nucleophilic attack at the carbonyl group by EG for the PET degradation.

$$\text{PET} \xrightarrow{\textit{fast}} \text{Oligomers} \xrightarrow{\textit{slow}} \text{BHET}$$



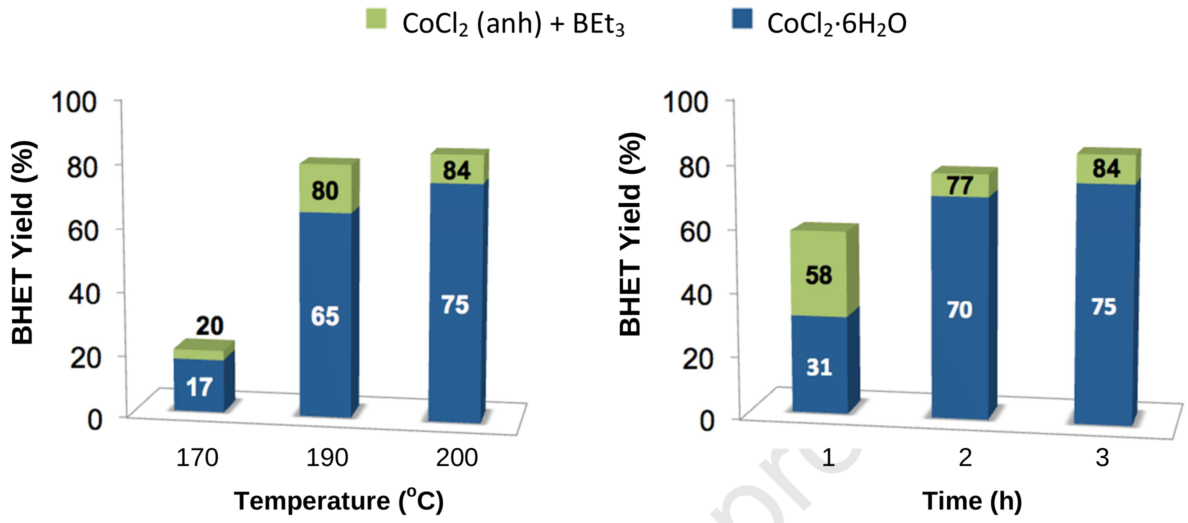
Scheme 1. PET degradation at 200°C with ethylene glycol, using 1 weight % of $CoCl_2{\cdot}6H_2O$ as a catalyst precursor. The mol % of oligomers was obtained by the difference between the undepolimerized PET and BHET yield.

As seen in **Scheme 1**, as the polymer size decreases, the transesterification reactions are slower. Furthermore, the presence of a soluble small quantity of the dimer was identified by ^{1}H-NMR in the reaction mixture (Figure S4), confirming that the degradation occurs via a transesterification mechanism with the formation of a dimer prior to the monomer BHET. No significant changes were observed between 1.5 and 3 hours; therefore, the last step could be described as a slow equilibrium between the dimer and BHET, as described in **Scheme 2**.



Scheme 2. Mechanistic proposal for PET degradation trough transesterification reactions with $CoCl_2{\cdot}6H_2O$.

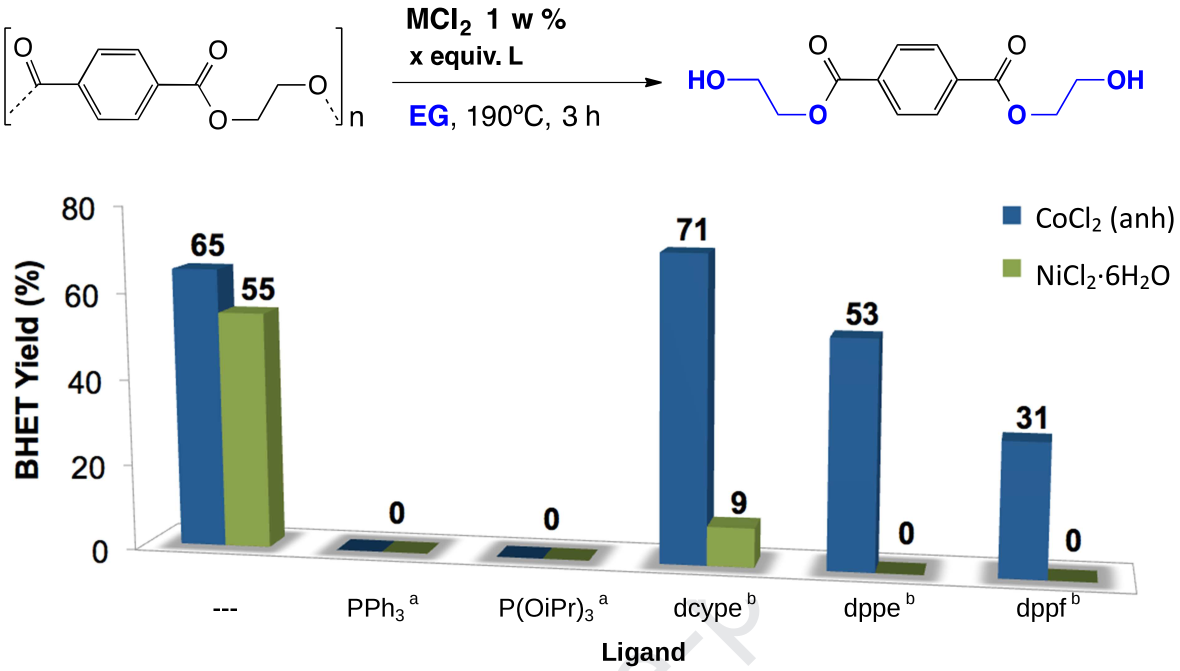
The addition of triethylborane increased the yield of BHET between 1-3 hours and 170-200°C (**Scheme 3**), giving the highest yields even compared with an increase of cobalt chloride, probably due the synergic effect of both precursors.



Scheme 3. Use of triethylborane in PET degradation with cobalt chloride. a) Effect of temperature at 3 hours; b) Effect of time at 200°C. *All reactions were carried out in a Schlenk flask (50 mL), with 1 g of PET, 10 mL of ethylene glycol, 1 weight % of $CoCl_2$ (anh) and 1 weight % of BEt_3.

1.2. Use of Metal salts with phosphine/phosphite ligands

In order to improve the PET degradation, we studied the effect of phosphine/phosphite ligands with $CoCl_2$ and $NiCl_2{\cdot}6H_2O$, using ethylene glycol as solvent and transesterification agent as well and an excess of ligand (**Scheme 4**).

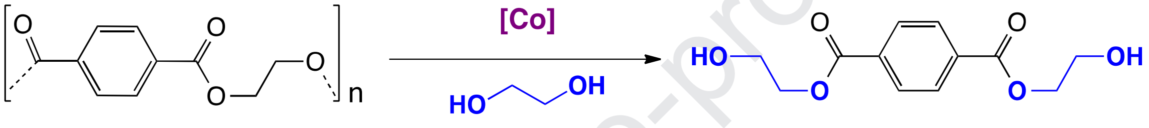


Scheme 4. PET degradation with metal salts and phosphine/phosphite ligands at 190^{o}C and 3 hours. ^{a}mol ratio of 1:6 of metal salt and monodentate ligand, respectively (x=6); ^{b}mol ratio of 1:3 of metal salt and bidentate ligand, respectively (x=3).*All reactions were carried out in a Schlenk flask (50 mL), with 1 g of PET, 10 mL of ethylene glycol and 1 weight % of the corresponding metal salts.

The use of monodentate ligands led to the complete inhibition of the degradation process, while bidentate ligands showed to favour the process but only with σ-donors like dcype. Thus, compounds formed between cobalt and bidentate ligands were more stable in ethylene glycol under the reaction conditions compared with those with monodentate ligands where decomposition was observed. Additional experiments to assess the influence of the amount of ligand in the degradation process with $NiCl_2{\cdot}6H_2O$ were made, they confirmed that monodentate ligands did not facilitated the degradation process (**Scheme S11**), while with the use of bidentate ligands the yield of BHET increased as the ligand amount decreased (**Table S11**).

The reactivity of the mixture $CoCl_2$:dcype in PET degradation was further optimised (**Table 2**). The yield of BHET recovered with different amounts of ligand (entries 1-2) and the use of complex [Co(dcype)Cl_2] (***1***) (entry 3) was practically the same, leading to conclude that (***1***) may be formed in the reaction mixture. The use of an increased load of complex ***1*** increased the BHET recovery.

Table 2. Reactivity of $CoCl_2$:dcype system in PET degradation using ethylene glycol.



Entry	Cat. Precursor	Load (mol %)	Temperature (°C)	Time (h)	BHET Yield (%)
1	$CoCl_2$ 1:3 dcype	1.5	190	3	10
2	$CoCl_2$ 1:1 dcype	1.5	190	1	58
3	[Co(dcype)Cl_2]	1.5	170	3	10
4	[Co(dcype)Cl_2]	1.5	190	1	58
5	[Co(dcype)Cl_2]	1.5	190	2	75
6	[Co(dcype)Cl_2]	1.5	190	3	75 / 70[a] / 5[b]
9	[Co(dcype)Cl_2]	3.0	190	3	82

*All reactions were carried out in a Schlenk flask (50 mL), with 1 g of PET, 10 mL of ethylene glycol and 1.5 or 3.0 mol % of $CoCl_2$ (anh) or catalyst precursor. [a]Mercury drop test. [b]Addition of DMSO drops.

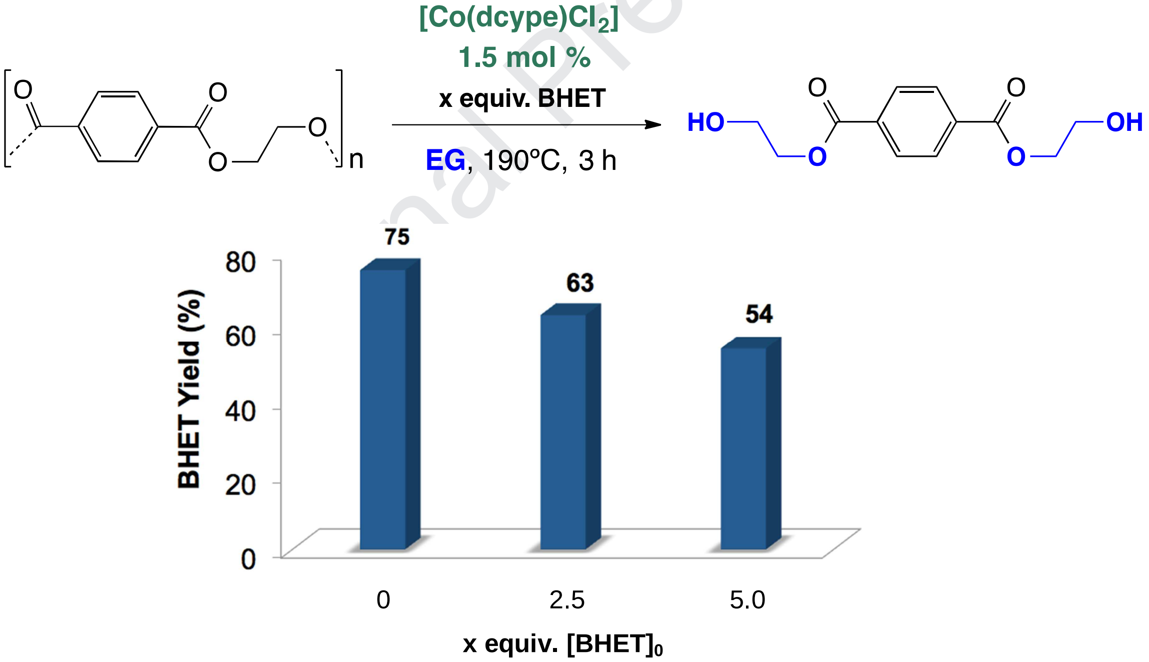
A mercury drop test showed no significant change in BHET yield (**Table 2**, entry 6). Additionally, the initial addition of DMSO decreased the monomer recovery almost completely, suggesting that the presence of a highly coordinating solvent modifies the catalytically active species by decreasing the vacant sites.

Based on the above experimental observations, two mechanisms can be envisaged:

1) A Lewis acid-catalysed mechanism, where ligands with higher π-acidity generate acid metal centres that interact with donor moieties in the intermediates and the final product (BHET), leading to product inhibition.

2) A Co(I)-Co(III)-Co(I) cycle, where Co(I) is generated in situ from Co(II), which might be reduced in the presence of phosphines and ethylene glycol.

To shed some light in order to identify the possible mechanism, we carried out experiments using initial amounts of BHET at the same reaction conditions, as shown in **Scheme 5**.



Scheme 5. Inhibition by product with BHET. *All reactions were carried out in a Schlenk flask (50 mL), with 1 g of PET, 10 mL of ethylene glycol and 1.5 mol % of catalyst precursor.

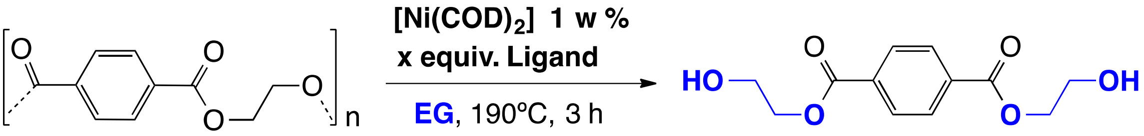
As a result, the addition of initial amounts of monomer decreased the final yield of BHET, probably due to a coordination of this monomer to the Lewis acids involved in the reaction mechanism. Additionally, the difference between cobalt and nickel could lie in the possibility of creating vacant sites in solution, d^7 Cobalt complexes could generate vacant sites easier by octahedral-tetrahedral coordination equilibrium, while d^8 square nickel complexes create them through a high-energy associative mechanism or ligand dissociation instead.

1.3. [Ni(COD)$_2$].

In sharp contrast, we decided to assess the reactivity of an electron rich metal centre using [Ni(COD)$_2$] with and without phosphine/phosphite ancillary ligands for PET degradation, as shown in **Table 3**. Surprisingly, the reactivity trend was similar to the one previously observed with Co(II): the use of monodentate ligands gave low yields (entries 2-3), while bidentate ligands gave higher yields (entries 4-6). Again, the intermediates formed with monodentate ligands could be unstable in ethylene glycol under the reaction conditions, while bidentate ligands gave good results.

To note, the use of [Ni(COD)$_2$] without ligands was highly active in PET degradation (entry 1), possibly due the formation of nickel (COD)-solvent compounds or nickel nanoparticles (NiNPs) (vide infra). The highest yield of BHET monomer, between bidentate ligands, was achieved with dppe (67%, entry 5), compared to dcype (59%, entry 4) and dppf (15%, entry 6).

Table 3. Reactivity of [Ni(COD)$_2$] in PET degradation.

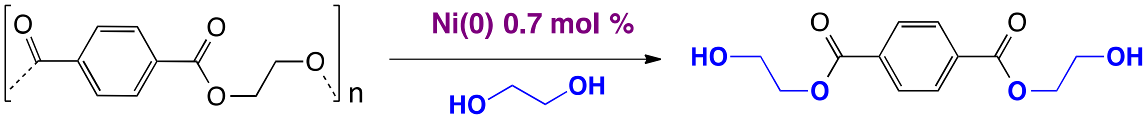


Entry	Ligand	PET Conversion (%)	BHET Yield (%)
1	---	100	55
2^a	PPh$_3$	27	13
3^a	P(OiPr)$_3$	0	0
4^b	dcype	100	59
5^b	dppe	100	67
6^b	dppf	30	15

*All reactions were carried out in a Schlenk flask (50 mL) and heated at 190°C per 3 hours, with 1 g of PET, 10 mL of ethylene glycol and 1 weight % of [Ni(COD)$_2$]. [a]mol ratio of 1:4 of nickel precursor and monodentate ligand, respectively (x=4); [b]mol ratio of 1:2 of nickel precursor and bidentate ligand, respectively (x=2).

The effect of the variation in the amount of ligand dppe, temperature and time were examined, the results are summarised in **Table 4**. The highest yield was obtained with 2 equivalents of dppe, compared to the addition of 1 equivalent of dppe only or the use of the complex [(COD)Ni(dppe)], where catalyst precursor decomposition was observed in both cases. Additionally, mercury drop tests were also performed for entries 1, 3 and 6, with no decrease in BHET yield, from which can be concluded the homogeneity of the catalytic reaction is likely. In entry 1, mercury drop test is not totally conclusive, if we consider that PET degradation occurs through reversible transesterification reactions, both glycolysis and polymerisation processes could be mediated by NiNPs and be just partially inhibited.

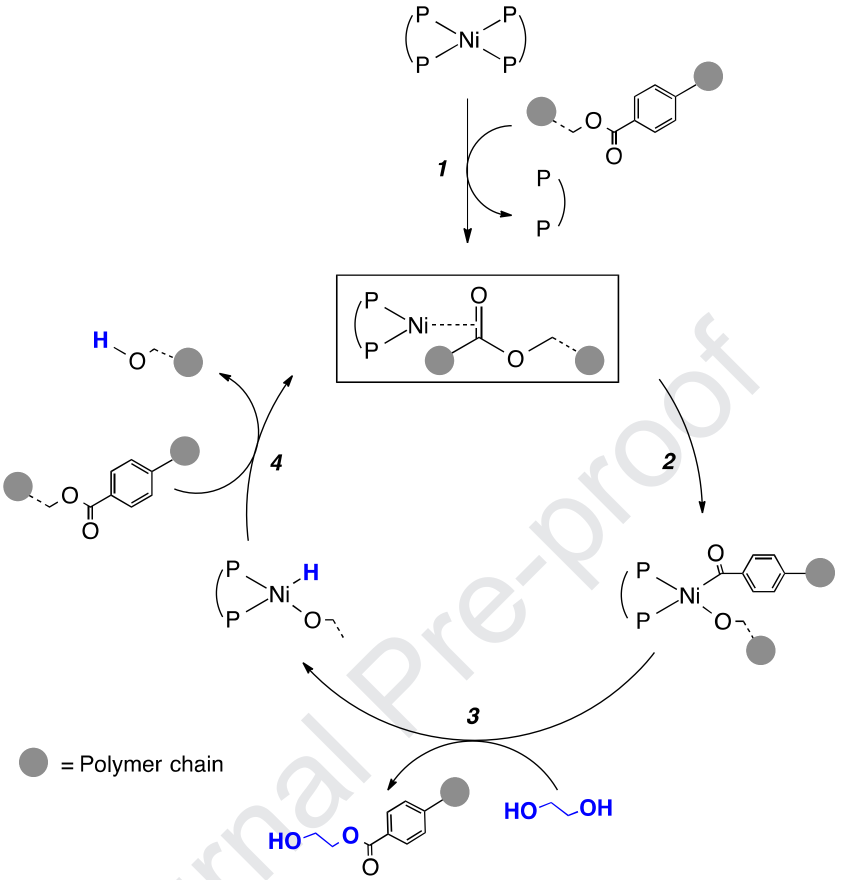
Table 4. Reactivity of [Ni(COD)$_2$]: dppe system in PET degradation.



Entry	System	Temperature (ºC)	Time (h)	BHET Yield (%)
1	[Ni(COD)$_2$]	190	3	55 / 60[a]
2	[(COD)Ni(dppe)]	190	3	44
3	[Ni(COD)$_2$] 1:1 dppe	190	3	45 / 48[a]
4	[Ni(COD)$_2$] 1:2 dppe	190	1	30
5	[Ni(COD)$_2$] 1:2 dppe	190	2	57
6	[Ni(COD)$_2$] 1:2 dppe	190	3	67 / 64[a]
7	[Ni(COD)$_2$] 1:2 dppe	190	5	59
8	[Ni(COD)$_2$] 1:2 dppe	200	3	71

*All reactions were carried out in a Schlenk flask (50 mL), with 1 g of PET, 10 mL of ethylene glycol and 1 weight % of [Ni(COD)$_2$] or the same amount (in mol%) of catalyst precursor. [a] Mercury drop test.

Considering the current results and previous reports related to ester C-O activation with nickel and the fact that low valent nickel compounds coordinates *side-on* in the C=O moiety in carbonylic groups,[25-27] a mechanistic proposal for the PET degradation is presented in **Scheme 6**. The first step involves the η^2-C,O coordination (*side-on)* of the nickel centre at the carbonyl moiety with ligand dissociation (1), followed by the oxidative addition of the ester C-O bond (2). Later on a nucleophilic attack by ethylene glycol (3) generates a hydride complex, then a reductive elimination releases the hydrogenated polymer chain (4). This cycle is repeated until the formation of low-molecular weight oligomers and BHET monomer.



Scheme 6. Mechanistic proposal for PET degradation mediated by Ni(0).

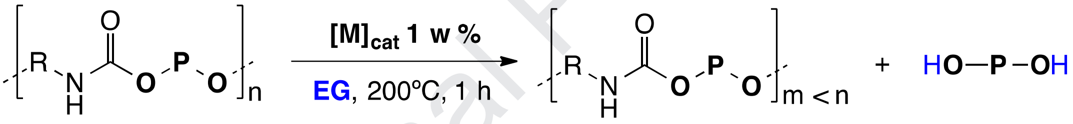
While the first steps are favoured with σ-donor bidentate ligands, the stability of formed species in solution at high temperatures gets compromised. Thus, the highest yield was obtained with an intermediate bearing a σ donor/π acceptor bidentate ligand, as dppe. To sum up, the best catalytic system in terms of activity and BHET yield was found to be the use of $CoCl_2.6H_2O$ as a cheap catalyst, compared with the already reported catalytic systems.[11-22] Noteworthy, the addition of BEt_3 improved the BHET yield and reaction time up to 84% yield in 3h with cobalt; also the use of an ancillary ligand can help to increase the activity but a careful selection of it must be considered.

2. Polyurethane degradation

2.1. Flexible PU foam

The degradation of flexible PU foam was carried out also using metal salts and Lewis acids as catalytic precursors and foam wastes in ethylene glycol. The GPC results (**Table 5**) showed the recovery of high-molecular weight polymers or oligomers with M_n values between (13 - 19) x 10^3; the polyol, with M_n values between (4-6) x 10^3, which is expected for flexible polyol and other by-products, including additives and the final structure of Di-Isocyanate, with molecular weights lower than 300.

Table 5. Flexible PU degradation with metal salts and Lewis acids.



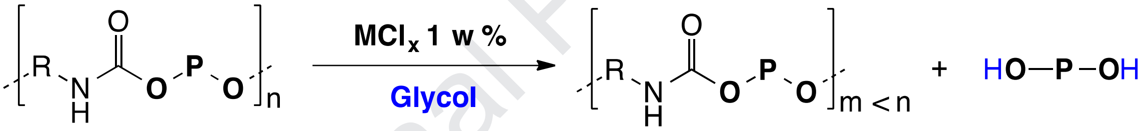
Entry	Catalytic Precursor	PO M_n (g/mol)	I_P	Polyol (%)
1	$ZrCl_4$	5,901	1.115	23
2	$MnCl_2{\cdot}6H_2O$	5,278	1.690	91
3	$FeCl_3{\cdot}6H_2O$	5,438	1.067	96
4	$CoCl_2{\cdot}6H_2O$	6,336	1.324	92
5	$NiCl_2{\cdot}6H_2O$	5,337	1.384	92
6	$AlCl_3$	5,298	1.394	92

*All reactions were carried out in a Parr Reactor (25 mL), with 0.5 g of PU, 10 mL of ethylene glycol and 1 weight % of catalytic precursor. Polyol % was determined by GPC.

In almost all cases, the catalytic precursors used were found to be quite active, since more than 90% of polyol was obtained, except for $ZrCl_4$. However, highly polarising metal cations, as Zr^{4+}, could favour both degradation and re-polymerisation processes, while intermediate hard metal cations and Lewis acids promote the PU foam degradation.

Since solubility was important for the reaction success the temperature and time of reaction were optimised and the type of diol used in the PU degradation (**Table 6**). Thus, no reaction was observed using temperatures lower than 160°C. Between 160-200°C, the amount of recovered polyol was greater as the temperature increased (entries 2-4 for $FeCl_3$ and entries 9-10 for $CoCl_2$). For longer reaction times at 200°C, no polyol was recovered (entries 5-6), due to the thermal decomposition of products. Comparing both glycols, the use of EG (entry 4) at 200°C, generated a higher polyol content product, compared with 1,4-butanediol (entry 8).

Table 6. Additional studies of PU foam degradation.



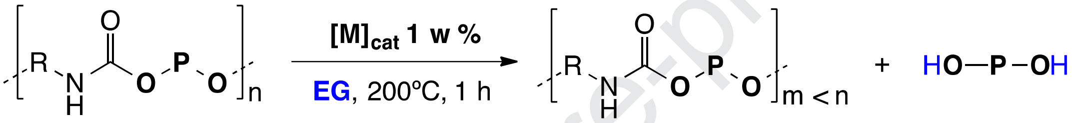
Entry	Catalytic Precursor	Time (h)	Temperature	Glycol	PO M_n (g/mol)	I_P	Polyol (%)
1	$FeCl_3·6H_2O$	1	140	EG	---	---	---
2	$FeCl_3·6H_2O$	1	160	EG	6,047	1.043	50
3	$FeCl_3·6H_2O$	1	180	EG	4,062	1.319	59
4	$FeCl_3·6H_2O$	1	200	EG	5,438	1.067	96
5	$FeCl_3·6H_2O$	2	200	EG	---	---	---
6	$FeCl_3·6H_2O$	3	200	EG	---	---	---
7[a]	$FeCl_3·6H_2O$	1	200	EG	4,814	1.166	84
8	$FeCl_3·6H_2O$	1	200	1,4-BD	4,990	1.124	60
9	$CoCl_2·6H_2O$	1	180	EG	6,120	1.113	46
10	$CoCl_2·6H_2O$	1	200	EG	6,336	1.324	92
11	$CoCl_2·6H_2O$	0.5	200	EG	6,161	1.056	85

*All reactions were carried out in a Parr Reactor (25 mL), with 0.5 g of PU, 10 mL of glycol and 1 weight % of catalytic precursor. Polyol % was determined by GPC. [a] 5 mL of glycol.

2.2. Rigid PU

The degradation of rigid PU was carried out using *Polyurethane Selectophore*^{TM} in ethylene glycol (**Table 7**). The GPC results showed the recovery of high-molecular weight polymers or oligomers with M_n values between (4-23) x 10^3; the polyol, with M_n values between (2-11) x 10^2, as expected for rigid PU and other by-products, including additives and the final di-Isocyanate.

Table 7. Rigid PU degradation with several catalyst precursors.



Entry	Catalytic Precursor	GPC Product Composition (%)	
		High-Molecular Weight Products	Polyol
1	$FeCl_3$	56	44
2	$FeCl_2$	83	17
3	$Zn(OAc)_2$	98	2
4	$ZnCl_2$	77	23
5	$CoCl_2$	99	1
6	$NiCl_2$	99	1
7	$[Ni(COD)_2]$ 1:2 dppe	95	0
8	$CoCl_2$ 1:1 dcype	96	0

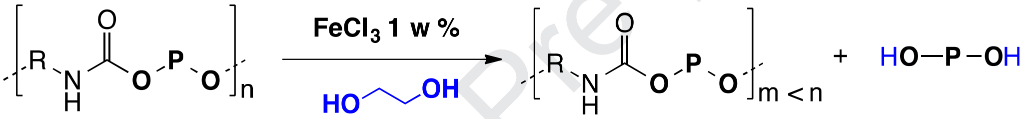
*All reactions were carried out in a Schlenk Flask (50 mL), with 0.3 g of PU, 2 mL of ethylene glycol and 1 weight % of catalyst precursor. Products composition determined by GPC.

The reactivity of metal chlorides seems to be related with their corresponding cation charge density and hardness, according to the following order: Fe^{3+} (232 C/mm^3) > Zn^{2+}

(112 C/mm^3) > Co^{2+} (108 C/mm^3). This can be seen on comparing the results obtained with both iron chlorides (entries 1-2). Therefore, more electron-rich metal precursors (entries 7-8), led to a lower polyol recovery, in sharp contrast with the results obtained for flexible foam.

Further optimisation studies with $FeCl_3$ showed that yield increased with temperature reaching a maximum of polyol recovery at 200°C, after 5 h of reaction, giving an increase in polyol molecular weight (**Table 8**, entries 3-4), probably due to a re-polymerisation process at longer reaction times.

Table 8. Rigid PU degradation with $FeCl_3$



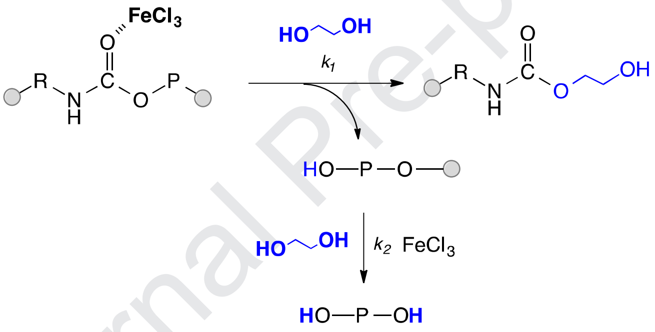
Entry	Time (h)	Temperature (°C)	PO M_n (g/mol)	I_p	Polyol (%)
1	1	160	440	1.221	2
2	1	180	361	1.509	27
3	1	200	1,113	2.299	44
4	5	200	4,996	2.460	95

*All reactions were carried out in a Schlenk Flask (50 mL), with 0.3 g of PU, 2 mL of ethylene glycol and 1 weight % of anhydrous $FeCl_3$. Products composition was determined by GPC.

A simplified cartoon-type representation of flexible and rigid PU is depicted in **Scheme 7** and **Figure 1**, showing the types of transesterification reactions during PU degradation:

Type 1) those where the polymer is only degraded without polyol release via k_1 (see **Scheme 7** and **Figure 1**).

Type 2) those where polyol is released via k_2, making easier to recover selectively the polyol (I_P = 1.0 - 1.4), while PU degrades if $k_2 > k_1$. On using rigid PU foam the last is less favoured due to its high cross-linked structure and the high functionality of the polyol, consequently a stronger Lewis acid is needed to increase the possibility of a type 2 transformation. Most of this transesterification reactions led mainly to a molecular weight decrease instead polyol recovery ($k_1 > k_2$), as can be seen in **Table 9** using a non-highly active catalytic precursor ($CoCl_2$) for rigid PU degradation, where the molecular weight of the polyurethane main structure decreases with a low release of polyol, as time increases.



Scheme 7. Transesterification reactions in PU degradation

a)

b)

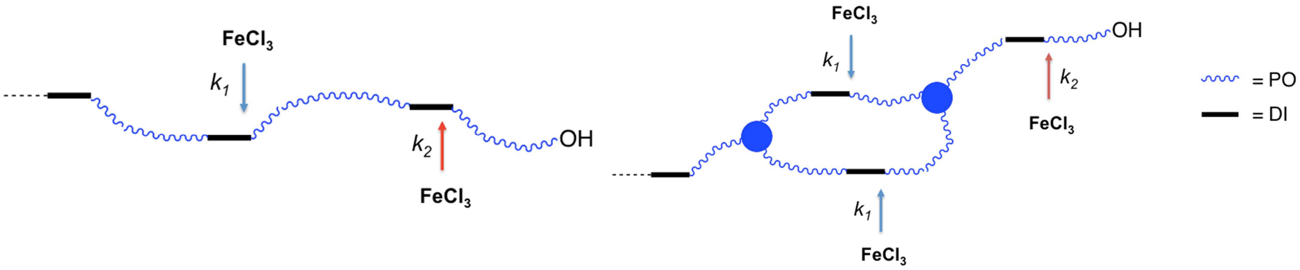
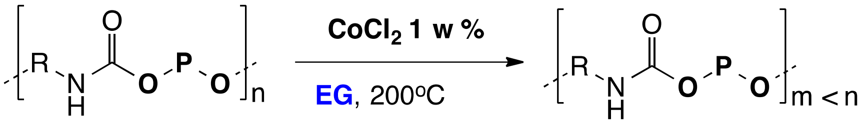


Figure 1. Transesterification reactions in PU degradation. a) Flexible PU foam; b) Rigid PU foam

Table 9. Rigid PU degradation with $CoCl_2$



Entry	Time (h)	Polymer M_n (g/mol)	I_P	Polyol (%)
1	1	8,753	1.732	1
2	3	7,099	2.235	4
3	5	5,608	2.464	7
4	10	4,700	2.030	8

*All reactions were carried out in a Schlenk Flask (50 mL), with 0.3 g of PU, 2 mL of ethylene glycol and 1 weight % of $CoCl_2$. Products composition was determined by GPC.

Conclusions

The metal-catalysed degradation by glycolysis or transesterification for PET and PU (rigid and flexible) was achieved to yield monomeric BHET and polyol respectively, in good yields. The use of ancillary σ donor/π acceptor bidentate phosphine ligands allowed the PET degradation process with Ni(0) and Co(II) systems. Furthermore, the use of soft Lewis acids in flexible PU degradation, led to the recovery of low-dispersity polyol with high polyol recovery. In contrast, catalytic precursors with metals in high oxidation state were more efficient in rigid PU degradation compared with those of low oxidation state. These results may be of interest for further design of new heterogeneous catalysts that provide important advantages such as catalyst recyclability.

Experimental Section

Unless otherwise mentioned, all manipulations were performed using the standard

Schlenk techniques in an inert-gas/vacuum double manifold or under an argon atmosphere (Praxair 99.998) in an MBraun glovebox (<1 ppm H_2O and O_2). All liquid reagents were purchased as reagent grade and were degassed before use. The solvents were dried using standard techniques and stored in the glovebox before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were stored under 4 Å molecular sieves for 24 h before use. NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer unless otherwise mentioned. ^1H-NMR spectra are reported relative to the residual protio-solvent. $^{13}C\{^1H\}$-NMR spectra give the characteristic carbon signal of each solvent. $^{31}P\{^1H\}$-NMR chemical shifts are reported relative to external 85% H_3PO_4. ^1H-NMR, $^{13}C\{^1H\}$-NMR and $^{31}P\{^1H\}$-NMR spectra were obtained in DMSO-d_6, $CDCl_3$ and/or THF-d_8. $[Ni(COD)_2]$ was purchased from Aldrich and purified on a Celite 545 plug, using THF or hexane. Anhydrous salts were obtained by heating above 140°C and drying for at least 6 hours in an inert-gas/vacuum double manifold below 0.005 mmHg and stored inside a glove box. IR (FTIR) spectra were recorded at room temperature on a Spectrum Two FTIR Bruker Spectrometer. GPC analyses were performed on a Waters 2695 ALLIANCE Separation Module. Post-consumer PET provided from a single source of plastic bottles, was cut until 1x1 mm^2 pieces, washed with organic solvents, heated at 100°C and dried for at least 4 hours. Flexible PU provided from commercial foams, was cut until 0.125 cm^3 pieces, washed with organic solvents and dried for at least 4 hours. Rigid PU (*Polyurethane Selectophore™)* was purchased from Aldrich.

General Procedure for PET Degradation studies. All reactions were made in a 25 mL Parr reactor or a 50 mL Schlenk Flask, typically charged with 1 weight % of catalyst precursor, 1 g of PET and 10 mL of ethylene glycol. If phosphine/phosphite ligands, triethylborane and/or [Ni(COD)$_2$] were used, all reactants were added to the Schlenk Flask in a MBraun glovebox. The solution was heated with vigorous stirring at the selected reaction temperature in an oil bath for the corresponding reaction time. If triethylborane was added to the reaction mixture, the solution was heated in a Schlenk Flash ensambled with a condenser, also using an inert-gas/vacuum double manifold. The reactor or Schlenk flask was opened after the reaction time in a well-vented hood prior to workup. Then, two parts of water were added to the reaction mixture, heated to boiling point. The under polymerised PET and other by-products, like oligomers and/or ligand residues, are separated by hot filtration. The under polymerised PET can be recovered from the residue, washed with water, organic solvents, and then dried. The conversion of PET is defined as

$$\text{Conversion of PET (\%)} = \frac{\mathrm{W_{PET,0}} - \mathrm{W_{PET,1}}}{\mathrm{W_{PET,0}}} \times 100\%$$

where $W_{PET,0}$ is the initial weight of PET, $W_{PET,1}$ is the weight of undepolymerized PET.

The collected filtrate was concentrated under vacuum and then stored in a fridge at 0^{o}C for at least 12 hours. White crystalline flakes of BHET were obtained and separated by filtration and dried. The yield of BHET is defined as

$$\text{Yield of BHET (\%)} = \frac{\mathrm{W_{BHET}}/\mathrm{MW_{BHET}}}{\mathrm{W_{PET,0}}/\mathrm{MW_{PET}}} \times 100\%$$

where $W_{PET,0}$ is the initial weight of PET and W_{BHET} is the weight of BHET. MW_{PET} and MW_{BHET} are the molecular weight of BHET (254 g/mol) and the PET repeating unit (192 g/mol), respectively.

General Procedure of flexible PU degradation studies. All reactions were made in a 25 mL Parr reactor, typically charged with 1 weight % of catalyst precursor, 0.5 g of PET and 10 mL of ethylene glycol. The solution was heated with vigorous stirring to the reaction temperature for the corresponding reaction time. After this, the reactor was opened in a well-vented hood prior to workup. One part of water was added to the reaction mixture and then transferred to 4 test tubes and centrifuged for 4 hours. The product mixture was recovered from the liquid phase by liquid-liquid extraction with two parts of CH_2Cl_2 or $CHCl_3$. The solvent was evaporated in an inert-gas/vacuum double manifold and the product mixture was dried for at least 4 hours.

General Procedure of rigid PU degradation studies. All reactions were made in a 50 mL Schlenk flash, typically charged with 1 weight % of catalyst precursor, 0.3 g of PET and 2 mL of ethylene glycol. If phosphine/phosphite ligands and/or [Ni(COD)$_2$] were used, all reagents were added to the Schlenk Flask in a MBraun glovebox. The solution was heated with vigorous stirring in an oil bath at reaction temperature for the corresponding reaction time. After this, the Schlenk flask was opened in a well-vented hood prior to workup. Two parts of water was added to the reaction mixture and then transferred to 4 test tubes and centrifuged for 4 hours. The product mixture was recovered from the liquid phase by liquid-liquid extraction with two parts of CH_2Cl_2 or $CHCl_3$. The solvent was evaporated in an inert-gas/vacuum double manifold and the product mixture was dried for at least 4 hours.

General Procedure for GPC. A 3-5 mg/mL solution of recovered product mixture in THF (HPLC-grade) was prepared for each sample, cleaned with a porous filter and transferred to HPLC vials. All the analyses were carried out on a Waters 2695 ALLIANCE Separation Module, with an integrated refractive index detector (Waters 2414), in-line de-gasifier; column furnace and a two-column bench (Waters HPLC): Styragel HR 5E with molecular weight range from 50 to 1 x 10^5, and Styragel HR 5E with molecular weight range from 2 x 10^3 to 4 x 10^6. THF is used as eluent at a flow rate of 1.0 mL/min at 35^{o}C. The calibration curve was performed with 18 polystyrene standards, with molecular weight range of 3.7 x 10^2 to 4.3 x 10^6.

Mercury Drop Test. Following the procedure described above for PET degradation studies, the very same reactions were prepared and two drops of elemental Hg were added to the reaction mixture.

Preparation of [(dppe)Ni(COD)]: The nickel (0) complex [(dppe)Ni(COD)] was prepared following the method of Freud *et* al[28] for the dcype complex. Solid dppe (48 mg, 0.12 mmol) was added in one portion to a yellow solution of $[Ni(COD)_2]$ (33 mg, 0.12 mmol) in THF (3 mL) and was stirred at room temperature. After the dppe was dissolved, the solution was stirred for 30 minutes at room temperature. The solvent was evaporated and further dried for six hours under vacuum to yield a yellow solid. $^{31}P\{^{1}H\}$-NMR (121.32 MHz, THF-d_8, r.t.) 43.74 ppm (s).

ASSOCIATED CONTENT

Supporting Information available: Includes complete experimental procedures, additional experiments, selected IR, NMR spectra and GPC determinations.

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Conflict of interests

There are no conflicts to declare

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Highlights

- ✓ PET and PU degradation by glycolysis
- ✓ Catalytic methodology
- ✓ Air stable, earth abundant and cheap catalysts
- ✓ High recovery yields

Conflict of interests

There are no conflicts to declare