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Reductive Depolymerization of Polyesters and Polycarbonates with Hydroboranes by Using a Lanthanum(III) Tris(amide) Catalyst

Marie Kobylarski,[a] Jean-Claude Berthet[a,*] and Thibault Cantat[a,*]

The homogeneous reductive depolymerization of polyesters and polycarbonates with hydroboranes is achieved with the use of an f-metal complex catalyst. These polymeric materials are transformed into their value-added alcohol equivalents. Catalysis proceeds readily, under mild conditions, with $La[N(SiMe_3)_2]_3$ (1 mol%) and pinacolborane (HBpin) and shows high selectivity towards alcohols and diols, after hydrolysis.

Plastics form a wide range of polymers containing additives with innumerable and remarkable physico-chemical properties. They have become ubiquitous in all aspects of modern society, with applications in packaging, construction and furniture as well as in the medical and automotive industries. Their production has now reached 368 Mt per year and is expected to double in the next 20 years.[1,2] As a result of the linear economy of plastics, plastic waste has accumulated in the environment for years. Currently, their reprocessing is a complex and challenging task due to the presence of a wide range of materials of different chemical properties, their high resistance, and the use of various additives. Chemical recycling, which is the depolymerization of materials into valuable monomers or chemicals, has emerged as a long-term strategy complementary to mechanical recycling.[3] It opens up interesting perspectives for the recovery of carbonaceous matter, the avoidance of the exhaustion of petroleum resources and limiting the generation of pollution. Suitable pathways for efficient depolymerization under mild conditions are needed to shift towards a circular and environmentally friendly plastic economy. Solvolysis processes are well-known and enable the depolymerization of polymers formed from polycondensation reactions (polyesters, polyamides, polycarbonates) by hydrolysis, aminolysis or transesterification reactions. They are catalyzed by a number of bases, acids and ionic liquids.[4–10] They offer the recovery of pure monomers, useful for the production of new virgin plastics. Recently, the reductive cleavage of carbon–oxygen and carbon–nitrogen bonds by a molecular catalyst in presence of a hydride source has appeared as an alternative approach to access new value added products from plastics. Such reductive deconstruction methods are scarce and are all based on the use of H_2 or hydrosilanes as reductants. The catalytic hydrogenolysis of oxygenated and nitrogenated polymers (polyesters, polyamides and polyurethanes) was reported with Ru(II) and Ir(III) catalysts.[4,11–13] While high pressures and temperatures were required for these hydrogenolysis methods, the hydrosilylation of polyesters and polycarbonates took place under milder conditions with metal-based catalysts (Ir(III), Zn(II), Mo(VI)) or organocatalysts ($[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$).[9,10,14–16] With these catalysts, some oxygenated polymers were efficiently reduced into their corresponding silylated alcohols and/or even into alkanes thus raising selectivity issues. To further advance this field, the search for new catalysts as well as the use of other reductants is crucial in order to depolymerize household plastic waste and to improve the chemoselectivity of these transformations.

Because hydroboranes exhibit higher hydride donor ability than hydrosilanes and an additional pronounced Lewis acidity,[17,18] they can offer distinct reactivity and selectivity as evidenced in the catalytic reduction of carbohydrates, pyridines or CO_2 using $B(C_6F_5)_3$ as the catalyst.[19,20,21]

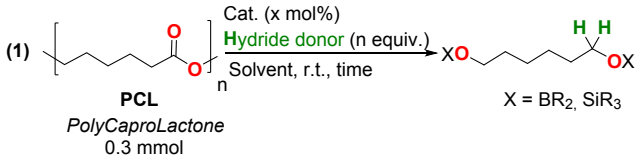
Recently, the group of Marks reported an efficient and selective catalytic reduction pathway of carbonyl compounds, such as mono-esters and mono-amides, with the borane HBpin when combined with the 4f-metal complex $La[N(SiMe_3)_2]_3$ (LaN^*_3), a powerful catalyst in organic synthesis.[22,23–25] Alkyl and aryl esters were thus cleaved into the corresponding alkoxyboranes while the amides were transformed into the tertiary and secondary amines through deoxygenative reactions. In 2019, the group of Xue revealed that the same reducing system (LaN^*_3/HBpin) could perform the hydroboration of some organic carbonates.[26] We thus considered the potential of the LaN^*_3/borane system to carry out C-O and C=O bonds cleavages in oxygenated plastic materials.

Here we report that under mild conditions, LaN^*_3 with hydroboranes as reductants, catalyzes the efficient cleavage of some polyester and polycarbonate materials. This work highlights the first use of a 4f-metal complex as a catalyst, as well as the first use of hydroboranes as a hydride source for the reductive depolymerization of carbonylated polymers.

Polycaprolactone (**PCL**), a biodegradable synthetic polyester mainly used in the biomedical field, displays a low melting point (mp = 60 °C) and was selected as the substrate of reference in our attempts to reductively depolymerize oxygenated plastics with the LaN^*_3/hydroborane system.[23–25] Indeed, among some polyesters and polycarbonates, **PCL** previously proved the easiest to cleave with hydrosilanes.[15] Its reactivity was attributed in part to its low melting point and its good solubility in a variety of

organic solvents (C_6H_6, CH_2Cl_2, THF, C_6H_5Cl) where it dissolved readily after 30 min stirring at room temperature (r.t.) or when exposed to ultrasonic waves. This relationship between reactivity and solubility of the polymer has already been reported and documented.[15]

Table 1. Optimization of the reaction conditions for the depolymerization of **PCL** catalyzed by LaN^*_3 with boron or silicon hydride donors.



Entry	Cat. (mol%)	Hydride donor (equiv. of H)	t (h)	Solvent	Yield (%)
1	LaN^*_3 (1)	HBpin (2.2)	1	C_6D_6	99
2	LaN^*_3 (1)	-	24	C_6D_6	0
3	-	HBpin (2.2)	24	C_6D_6	0
4	LaN^*_3 (1)	HBpin (2.2)	1	CD_2Cl_2	99
5	LaN^*_3 (1)	HBpin (2.2)	1	THF-d_8	99
6	LaN^*_3 (1)	HBpin (2.2)	1	C_6H_5Cl	99
7	LaN^*_3 (1)	HBpin (2.2)	1	CD_3CN	27
8	LaN^*_3 (1)	HBpin (2.2)	1	Anisole	79
9	LaN^*_3 (1)	$HB(Cy)_2$ (2.2)	1	C_6D_6	86
10[a]	LaN^*_3 (1)	CatBH (2.2)	1	C_6D_6	16
11[b]	LaN^*_3 (1)	9-BBN dimer (2.2)	1	C_6D_6	78
12[c]	LaN^*_3 (1)	$PhSiH_3$ (4.4)	24	C_6D_6	n.d.
13[c]	LaN^*_3 (1)	Et_3SiH (4.4)	24	C_6D_6	n.d.
14[c]	LaN^*_3 (1)	$(EtO)_2MeSiH$ (4.4)	24	C_6D_6	n.d.
15[c]	LaN^*_3 (1)	$(MeO)_3SiH$ (4.4)	24	C_6D_6	n.d.
16[cd]	LaN^*_3 (1)	PMHS (4.4)	24	C_6D_6	n.d.

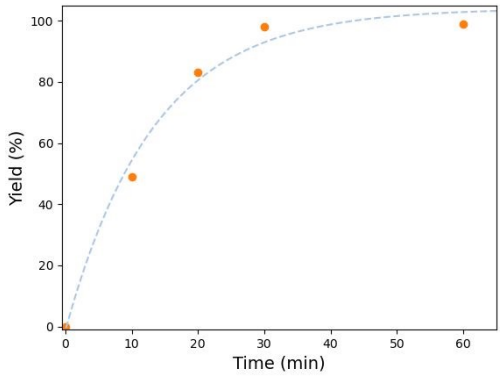
Conversions and yields measured by ^1H NMR with mesitylene as internal standard. n.d.= not detected
[a] After 22 h, 88% of $CatBO(CH_2)_6OBCat$. [b] At 100 °C, 1.1 equiv. of 9-BBN dimer (= 2.2 equiv of H). [c] At 100 °C. [d] 2.2 equiv. of H from the monomer.

Within the optimal reaction conditions reported by Marks *et al.* for the cleavage of esters,[24] LaN^*_3 (1 mol%) and HBpin (2.2 equiv. per ester group) were added into a suspension of commercial pellets of **PCL** in C_6D_6. After 1 h stirring at r.t., the pellets completely disappeared giving a clear colorless solution. The ^1H and ^{13}C NMR spectra of the reaction mixture (see SI) evidenced the complete and selective depolymerization of **PCL** giving a yield of 99% of 1,6-(hexanedioxyborane), *i.e.* $pinBO(CH_2)_6OBpin$ (Table 1, Entry 1). This reductive depolymerisation of **PCL** was almost complete after 30 min at r.t. (Figure 1) and the corresponding 1,6-hexanediol was isolated in 53% yield after hydrolysis (see SI).

To properly compare the efficiency of the La(III) catalyst with the catalysts used in hydrosilylative depolymerizations, we tested LaN^*_3 combined with hydrosilanes as hydride donors to perform the reduction of **PCL**. Regardless of the choice of hydrosilane ($PhSiH_3$, Et_3SiH, PMHS, $(EtO)_2MeSiH$, $(EtO)_3SiH$) the catalysis did not proceed at all (Table 1, Entries 12-16), even after heating up to 100°C and adding a larger amount of hydride donor to the reaction mixture (Table 1, Entries 12-16). The NMR spectra only featured signals of **PCL** and of the starting silane.

Control experiments at r.t. without the catalyst or the borane (HBpin) (Table 1, Entries 2 and 3) clearly evidenced that the depolymerization of **PCL** only occurred in presence of both compounds. In these two experiments, we only observed the dissolution of the pellets of **PCL** and no traces of other compounds were detected.

Figure 1. ^1H NMR monitoring of the formation of $pinBO(CH_2)_6OBpin$ as a function of time.



As reported above, the choice of the organic solvent was of importance to increase solubility and reactivity of the polymer. Although benzene was well suited for the hydroboration of **PCL** (Table 1, Entry 1), it is classified as CMR chemical (CMR = Carcinogen, Mutagen, Reprotoxic) and its use is severely restricted. Alternative solvents, *eg* CH_2Cl_2, THF, C_6H_5Cl, CH_3CN and anisole, viewed as less toxic from the CHEM21 solvent guide,[27] were therefore tested. When using the "*problematic solvents*" (CH_2Cl_2, THF, C_6H_5Cl, CH_3CN),[27] the depolymerizations were as efficient as in benzene (Table 1, Entries 4-6) affording 99% of $pinBO(CH_2)_6OBpin$, except for CH_3CN where **PCL** was poorly soluble. In anisole, a "*recommended solvent*", [27] the depolymerization proceeded somewhat less efficiently, providing $pinBO(CH_2)_6OBpin$ in 79% yield after 1 h.

The influence of the hydroborane was evaluated with the use of dicyclohexylborane ($(Cy)_2BH$), catecholborane (CatBH) and 9-borabicyclo[3.3.1]nonane (9-BBN) in the reduction of **PCL** (Table 1, Entries 9-11). All these hydroboranes proved less efficient than HBpin affording, after 1 h, $R_2BO(CH_2)_6OBR_2$ in 86%, 16% and 78% yield, respectively. This is in agreement with the observation of Marks *et al.* on the reduction of mono-esters.[24]

These results evidence that the yields in $R_2BO(CH_2)_6OBR_2$ are not strictly related to the hydridic character of the hydroborane which follows the order HBpin > CatBH > 9-BBN for the cyclic boranes.[28] Marks et al attributed the excellent reductive ability of HBpin towards esters to its initial coordination to the La^{3+} ion through one of its oxygen atom.[24] In the presence of polyesters, such a coordination is not necessary to ensure a fast turnover, as highlighted with the good performances of the alkyl hydroboranes $(Cy)_2BH$ and 9-BBN.

The successful reductive depolymerization of **PCL** led us to expand the scope to other aliphatic and aromatic polyesters. With the same reduction conditions as for **PCL** (Table 1, Entry 1), a

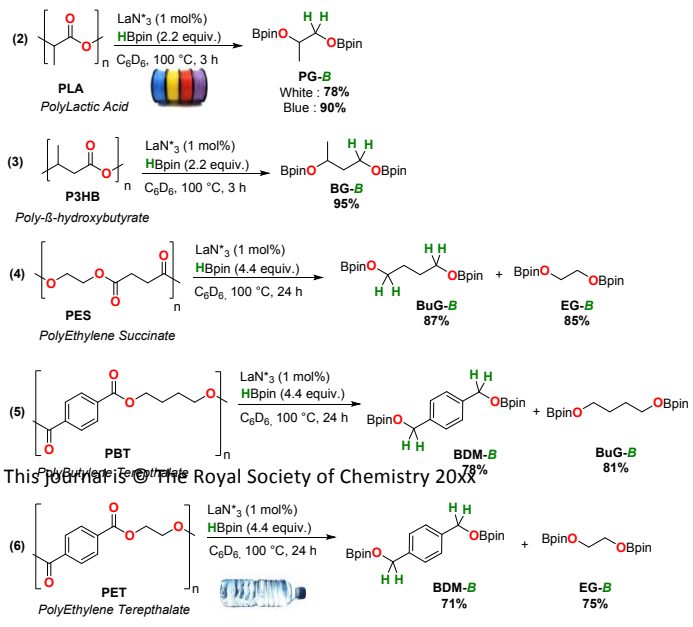
number of polyesters (**P3HB**, **PLA**, **PES**, **PBT**, **PET**), whether chemically pure or from household plastics (for **PLA** and **PET**), were found inert at r.t., presumably due to their high melting points or their low solubility.

PLA and **P3HB**, the most common polyhydroxyalkanoates (PHAs) are two biobased and biodegradable polyesters.[29,30]

Large insoluble pieces of colored **PLA** filaments (L X D ≈ 0.5 × 0.3 cm (white) and ≈ 0.6 × 0.2 cm (blue)), utilized in 3D printers, were used in order to evaluate the influence of additives on the nature and yields in depolymerization products. Within 3 h at 100 °C, all the plastic fragments disappeared and the colorless or blue solution with a small amount of undissolved white or blue solid remaining which was attributed to insoluble contaminants. NMR spectra of these solutions revealed the presence of the diborylated propylene glycol (**PG-*B***), as the sole product in 78% or 90% yield, respectively (Scheme 1, Eq. 2). The relatively high yields of **PG-*B*** evidenced a high tolerance of LaN*$_3$ toward contaminants and the distinct yields are related to the different charges in additives (see SI). Interestingly, the yields in **PG-*B*** were unchanged in presence of excess borane (4.4 equiv) and no over-reduced products such as borylated hexanol or propane could be detected by NMR analysis. Similarly, pure and finely ground commercial **P3HB** powder, when treated with LaN*$_3$ and 2.2 equiv. or an excess (4.4 equiv.) of HBpin, rapidly decomposed into **BG-*B*** obtained in excellent yield (95%) after 3 h at 100 °C (Scheme 1, Eq. 3).

To reduce commercial pellets of **PES**, an aliphatic biodegradable copolymer of ethylene glycol and butanedioic acid, 4 equiv. of reductant were needed to cleave the ester groups into the borylated monomeric derivatives. With 4.4 equiv. or an excess (8.8 equiv.) of HBpin, using the same conditions as with **PLA** or **P3HB**, the depolymerization of **PES** (> 85%) into the bis(borylated)butanediol (**BuG-*B***) and bis(borylated)ethyleneglycol (**EG-*B***) took eight times longer than **PLA** or **P3HB** (Scheme 1, Eq. 4). This effect could be attributed to the distinct solubilities of these polymers related to their granulometry (see SI).

The two aromatic thermoplastics containing the terephthalate group, **PBT** and **PET**, obtained from small chunks of commercial pellets and Evian© bottles, respectively, behaved similarly to **PES** under the same reaction conditions. After 24 h at 100 °C and with a slight excess of HBpin (4.4 equiv.), both **PBT** and **PET** were depolymerized into their corresponding dialkoxyboranes (Scheme 1, Eqs. 5 and 6).



Good NMR yields of the borylated 1,4-benenedimethanol (**BDM-*B***) were obtained, reaching 78% and 71% from **PBT** and **PET**, respectively. The yields in **BuG-*B*** or **EG-*B*** were similar to the yields of **BDM-*B*** within the NMR integration errors. The hardly lower yields in monomers obtained from **PET** might be related to the distinct purities of **PBT** and **PET** samples.

Scheme 1. Reductive depolymerization of the polyesters **PLA**, **P3HB**, **PES**, **PBT** and **PET** with HBpin and catalyst LaN*$_3$.

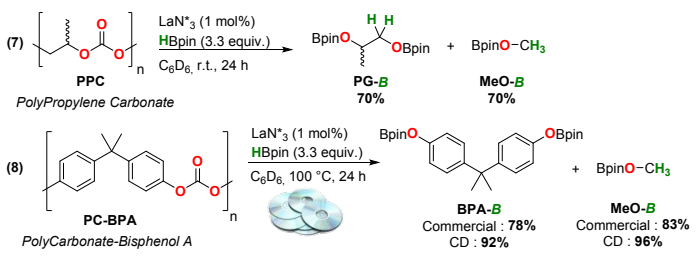
In the above polyester reductions (Scheme 1, Eqs. 1-6), the LaN*$_3$/HBpin system showed high selectivities towards the borylated diols which were obtained in good yields (70%–99%). Over-reduced products (monoborylether derivatives and the alkanes : butane, ethane, propane or *p*-xylene) often obtained under hydrosilylation conditions with $B(C_6F_5)_3$, Ir(III), Zn(II) or Mn(VI) catalysts[14–16,31] were not observed. Under hydrosilylation conditions, the reduction of polycarbonates suffered from poor chemoselectivity which appeared to be strongly dependent of the reaction conditions, the nature of the reductant and its quantity. For example, with the Ir(III) catalyst [(POCOP)IrH(THF)][$B(C_6F_5)_4$] and 3 equiv. of Et_3SiH at 65 °C, **PLA** was degraded into a mixture of the mono and bisilylated derivatives of propyleneglycol (31% and 64%, respectively) and ethane was found together with $(Et_3Si)_2O$. With excess Et_3SiH at 90 °C, monosilylated propyleneglycol was the major product (92%), with ethane (8%) and siloxane.[15]

With a more electrophilic carbonyl carbon, esters are more easily reduced than organic carbonates. As mentioned previously, recently, Xue *et al.* proved the efficiency of the LaN*$_3$/HBpin system in the reduction of carbonates into alkoxyboranes.[26] In the field of polymers, the catalytic reduction of polycarbonates has only been described by our group with hydrosilanes and $B(C_6F_5)_3$ or Ir(III) as catalyst, while Robertson *et al.*, reported in a seminal work their catalytic controlled hydrogenative deconstruction with a Ru(II) pincer catalyst.[11]

The reduction of polycarbonates was considered, in particular polypropylene carbonate (**PPC**) and the polycarbonate of bisphenol A (**PC-BPA**, commercial pellets and compact disk chunks (CD)), which are common plastics with numerous applications (glass, food contact, medical, construction, etc.).[32]

3 equiv. of HBpin per carbonate group were required to reduce these polymers into the corresponding monomeric alkoxyboranes (Scheme 2, Eqs. 7 and 8).

Scheme 2. Reductive depolymerization of the polycarbonate **PPC** and **PC-BPA** with HBpin and LaN*$_3$



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When pellets of **PC-BPA** or **PPC** were introduced in a benzene solution of LaN*$_3$ (1 mol%) and HBpin (3.3 equiv.), we observed after 24 h at 100 °C the decomposition of **PPC** into **PG-*B*** and **MeO-*B*** (70% yield) while **PC-BPA** was transformed into **BPA-*B*** (78%) and **MeO-*B*** (83%). For both substrates, as for the polyesters, no over-reduced by-products could be detected, even in the presence of an excess of HBpin (6.6 equiv.). In comparison, the treatment of **PPC** by the Ir(III) catalyst (0.5 mol%) in presence of Et_3SiH (4 equiv.) gave excellent selectivity (99%) for the bisilylated propanol and silylated methanol, after 3 h at 65 °C.[15] Concerning the depolymerization of **PC-BPA**, the organocatalyst $B(C_6F_5)_3$ (2 mol%) with TMDS (2.2 equiv.), was by far the most active catalyst, affording the silylated bisphenol-A (98%), rapidly (1 h) and without any heating.[16]

In conclusion, this work highlights the first use of hydroboranes to carry out efficient catalytic reductive depolymerization of polyesters and polycarbonates into their corresponding borylated alcohols. This transformation proceeded under mild conditions and was achieved by using a powerful lanthanide catalyst (LaN*$_3$ in 1 mol%). This is the first use of an f-element complex in the chemical depolymerization of polymers. In contrast to the few systems using hydrosilanes as hydride sources, the LaN*$_3$/HBpin system, even in presence of an excess of reductant, offers excellent yields and selectivities towards alkoxyboranes by avoiding the formation of over-reduced derivatives.

Conflicts of interest

There are no conflicts to declare.

Note and references

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