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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, b and Thibault Cantat a, b

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(SiMe3)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 (polymers, 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 H2 or hydroxilanes 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,C][B(C6F5)4] and B(C6F5)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 hydroxilanes and an additional pronounced Lewis acidity17, 18 they can offer distinct reactivity and selectivity as evidenced in the catalytic reduction of carbohydrates, pyridines or CO2 using B(C6F5)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(SiMe3)3] (LaN3), 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 (LaN3/HBpin) could perform the hydroboration of some organic carbonates.26 We thus considered the potential of the LaN3/borane system to carry out C-O and C=O bonds cleavages in oxygenated plastic materials.

Here we report that under mild conditions, LaN3 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 carboxylated polymers.

Polycapro lactone (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 LaN3/HBpin system.23, 25 Indeed, among some polyesters and polycarbonates, PCL previously proved the easiest to cleave with hydroxilanes.15 Its reactivity was attributed in part to its low melting point and its good solubility in a variety of...
organic solvents (C\textsubscript{6}H\textsubscript{5}O, CH\textsubscript{3}Cl\textsubscript{2}, THF, C\textsubscript{6}H\textsubscript{5}Cl) 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.\textsuperscript{15}

Table 1. Optimization of the reaction conditions for the depolymerization of PCL catalyzed by LaN\textsuperscript{*}3 with boron or silicon hydride donors.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat. (mol%)</th>
<th>Hydride donor (equiv. of H)</th>
<th>t (h)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>HBpin (2.2)</td>
<td>1</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>-</td>
<td>24</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>HBpin (2.2)</td>
<td>24</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>HBpin (2.2)</td>
<td>1</td>
<td>CD\textsubscript{2}Cl\textsubscript{2}</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>HBpin (2.2)</td>
<td>1</td>
<td>THF-\textsubscript{d}6</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>HBpin (2.2)</td>
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<td>C\textsubscript{6}H\textsubscript{5}Cl</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>HBpin (2.2)</td>
<td>1</td>
<td>CD\textsubscript{3}CN</td>
<td>27</td>
</tr>
<tr>
<td>8</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>HBpin (2.2)</td>
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<td>Anisole</td>
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<td>9</td>
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<td>HB(C\textsubscript{6}H\textsubscript{5})\textsubscript{3} (2.2)</td>
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<td>C\textsubscript{6}D\textsubscript{5}</td>
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<td>10\textsuperscript{a}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>CatBH (2.2)</td>
<td>1</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>16</td>
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<tr>
<td>11\textsuperscript{b}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>9-BBN dimer (2.2)</td>
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<td>78</td>
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<tr>
<td>12\textsuperscript{c}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>PhSi\textsubscript{2}H\textsubscript{2} (4.4)</td>
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<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>n.d.</td>
</tr>
<tr>
<td>13\textsuperscript{d}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
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<td>24</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>n.d.</td>
</tr>
<tr>
<td>14\textsuperscript{e}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>(EtO)\textsubscript{2}MeSi\textsubscript{2}H\textsubscript{2} (4.4)</td>
<td>24</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>n.d.</td>
</tr>
<tr>
<td>15\textsuperscript{f}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>(MeO)\textsubscript{2}SiH\textsubscript{2} (4.4)</td>
<td>24</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>n.d.</td>
</tr>
<tr>
<td>16\textsuperscript{g}</td>
<td>LaN\textsuperscript{*}3 (1)</td>
<td>PMH\textsubscript{2}S\textsubscript{2}H\textsubscript{2} (4.4)</td>
<td>24</td>
<td>C\textsubscript{6}D\textsubscript{5}</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Conversions and yields measured by \textsuperscript{1}H NMR with mesitylene as internal standard. n.d.\textsuperscript{a} = not detected
\textsuperscript{a} After 22 h, 88% of CatBO(CH\textsubscript{3})\textsubscript{3}OBCat. \textsuperscript{b} At 100 °C, 1.1 equiv. of 9-BBN dimer (= 2.2 equiv of H). \textsuperscript{c} At 100 °C. \textsuperscript{d} 2 equiv. of H from the monomer.

Within the optimal reaction conditions reported by Marks et al. for the cleavage of esters,\textsuperscript{24} LaN\textsuperscript{*}3 (1 mol\%) and HBpin (2.2 equiv. per ester group) were added into a suspension of commercial pellets of PCL in C\textsubscript{6}D\textsubscript{5}. After 1 h stirring at r.t., the pellets completely disappeared giving a clear colorless solution. The \textsuperscript{1}H and \textsuperscript{1}3C NMR spectra of the reaction mixture (see SI) evidenced the complete and selective depolymerization of PCL giving a yield of 99% of 1,6-(hexanedi oxyborane), i.e. pinBO(CH\textsubscript{3})\textsubscript{2}O\textsubscript{2}Pin (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\textsuperscript{*}3 combined with hydride donors as hydride donors to perform the reduction of PCL. Regardless of the choice of hydrosilane (PhSi\textsubscript{2}H\textsubscript{2}, Et\textsubscript{2}Si\textsubscript{2}H, PMH\textsubscript{2}S\textsubscript{2}H\textsubscript{2}, (EtO)\textsubscript{2}MeSi\textsubscript{2}H\textsubscript{2}, (EtO)\textsubscript{2}SiH\textsubscript{2}) 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. \textsuperscript{1}H NMR monitoring of the formation of pinBO(CH\textsubscript{3})\textsubscript{2}O\textsubscript{2}Pin 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\textsubscript{3}Cl\textsubscript{2}, THF, C\textsubscript{6}H\textsubscript{5}Cl, CH\textsubscript{3}CN and anisole, viewed as less toxic from the CHEM21 solvent guide,\textsuperscript{27} were therefore tested. When using the “problematic solvents” (CH\textsubscript{3}Cl\textsubscript{2}, THF, C\textsubscript{6}H\textsubscript{5}Cl, CH\textsubscript{3}CN),\textsuperscript{27} the depolymerizations were more efficient as in benzene (Table 1, Entries 4-6) affording 99% of pinBO(CH\textsubscript{3})\textsubscript{2}O\textsubscript{2}Pin, except for CH\textsubscript{3}CN where PCL was poorly soluble. In anisole, a “recommended solvent”,\textsuperscript{27} the depolymerization proceeded somewhat less efficiently, providing pinBO(CH\textsubscript{3})\textsubscript{2}O\textsubscript{2}Pin in 79% yield after 1 h.

The influence of the hydroborane was evaluated with the use of dicyclohexylborane ((Cy)\textsubscript{2}BH), 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\textsubscript{2}BO(CH\textsubscript{3})\textsubscript{2}O\textsubscript{2}R\textsubscript{3} in 86%, 16% and 78% yield, respectively. This is in agreement with the observation of Marks et al. on the reduction of mono-esters.\textsuperscript{24} These results evidence that the yields in R\textsubscript{2}BO(CH\textsubscript{3})\textsubscript{2}O\textsubscript{2}R\textsubscript{3} are not strictly related to the hydridic character of the hydroborane which follows the order HBpin > CatBH > 9-BBN for the cyclic boranes.\textsuperscript{28} Marks et al attributed the excellent reductive ability of HBpin towards esters to its initial coordination to the La\textsuperscript{3+} ion through one of its oxygen atom.\textsuperscript{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)\textsubscript{2}BH 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)ethylene glycol (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-benzenedimethanol (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(C6F5)3, Ir(III), Zn(II) or Mn(VI) catalysts14–16,31 were not observed. Under hydrosilylation conditions, the reduction of polycarbonates suffered from poor chemoselectivity which appeared to be strongly dependent on the reaction conditions, the nature of the reductant and its quantity. For example, with the Ir(III) catalyst [(POCOP)Ir(H)(THF)]B(C6F5)3 and 3 equiv. of Et3SiH at 65 °C, PLA was degraded into a mixture of the mono and bisilylated derivatives of propylene glycol (31% and 64%, respectively) and ethane was found together with (Et3Si)2O. With excess Et3SiH at 90 °C, monosilylated propylene glycol 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 alkoxboranes.26 In the field of polymers, the catalytic reduction of polycarbonates has only been described by our group with hydrosilanes and B(C6F5)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 disc 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 alkoxboranes (Scheme 2, Eqs. 7 and 8).

Scheme 2. Reductive depolymerization of the polycarbonate PPC and PC-BPA with HBpin and LaN*3.
When pellets of PC-BPA or PPC were introduced in a benzene solution of LaN\textsuperscript{3+} (1 mol\%) and HBpin (3.3 equiv.), we observed after 24 h at 100 °C the decomposition of PPC into PG-\textit{B} and MeO-\textit{B} (70% yield) while PC-BPA was transformed into BPA-\textit{B} (78%) and MeO-\textit{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\textsubscript{3}SiH (4 equiv.) gave excellent selectivity (99%) for the bisilylated propanol by the Ir(III) catalyst (0.5 mol\%) in presence of Et\textsubscript{3}SiH (4 equiv.) was by far the most active catalyst, affording the silylated bisphenol-A (98%), rapidly (1 h) and without any heating.\textsuperscript{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\textsuperscript{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\textsuperscript{3+}/HBpin system, even in presence of an excess of reductant, offers excellent yields and selectivities towards alkoxylboranes by avoiding the formation of over-reduced derivatives.

**Conflicts of interest**

There are no conflicts to declare.

**Note and references**

For financial support, we acknowledge CEA, CNRS, the University Paris-Saclay, and the European Research Council (ERC Consolidator Grant Agreement no. 818260). T.C. thanks the Fondation Louis D.–Institut de France for its major support.

29. Note: PLA is synthesized from lactic acid obtained through the fermentation of sugars or starches. PHAs are naturally produced by microorganisms from various carbon sources and stored inside cells as an energy source to metabolize. T. Gérard, Doctoral dissertation, École Nationale Supérieure des Mines de Paris, 2013.