Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2022

Supporting Information

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

Marie Kobylarski, Jean-Claude Berthet*, Thibault Cantat*

NIMBE, CEA Paris-Saclay, 91191 Gif-sur-Yvette Cedex (France)

E-mails : jean-claude.berthet@cea.fr, thibault.cantat@cea.fr

Table of Contents

1.	General considerations	3
2.	General catalytic procedures	4
3.	Results	7
4.	¹ H and ¹³ C{ ¹ H}NMR	8
5.	References	26

1. General considerations

Unless otherwise stated, all reactions and manipulations were performed at 20 °C in a recirculating *mBraunLabMasterDP* inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 80 °C. NMR spectra were obtained using a *Bruker AVANCE Neo 400 MHz* spectrometer. Chemical shifts for ¹H, ¹³C NMR and ¹¹B{¹H} were referenced to solvent impurities.

The 4 Å molecular sieve (Aldrich) was activated by drying under dynamic vacuum at 250 °C for 48 h prior to use. Mesitylene (Aldrich) was stored over activated 4 Å molecular sieves and used directly without further purification. d_6 -benzene (C₆D₆) and d-chloroform (CDCl₃) were purchased from Eurisotop and used without further purification.

La[N(SiMe₃)₂]₃ was purchased from Aldrich, degassed and stored in the gloves box. Likewise, all the hydroboranes and hydrosilanes were obtained from Aldrich and used as received after degassing and storage under argon. Polymers such as polycaprolactone (PCL), white poly(lactic acid) (PLA), poly(3-hydroxybutyrate) (P3HB), polyethylene(succinate) (PES), polybutylene terephthalate (PBT), poly(propylene carbonate) (PPC) and poly(bisphenol A carbonate) (PC-PBA) were purchased from Aldrich, stored in the gloves box and used without further purification. Blue poly(lactic acid) (PLA) was obtained from 3D printer wires. Polyethylene terephthalate (PET) chunks were obtained from a commercial Evian[®] water bottle and used without additional treatment. Poly(bisphenol A carbonate) chunks were obtained from Compact Disks (PC-BPA (CD)) and put in reaction without further treatment.



Figure S1. Commercial polymers and plastics depolymerized

2. General catalytic procedures

The different experiments were prepared and conducted following the procedures described below. The number of moles and equivalents of the different polymers and plastics correspond to those of the corresponding monomers. For all the reactions the commercial pellets of polymers were weighted without cutting and the other reagents were added according to this weighted mass.



Figure S2. Molecular weight of the corresponding monomers of the different polymers depolymerized

- Procedure for the optimization of the reaction

A J. Young NMR tube was charged with **PCL** (34 mg, 0.30 mmol, 1 equiv.) and La[N(SiMe₃)₂]₃ (1.9 mg, 0.003 mmol, 1 mol%) followed by the deuterated solvent, C₆D₆ (0.3 mL, 3.4 mmol, 11 equiv.) and the mesitylene as an internal standard (21 μ L, 0.15 mmol, 0.5 equiv.). To the resulting colorless solution was added the hydride donor (0.66 mmol, 2.2 equiv.). The tube was then sealed and rotated at room temperature (r.t.) or warmed in a silicon oil bath maintained at 100 °C during the required time. Yields in monomers were determined by integration of the ¹H NMR signals versus those of mesitylene ($\delta_{H} = 6.58$ and 2.08 ppm in C₆D₆).

After the catalysis, the pellets of PCL were completely dissolved or depolymerized. All the homogenous reaction mixtures were colorless except for the hydrosilanes where they were yellowish.

- Procedure for the scale up depolymerization of PCL followed by hydrolysis

A 25 mL round bottom flask was charged with **PCL** (118 mg, 1 mmol, 1 equiv.), La[N(SiMe₃)₂]₃ (9 mg, 0.01 mmol, 1 mol%) and then the pinalcolborane (320 μ L, 2.2 mmol, 2.2 equiv.) followed by THF (1mL, 12.3 mmol, 12 equiv.). The reaction mixture was stirred vigorously at room temperature during 24 h. At the end, the mixture was a homogeneous colorless solution. After evaporating under vacuum the excess of HBpin and the solvent, the borylated alcohol PinBO(CH₂)₆OBpin was collected as a colorless oil. It was hydrolyzed in a 1M NaOH aqueous solution (10 mL) and MeOH (10 mL) at 50 °C for 24 h. The alcohol HO(CH₂)₆OH was extracted in dichloromethane (4x20 mL) and the organic phases were dried other MgSO₄. Then, the crude (colorless oil) was obtained after removing the solvent under vacuum and purified by silica gel column chromatography using EtOAc and pentane (gradient from 5/5 to 3/1). Final yield of 1,6-hexanediol (white solid): 87%.

- Procedure for polyesters with one ester group (PCL, PLA, P3HB)

A J. Young NMR tube was charged with pellets, chunks or powder of a plastic polymer (0.30 mmol, 1 equiv.), La[(N(SiMe_3)_2]_3 (1.9 mg, 0.003 mmol, 1 mol%), the deuterated solvent C₆D₆ (0.3 mL, 3.4 mmol, 11 equiv.) and mesitylene as an internal standard (21 μ L, 0.15 mmol, 0.5 equiv.). To the colorless solution (containing the plastic fragments) was added the pinalcolborane (96 μ L, 0.66 mmol, 2.2 equiv.). The tube was then sealed and rotated at room temperature or warmed in a silicon oil bath at 100 °C during the required time. Yields in borylated alcohols were determined by integration of the ¹H NMR signals versus those of mesitylene ($\delta_{H} = 6.58$ and 2.08 ppm in C₆D₆).

After the catalysis, the pellets/chunks of the polymer have completely or partially disappeared depending on the efficiency of the depolymerization reaction. In blue or white PLA reaction mixtures, the solution are colorless and contain blue or white suspension and deposits of the additives (see Figure).



Figure S3. NMR tubes after depolymerization of blue and white **PLA** : left (deposit of the solid in the crude mixture), right : isolated solid

From an NMR tube containing 23.9 mg of the blue **PLA** chunks, at the end of the catalysis (3h or 60h at 100°C), we recovered \approx 2 mg of blue solid after washings with diethyl ether and drying under vacuum.

From an NMR tube containing 21.2 mg of the white **PLA** chunks, at the end of the catalysis (3h or 60h at 100°C), we recovered a mean values of \approx 4.4 mg of white solid after washings with diethyl ether and drying under vacuum.

In order to check if the reduction could go further with formation of alkanes instead of alcohol derivatives, pinalcolborane (96 μ L, 0.66 mmol, 2.2 equiv.) was added to the ended mixture. After rotation of the tube at room temperature or heating at 100 °C for 2 days no evolution was observed except an increase in the yields of borylated alcohols.

- Procedure for polyesters with two ester groups (PES, PET, PBT)

A J. Young NMR tube was charged with pellets or chunks of the considered polymer (0.30 mmol, 1 equiv.), La[N(SiMe_3)_2]_3 (1.9 mg, 0.003 mmol, 1 mol%), the solvent C₆D₆ (0.3 mL, 3.4 mmol, 11 equiv.) and mesitylene as an internal standard (21 μ L, 0.15 mmol, 0.5 equiv.). To the colorless solution (containing the plastic fragments) was added the pinalcolborane (192 μ L, 1.32 mmol, 4.4 equiv.). The tube was then sealed and warmed in a silicon oil bath at 100 °C at room temperature during the required time. Yields in borylated alcohols were determined by integration of the ¹H NMR signals versus those of mesitylene ($\delta_{H} = 6.58$ and 2.08 ppm in C₆D₆).

After the catalysis, the pellets/chunks of the polymer have completely or partially disappeared depending on the efficiency of the depolymerization reaction. With PET, the reaction mixture was found colorless. With PBT and PES, the resulting cloudy suspension were whitish and yellowish,

respectively while with PES, white flakes were also observed in the resulting suspension. The deposits and colors are likely insoluble dies and additives.

In order to check if the reduction reaction could go further with transformation of the alcohol derivatives into the corresponding alkanes, pinalcolborane (192 μ L, 1.32 mmol, 4.4 equiv.) was added. After rotation of the tube at room temperature or heating at 100 °C for 2 days no evolution was observed except an increase in the yields of borylated alcohols.

- Procedure for polycarbonate (PPC, PC-BPA, PC-BPA(CD))

A J. Young NMR tube was charged with plastic polymer (0.30 mmol, 1 equiv.), $La[N(SiMe_3)_2]_3$ (1.9 mg, 0.003 mmol, 1 mol%), the solvent C₆D₆ (0.3 mL, 3.4 mmol, 11 equiv.) and mesitylene as an internal standard (21 µL, 0.15 mmol, 0.5 equiv.). To the resulting colorless solution containing the plastic fragments was added the pinalcolborane (144 µL, 0.99 mmol, 3.3 equiv.). The tube was sealed and rotated at room temperature or warmed in a silicon oil bath at 100 °C during the required time. Yields in borylated alcohols were determined by integration of the ¹H NMR signals versus those of mesitylene ($\delta_{H} = 6.58$ and 2.08 ppm in C₆D₆).

After the catalysis, the pellets/chunks of the polymer have completely or partially disappeared depending on the efficiency of the depolymerization reaction. All the ended mixtures were colorless except with **PC-BPA (CD)** where a fine white suspension was observed (particles of the printed white film on the CD).

In order to check if the reduction reaction could afford alkanes instead of borylated alcohol, pinalcolborane (144 μ L, 0.99 mmol, 3.3 equiv.) was added to the above reacted mixture. The tube was rotated at room temperature or heated at 100 °C for 2 days. Except an increasing of the yields in alcohols derivatives, no alkane products could be detected.

3. Results



Entry	Cat. (mol%)	Borane (equiv. of H)	t (h)	Solvant	Yield (%)
1ª	La[N(SiMe ₃) ₂] ₃ (1)	HBpin (2.2)	1	C ₆ D ₆	99
2	La[N(SiMe ₃) ₂] ₃ (1)	-	24	C_6D_6	n.d.
3	-	HBpin (2.2)	24	C_6D_6	n.d.
4	La[N(SiMe ₃) ₂] ₃ (1)	HBpin (2.2)	1	CD_2Cl_2	99
5	La[N(SiMe ₃) ₂] ₃ (1)	HBpin (2.2)	1	THF-d ₈	99
6	La[N(SiMe ₃) ₂] ₃ (1)	HBpin (2.2)	1	C_6H_5CI	99
7	La[N(SiMe ₃) ₂] ₃ (1)	HBpin (2.2)	1	CD ₃ CN	27
8	La[N(SiMe ₃) ₂] ₃ (1)	HBpin (2.2)	1	Anisole	79
9	La[N(SiMe ₃) ₂] ₃ (1)	HB(Cy) ₂ (2.2)	1	C_6D_6	86
10 ^b	La[N(SiMe ₃) ₂] ₃ (1)	CatBH (2.2)	1	C_6D_6	16
11 ^c	La[N(SiMe ₃) ₂] ₃ (1)	9-BBN dimer (2.2)	1	C_6D_6	78
12 ^d	La[N(SiMe ₃) ₂] ₃ (1)	PhSiH₃ (4.4)	24	C_6D_6	n.d.
13 ^d	La[N(SiMe ₃) ₂] ₃ (1)	Et ₃ SiH (4.4)	24	C_6D_6	n.d.
14 ^d	La[N(SiMe ₃) ₂] ₃ (1)	(EtO) ₂ MeSiH (4.4)	24	C_6D_6	n.d.
15 ^d	La[N(SiMe ₃) ₂] ₃ (1)	(MeO)₃SiH (4.4)	24	C_6D_6	n.d.
16^{de}	$La[N(SiMe_3)_2]_3(1)$	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 Without rotation of the tube, at RT, the reaction time is longer (45% yield after 1 h and 86% yield after 24 h). ^b After 22 h, 88% of CatBO(CH₂)₆OBCat. ^c At 100 °C, 1.1 equiv. of 9-BBN dimer (= 2.2 equiv of H). ^d At 100 °C, **PCL** pellets were completely dissolved after 30 min. ^e 2.2 equiv. of H from the monomer.

Table S1. Optimization of the depolymerization reaction of PCL promoted by $La[N(SiMe_3)_2]_3$ in presence of hydroboranes or hydrosilanes

The 9-BBN dimer is insoluble at room temperature in C_6D_6 and the depolymerization reaction did not proceed. Heating at 100 °C helped the dissolution of 9BBN dimer and induced the depolymerization of the **PCL** pellets.

4. ¹H and ¹³C{¹H} NMR

In the ¹H NMR and ¹³C NMR analyses, the signals of the catalyst La[N(SiMe₃)₂]₃ were observable (singlets at $\delta_{\rm H}$ = 0.06 ppm and at $\delta_{\rm C}$ = 2.26 ppm for the Me groups, respectively). In some case, traces of unidentified decomposition products of HBpin and La[N(SiMe₃)₂]₃ were observed in the NMR spectra, as described by Marks *et al.* in their stoichiometric studies.¹ C₆D₆ (solvent) showed a singlet at $\delta_{\rm H}$ = 7.15 ppm and a triplet at $\delta_{\rm C}$ = 127.63 ppm. CDCl₃ (singlet at $\delta_{\rm H}$ =7.29 ppm and triplet at $\delta_{\rm C}$ =77.02 ppm) was only used for the ¹H NMR and ¹³C NMR analyses of 1,6-hexanediol.



NMR data:



¹**H NMR** (400 MHz, C_6D_6) δ (ppm) = 3.82 (t, *J* = 6.6 Hz, 4H, (CH₂)_a), 1.43 (m, 4H, (CH₂)_b), 1.20 (m, 4H, (CH₂)_c), 1.06 (s, 24H, CH₃).

¹³C{¹H} NMR (400 MHz, C_6D_6) δ (ppm) = 81.93 (C_q), 64.54 ((CH_2)_a), 31.57 ((CH_2)_b), 25.31 ((CH_2)_c), 24.34 (CH_3).



Figure S4. Characterization of the monomer pinBO(CH₂)₆OBpin in the ¹H and ¹³C NMR spectra of the reductive depolymerization of **PCL** in C₆D₆ at RT (**PCL** with 1 mol% of La[N(SiMe₃)₂]₃, 2.2 equiv. of HBpin).





¹**H NMR** (400 MHz, CDCl₃) δ (ppm) = 3.68 (t, *J* = 6.6 Hz, 4H, (C*H*₂)_a), 1.61 (m, 4H, (C*H*₂)_b), 1.45-1.35 (m, 4H, (C*H*₂)_c), 1.37 (bs, 2H, OH).

¹³C{¹H} NMR (400 MHz, CDCl₃) δ (ppm) = 62.93 ((CH₂)_a), 32.70 ((CH₂)_b), 25.56 ((CH₂)_c).



Figure S5. ¹H and ¹³C NMR spectra of 1,6-hexanediol obtained from the hydrolysis of PinBO(CH₂)₆OBpin.





¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 4.44 (h, *J* = 6.2 Hz, 1H, *H*_b), 3.80 (d, *J* = 5.0 Hz, 2H, (C*H*₂)_a), 1.09 (s, 12H, C*H*₃), 1.07 (s, 12H, C*H*₃), 1.04 (d, *J* = 6.2 Hz, 3H, (C*H*₃)_c).

¹³C{¹H} NMR (400 MHz, C_6D_6) δ (ppm) = 82.16 (C_q), 82.01 (C_q), 70.31 (C_a), 69.17 (C_b), 24.41 (CH_3), 24.38 (CH_3), 24.34 (CH_3), 24.27 (CH_3), 18.19 (C_c).



Figure S6. ¹H and ¹³C NMR spectra of the crude mixture obtained from the reductive depolymerization of blue **PLA** at 100 °C in benzene (**PLA** with La[N(SiMe₃)₂]₃ (1 mol%), 2.2 equiv. of HBpin). Characterization of the borylated monomer.





¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 4.45 (m, 1H, H_c), 4.00 (m, 2H, (CH₂)_a), 1.73 (m, 2H, (CH₂)_b), 1.13 (d, J= 6.2 Hz, 3H, (CH₃)_d), 1.05 (s, 24H, CH₃).

¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 81.99 (C_q), 81.85 (C_q), 67.68 (C_a), 61.60 (C_c), 39.92 (C_b), 24.35 (CH_3), 24.32 (CH_3), 24.28 (CH_3),

22.49 (C_d).



Figure S7. ¹H and ¹³C NMR spectra of the reaction mixture obtained from the reductive depolymerization of **P3HB** at 100 °C in C_6D_6 . (**P3HB** with $La[N(SiMe_3)_2]_3$ (1 mol%), 2.2 equiv. of HBpin). Identification of the characteristic peaks of the borylated monomer.





¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 3.79 (m, 4H, (CH₂)_a), 1.52 (m, 4H, (CH₂)_b), 1.04 (s, 24H, CH₃).

¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 81.95 (C_q), 64.17 ((CH₂)_a), 27.76 ((CH₂)_b), 24.32 (CH₃).



¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 3.85 (s, 4H, CH₂), 1.06 (s, 24H, CH₃).

¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 81.95 (C_q), 64.95 (CH₂), 24.32 (CH₃).



Figure S8. ¹H and ¹³C NMR spectra of the crude mixture obtained from the reductive depolymerization of **PES** at 100 °C in C_6D_6 (**PES** with $La[N(SiMe_3)_2]_3$ (1 mol%) and 4.4 equiv. of HBpin). Characterization of the borylated monomers.





¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 3.80 (m, 4H, (CH₂)_a), 1.53 (m, 4H, (CH₂)_b), 1.04 (s, 24H, CH₃).

¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 81.96 (C_q), 64.18 ((CH₂)_a), 27.78 ((CH₂)_b), 24.31 (CH₃).

¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 7.20 (s, 4H, H_{Ar}), 4.84 (s, 4H,C H_2), 1.04 (s, 24H, C H_3).

¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 138.70 ($C_{q Ar}$), 126.64 (C_{Ar}), 82.31 (C_q), 66.26 (CH_2), 24.31 ($C(CH_3)_2$).



Figure S9. ¹H and ¹³C NMR spectra of the crude mixture obtained from the reductive depolymerization of **PBT** at 100 °C in C_6D_6 (**PBT** with $La[N(SiMe_3)_2]_3$ (1 mol%) and 4.4 equiv. of HBpin). Characterization of the borylated monomers.



PolyEthylene Terephtalate 0.28 mmol

NMR data:



¹H NMR (400 MHz, C₆D₆) δ (ppm) = 3.87 (s, 4H, CH₂), 1.06 (s, 24H, CH₃). ¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 82.14 (C_q), 64.97 (CH₂), 24.30 (CH₃).

¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 7.20 (s, 4H, H_{Ar}), 4.84 (s, 4H,C H_2), 1.04 (s, 24H, C H_3).

¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 138.70 ($C_{q Ar}$), 126.65 (C_{Ar}), 82.31 (C_q), 66.26 (CH_2), 24.32 ($C(CH_3)_2$).



Figure S10. ¹H and ¹³C NMR spectra of the crude mixture obtained from the reductive depolymerization of **PET** at 100 °C in C_6D_6 (**PET** with La[N(SiMe_3)_2]_3 (1 mol%) and 4.4 equiv. of HBpin). Characterization of the borylated monomers.





¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 3.46 (s, 3H, OCH₃), 1.07 (s, 12H, CH₃). ¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 82.08 (C_q), 51.91 (OCH₃), 24.32 (CH₃).



¹**H NMR** (400 MHz, C₆D₆) δ (ppm) = 4.40 (h, J = 6.2 Hz, 1H, H_b), 3.77 (d, J = 5.0 Hz, 2H, (CH₂)_a), 1.09 (d, J = 6.2 Hz, 3H, (CH₃)_c), 1.04 (s, 24H, CH₃). ¹³C{¹H} **NMR** (400 MHz, C₆D₆) δ (ppm) = 82.16 (C_q), 81.98 (C_q), 70.25 (C_a), 69.11 (C_b), 24.32 (CH₃), 18.17 (C_c).



Figure S11. ¹H and ¹³C NMR spectra of the crude mixture obtained from the reductive depolymerization of **PPC** at R.T. in benzene (**PPC** with $La[N(SiMe_3)_2]_3(1 \text{ mol}\%)$ and 3.3 equiv. of HBpin). Characterization of the borylated monomers.





¹**H NMR** (400 MHz, C_6D_6) δ (ppm) = 7.00 (m, 8H, H_{Ar}), 1.42 (s, 6H, $C(CH_3)_2(Ar)_2$), 1.05 (s, 24H, CH_3). ¹³C{¹H} NMR (400 MHz, C_6D_6) δ (ppm) = 151.69 (C_{qAr}), 145.14 (C_{qAr}), 127.56 (C_{Ar}), 119.00 (C_{Ar}), 82.78 (C_q), 41.72 ($C(CH_3)_2(Ar)_2$), 30.80 ($C(CH_3)_2(Ar)_2$), 24.23 (CH_3).



¹H NMR (400 MHz, C₆D₆) δ (ppm) = 3.46 (s, 3H, OCH₃), 1.04 (s, 12H, CH₃). ¹³C{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = 82.11 (C_q), 51.95 (OCH₃), 24.36 (CH₃).



Figure S12. ¹H and ¹³C NMR spectra of the of the crude mixture obtained from the reductive depolymerization of **PC-BPA** at 100 °C in benzene (**PC-BPA** with 1 mol% of $La[N(SiMe_3)_2]_3$, 3.3 equiv. of HBpin). Characterization of the borylated monomers.

5. References

1 C. J. Barger, A. Motta, V. L. Weidner, T. L. Lohr and T. J. Marks, ACS Catal., 2019, 9, 9015–9024.