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

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Plastics are ubiquitous in our modern society and their world annual production now reaches 368 Mt and is expected to double in the next 20 years. Most household wastes accumulates in landfills or are burnt due to the absence of efficient and economical recycling and valorization processes.¹ Such a situation causes severe damage to the environment and emissions of large amount of CO₂.²

The implementation of a circular economy of plastics lies on three main axes: drastic reduction of the leakage of wastes in the nature, the decoupling of plastic production from fossil resources and up-taking efficient recycling processes.

Today, while mechanical recycling is the most useful method to valorized plastic, the matter is however degraded by melting and most of the recycled polymer must be combined with virgin resins to retain the desired physical properties. Chemical recycling, which is the depolymerization of materials into valuable monomers useful for the production of recycled virgin quality plastics or chemicals for industry, now emerged as a long-term strategy complementary to mechanical recycling.³ Some well-known catalytic methods have been developed for depolymerizing oxygen and nitrogen containing polymers such as the solvolysis processes (hydrolysis, aminolysis, alcoholysis). They offer the recovery of pure monomers useful for the production of new virgin plastics.

Recently, reductive depolymerization methods appeared as alternative approaches to access new value added products from plastics.⁴ The goal is to develop catalytic systems able to selectively split and reduce polarized bonds of oxygenated (polyesters, polycarbonates and polyethers) and nitrogenated (polyamides, polyurethanes) polymers to obtain the corresponding monomers or some valuable derivatives (alcohols, amines or hydrocarbons).

Such ways are scarce. Hydrogenolysis methods require noble metals (Ru, Ir) and high pressure and temperature.⁵ In contrast, the hydrosilylation of polyesters and polycarbonates took place under milder conditions with metal-based catalysts (Ir(III), Zn(II), Mo(VI)) or boron-based organocatalysts.⁴ Surprisingly, hydroboranes reductants that could offer distinct reactivity and selectivity due to their higher hydride donor ability and additional pronounced Lewis acidity have never been tested.

Inspired by the work of T. J. Marks *et al.*⁶ on the reduction of esters, we successfully used hydroboranes and the 4f-catalyst La[N(SiMe₃)₂]₃ to successfully depolymerize a wide range of polyesters and polycarbonates into their corresponding borylated alcohols (Fig.1).⁷

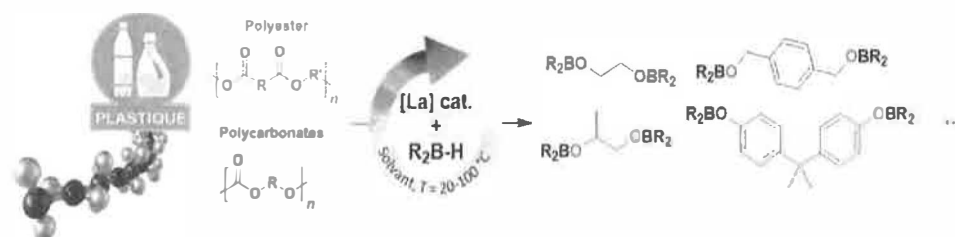


Fig. 1 Depolymerization of oxygenated plastics with the catalytic system La(III)/HBpin

¹ a) *Plastic - The Facts*, PlasticsEurope, 2020. <https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/> (on 2022/02/03); b) *The New Plastics Economy - Rethinking the future of plastics*, Ellen MacArthur Foundation & McKinsey Company, 2016; <https://ellenmacarthurfoundation.org/publications> (on 2022/02/03).

² Atlas du plastique 2020, https://fr.boell.org/sites/default/files/2020-03/Atlas%20du%20Plastique%20VF_0.pdf

³ Jehanno C., Pérez-Madriral M. M., Demarteau J., Sardon H., Dove A. P. *Polym. Chem.*, 2019, 10, 172.

⁴ Fernandes A. C., *Green Chem.* 2021, 23, 7330; b) Monsigny L., Berthet J.-C., Cantat T. *ACS Sustainable Chem. Eng.* 2018, 6, 10481.

⁵ Kumar A., Milstein D. et al, *J. Am. Chem. Soc.* 2020, 142, 14267.

⁶ Barger-C. J., Motta A., Weidner V. L., Lohr T. L., Marks T. J., *ACS Catal.* 2019, 9, 9015.

⁷ Kobylarski M., Berthet J.-C., Cantat T., *Chem. Commun.* 2022, <https://doi.org/10.1039/D2CC00184E>