

Supplementary information

Dioxomolybdenum complex as an efficient and cheap catalyst for the reductive depolymerization of plastic waste into value-added compounds and fuels

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1. General information

All the reactions were carried out under air atmosphere and without any dry solvent. Sodium molybdate, PhSiH_3 , DMPS, Et_3SiH , Pr_3SiH , Ph_3SiH and PMHS were obtained from commercial suppliers and were used without further purification. Polymers such as polycaprolactone (PCL), polydioxanone (PDO), and polybutylene terephthalate (PBT) were purchased as granulate from Sigma and Aldrich. Poly(lactic acid) (PLA) was obtained from a glass generously donated by C2Catering. Polyethylene terephthalate (PET) were obtained from a used Evian® water bottle and PDO sterile surgical suture (model MONOPLUS) was generously donated by B. Braun Medical Portugal.

^1H NMR spectra were measured on a Bruker Avance II⁺ 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. The ESI mass spectrum was obtained on a LCQFleet ion trap mass spectrometer equipped with an electrospray source (Thermo ScientificTM, Waltham, MA USA), operating in the positive ion mode.

Gas chromatography (GC) analyses were run on an Agilent Technologies 7820A series gas chromatograph (He as carrier gas) equipped with the FID detector and BP20/SGE (30 m × 0.22 mm × 0.25 μm) capillary column.

2. Reductive depolymerization of PCL with the catalytic system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PMHS}$

To a schlenk flask equipped with a J. Young tap containing PCL (57 mg, 0.5 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (2 mol%) and PMHS (1.0 mmol). The reaction mixture was stirred in the closed schlenk at 110 °C during 48 h. The product yield was determined by ^1H NMR spectroscopy using mesitylene as internal standard.

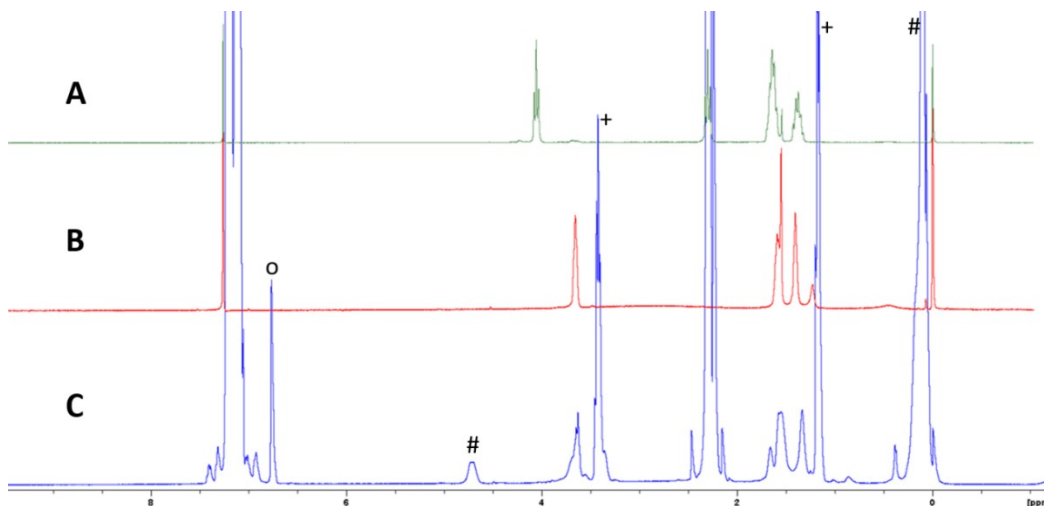


Figure S1 – ^1H NMR spectra of: A) PCL; B) 1,6-hexanediol; C) reaction mixture. $^\circ$ Mesitylene; $^+$ Diethyl ether; $\#$ PMHS.

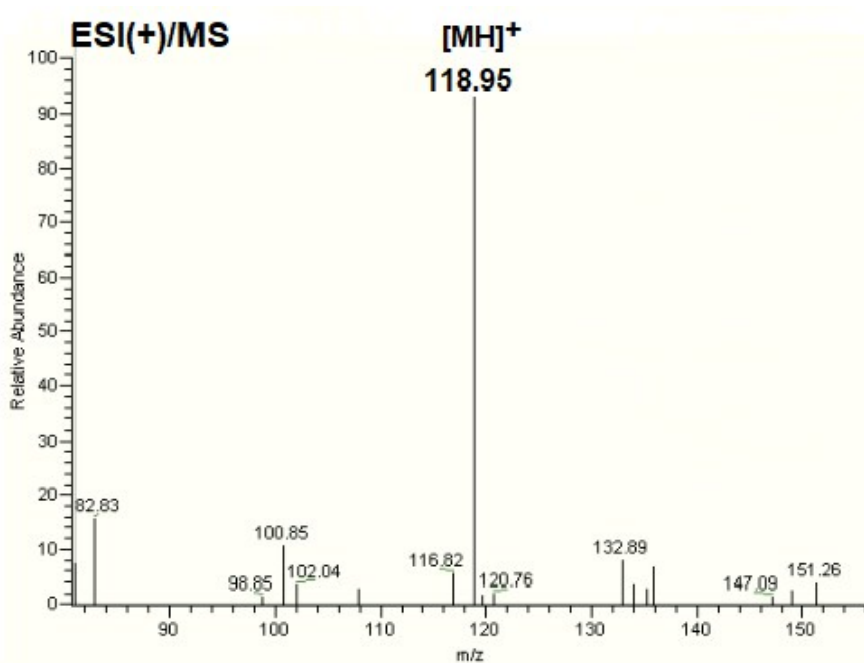


Figure S2 – Full mass spectrum of the protonated molecule of 1,6-hexanediol (m/z 119).

3. Reductive depolymerization of PCL with the catalytic system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PhSiH}_3$

To a schlenk flask equipped with a J. Young tap containing PCL (57 mg, 0.5 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (1 mol%) and PhSiH_3 (0.75 mmol). The reaction mixture was stirred in the closed schlenk at 110 °C during 20 h. The product yield was determined by ^1H NMR spectroscopy using mesitylene as internal standard.

4. Use of catalyst $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ in several cycles

To a schlenk flask equipped with a J. Young tap containing PCL (28.5 mg, 0.25 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (1 mol%) and PhSiH_3 (0.375 mmol). The reaction mixture was stirred in the closed schlenk at 110 °C during 24 h. After cooling, the product yield was determined by ^1H NMR spectroscopy using mesitylene (0.25 mmol) as internal standard. In the next catalytic cycles, PCL (0.25 mmol), PhSiH_3 (0.375 mmol) and mesitylene (0.25 mmol) were added to the reaction mixture and stirred for 24 h at 110 °C. The reaction mixture was cooled and the yields were determined by ^1H NMR spectroscopy.

Cycle number	Conversion (%)	Product (%)	TON
1	100	85	100
2	100	85	100
3	100	84	100
4	95	81	95
5	95	80	95
6	95	81	95
7	95	80	95
8	95	79	95

5. Reaction of 1,6-hexanediol with the system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PMHS}$

To a Schlenk flask equipped with a J. Young tap containing 1,6-hexanediol (59 mg, 0.5 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (1 mol%) and PMHS (1.0 mmol). The reaction mixture was stirred in the closed Schlenk at 110 °C during 48 h.

6. Reductive depolymerization of PLA with the catalytic system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PMHS}$

To a schlenk flask equipped with a J. Young tap containing small pieces of a glass of PLA (36 mg, 0.5 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (2 mol%) and PMHS (1.0 mmol). The reaction mixture was stirred in the closed schlenk at 110 °C during 40 h.

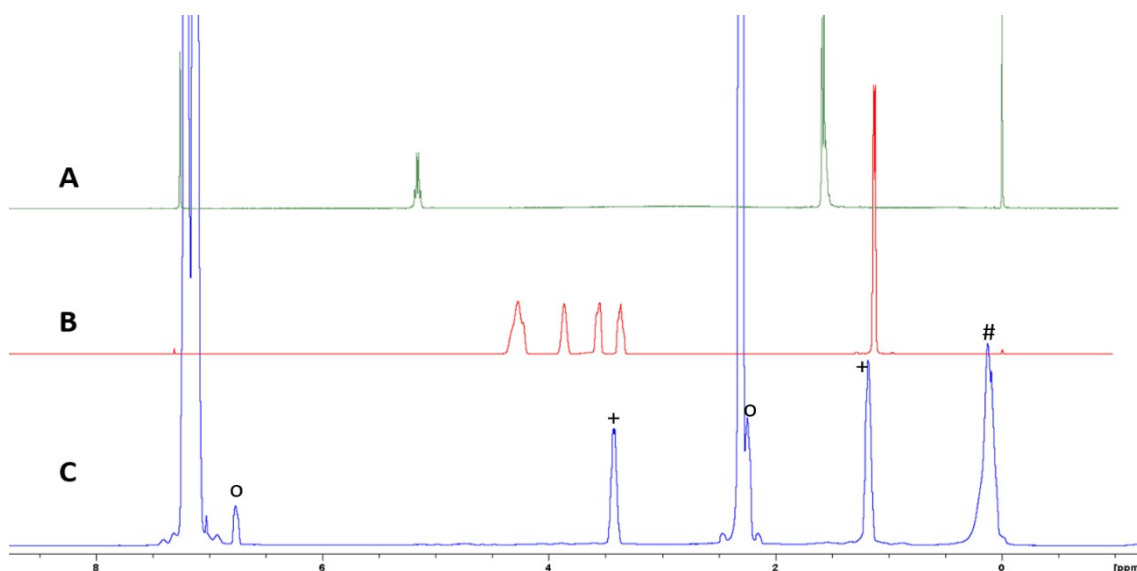


Figure S3 – ^1H NMR spectra of: A) PLA; B) 1,2-propanediol; C) Reaction mixture. ^oMesitylene; ⁺Diethyl ether; #PMHS.

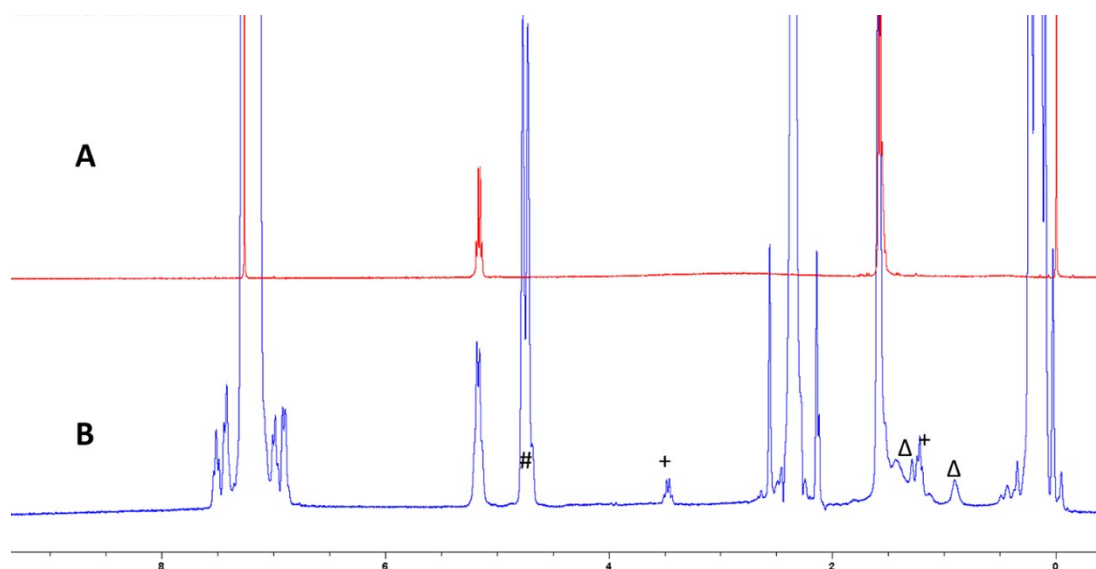


Figure S4 – ^1H NMR spectra of: A) PLA; B) reaction mixture after 20 h. Δ Propane; #PMHS; ⁺Diethyl ether.

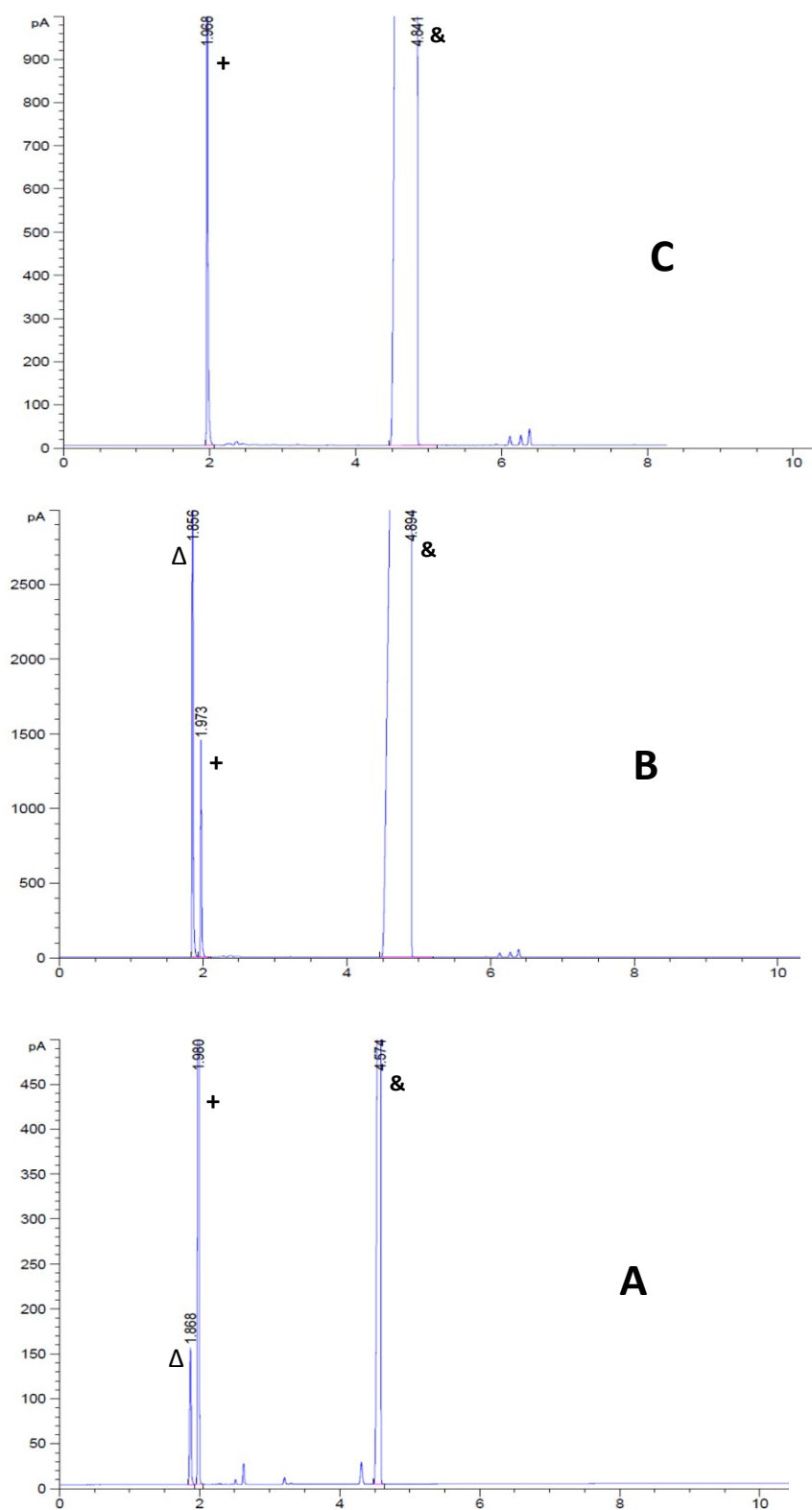


Figure S5 – GC chromatograms of: A) Gaseous phase of PLA reductive depolymerization; B) Solution toluene + diethyl ether + propane; C) Solution of toluene and diethyl ether. ΔPropane; +Diethyl ether; &Toluene.

7. Reductive depolymerization of PLA with the catalytic system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PhSiH}_3$

To a schlenk flask equipped with a J. Young tap containing small pieces of a glass of PLA (36 mg, 0.5 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (1 mol%) and PhSiH_3 (0.75 mmol). The reaction mixture was stirred in the closed schlenk at 110 °C during 20 h. The PLA conversion was determined by ^1H NMR spectroscopy using mesitylene as internal standard.

8. Reaction of 1,2-propanediol with the system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PhSiH}_3$

To a Schlenk flask equipped with a J. Young tap containing 1,2-propanediol (0.04 mL, 0.5 mmol) in toluene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (1 mol%) and PhSiH_3 (0.75 mmol). The reaction mixture was stirred in the closed schlenk at 110 °C during 30 h.

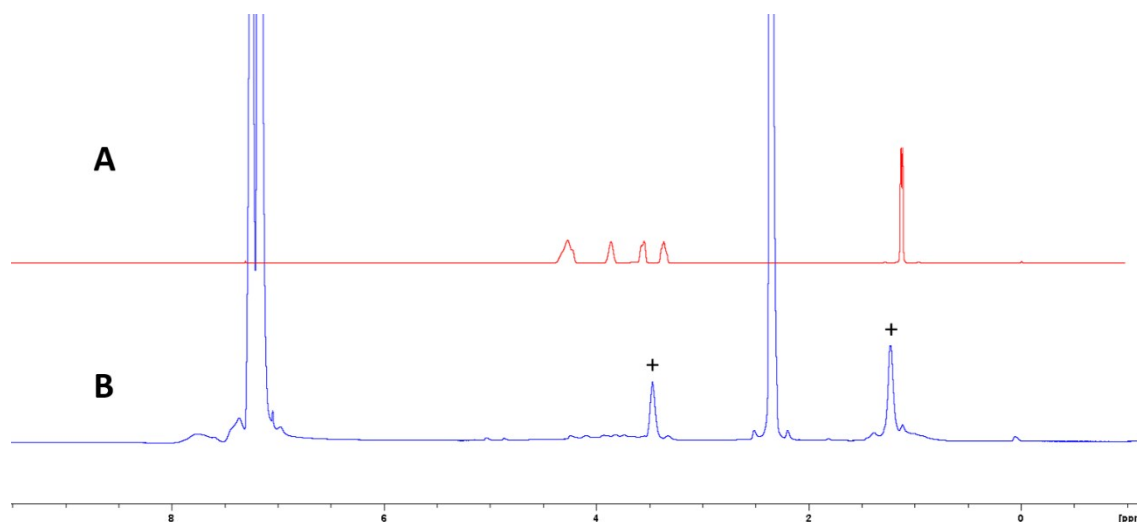


Figure S6 – ^1H NMR spectra of: A) 1,2-propanediol; B) Reaction mixture. +Diethyl ether.

9. Reductive depolymerization of PDO with the catalytic system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PhSiH}_3$

To a schlenk flask equipped with a J. Young tap containing PDO (51 mg, 0.5 mmol) in chlorobenzene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (2 mol%) and PhSiH_3 (1.0 mmol). The reaction mixture was stirred in a closed schlenk at 110 °C during 20 h. The ethylene glycol yield was determined by ^1H NMR spectroscopy using mesitylene as internal standard.

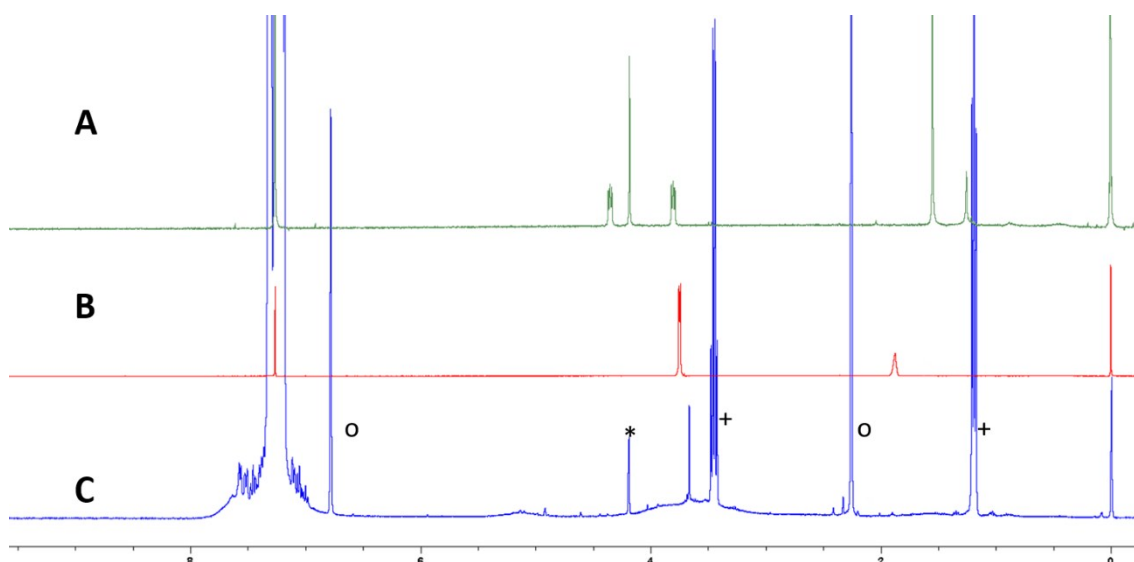


Figure S7 – ^1H NMR spectra of: A) PDO; B) Ethylene glycol; C) Reaction mixture. $^{\circ}$ Mesitylene; *PhSiH₃; +Diethyl ether.

10. Reductive depolymerization of PET with the system MoO₂Cl₂(H₂O)₂/PhSiH₃

To a schlenk flask equipped with a J. Young tap containing PET (48 mg, 0.25 mmol), obtained from a commercial Evian[®] water bottle finely ground, in chlorobenzene (2 mL) was added the ether solution of MoO₂Cl₂(H₂O)₂ (5 mol%) and PhSiH₃ (1.5 mmol). The reaction mixture was stirred in the closed schlenk at 160 °C during 4 days. The *p*-xylene yield was determined by ^1H NMR spectroscopy using furan as internal standard.

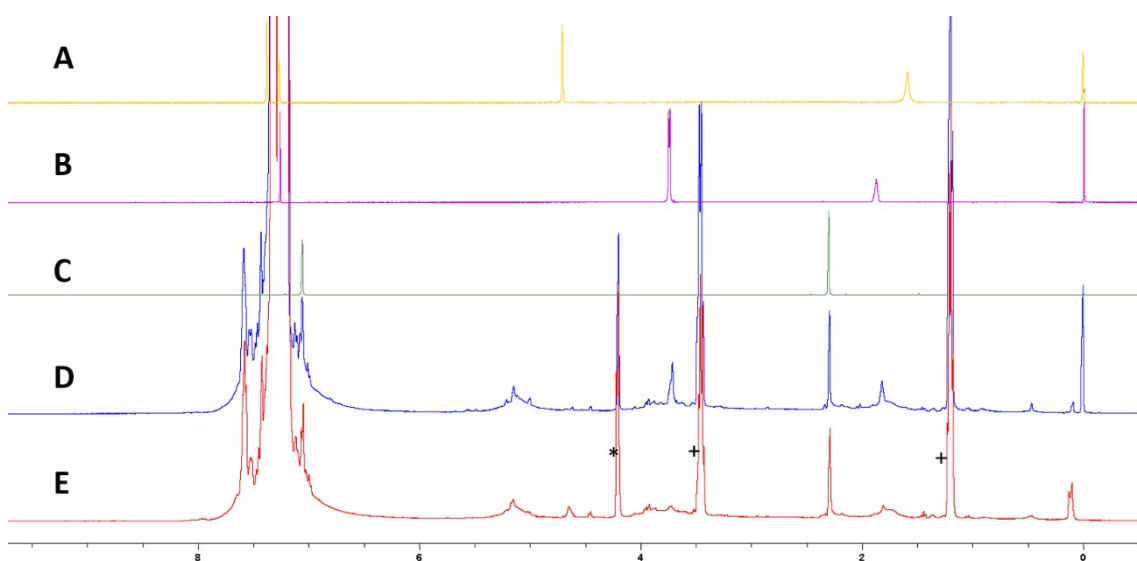


Figure S8 – ^1H NMR spectra of: A) 1,4-Benzenedimethanol; B) Ethylene glycol; C) *p*-Xylene; D) Reaction mixture after 4 days; E) Reaction mixture after 7 days. *PhSiH₃; +Diethyl ether.

11. Reaction of dimethyl terephthalate with the system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PhSiH}_3$

To a Schlenk flask equipped with a J. Young tap containing dimethyl terephthalate (48.5 mg, 0.25 mmol) in chlorobenzene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (5 mol%) and PhSiH_3 (1.5 mmol). The reaction mixture was stirred in the closed Schlenk at 110°C during 24 h.

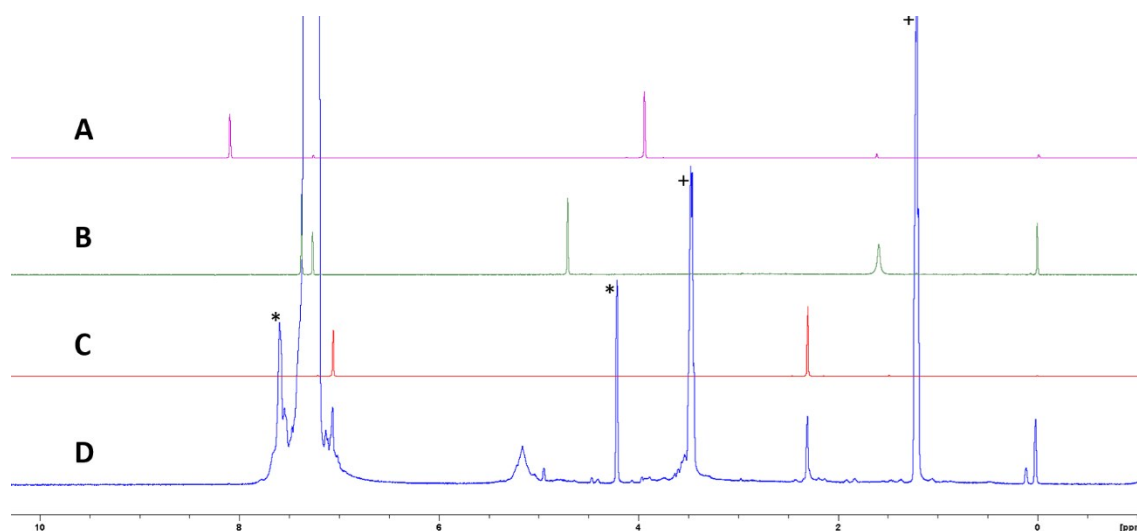


Figure S9 – ¹H NMR spectra of: A) Dimethyl terephthalate; B) 1,4-Benzenedimethanol; C) *p*-Xylene; D) Reaction mixture. * PhSiH_3 ; + Diethyl ether.

12. Reductive depolymerization of PBT with the system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PhSiH}_3$

To a schlenk flask equipped with a J. Young tap containing PBT (55 mg, 0.25 mmol) in chlorobenzene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (5 mol%) and PhSiH_3 (1.5 mmol). The reaction mixture was stirred in the closed schlenk at 160 °C during 4 days. The *p*-xylene yield was determined by ¹H NMR spectroscopy using furan as internal standard.

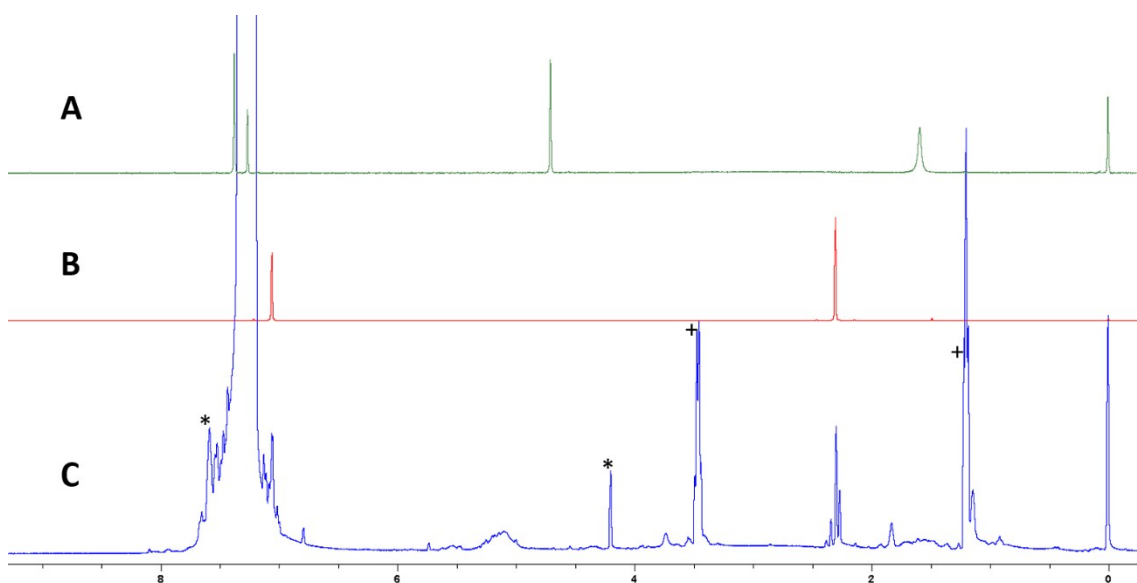


Figure S10 – ^1H NMR spectra of: A) Benzenedimethanol; B) *p*-Xylene; C) Reaction mixture. * PhSiH_3 ; +Diethyl ether.

13. Reductive depolymerization of a PCL, PLA and PET mixture with the system $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2/\text{PMHS}$

To a schlenk flask equipped with a J. Young tap containing PCL (57 mg, 0.5 mmol), PLA (36 mg, 0.5 mmol) and PET (48 mg, 0.5 mmol) in chlorobenzene (2 mL) was added the ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ (2 mol%) and PMHS (3.0 mmol) The reaction mixture was stirred in the closed schlenk at 110 °C during 48 h.

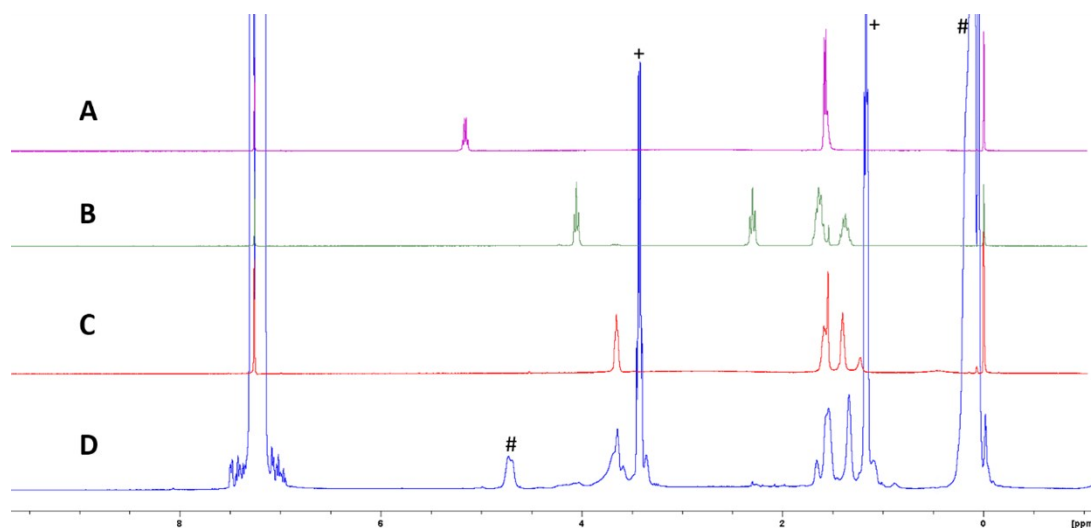


Figure S11 – ^1H NMR spectrum of: A) PLA; B) PCL; C) 1,6-hexanediol; D) reaction mixture. #PMHS; +Diethyl ether.

14. Photo and infrared spectrum of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ solution.

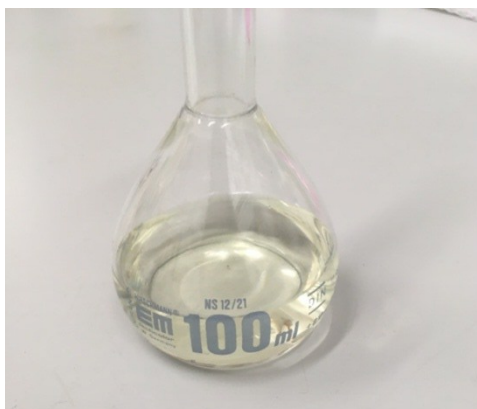


Figure S12 - Diethyl ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ 10 months after its preparation.

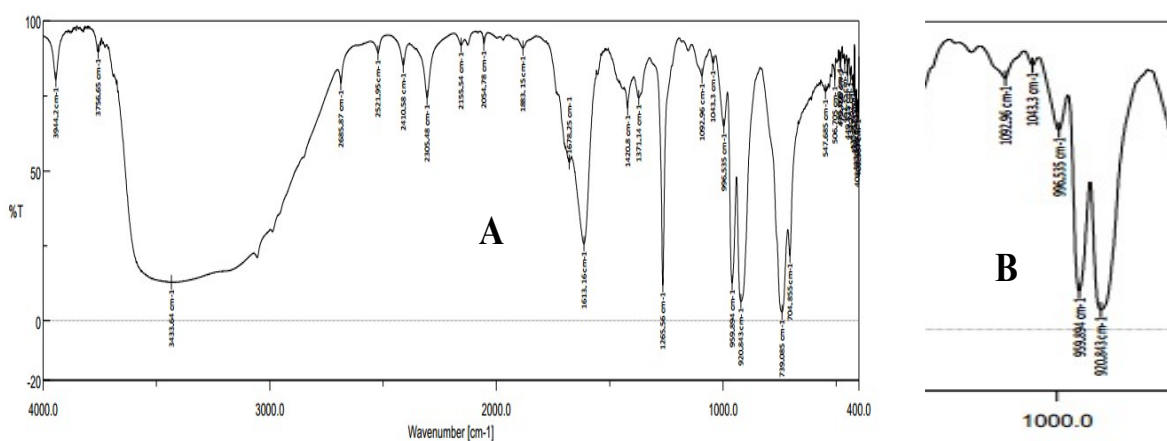


Figure S13 – Infrared spectrum of the dichloromethane solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$. To eliminate the bands of diethyl ether in the infrared spectrum in the zone between 1000-800 cm^{-1} , the diethyl ether solution of $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ was evaporated and, then, the oxo-molybdenum complex was dissolved in dichloromethane. The bands observed in the IR spectrum of this solution, 10 months after its preparation, are similar to those reported in the literature,¹ confirming its air stability.

Reference

1 - E. Soleimani, *Asian J. Chem.*, 2011, **23**, 1869-1870.