

Electronic Supplementary Information

Lanthanide dodecyl sulfates, a potent family of catalysts for the preparation of biobased epoxy thermosets

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I. Experimental Section

I.1 Materials and methods

Limonene dioxide (LDO) was purchased from the company Symrise Chemical. Epikure 3251 was purchased from the Hexion company. All lanthanide nitrates were purchased from the Strem company. All other chemicals were purchased from Sigma Aldrich. Fourier Transformed Infrared spectroscopy (FTIR) were acquired on a Bomem MB104 spectrometer, using a Golden Gate attenuated total reflectance (ATR) module from Specac. Spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 2 cm^{-1} using an average of 64 measurements in the final spectrum. Nuclear Magnetic Resonance (NMR) spectra were acquired on an Avance Neo 400 MHz spectrometer at ambient temperature using anhydrous benzene as internal standard. For solid-state NMR, ^{13}C cross-polarization (CP) spectra were acquired on a Bruker AVANCE NEO 400 MHz wide bore spectrometer (Bruker Biospin, Milton, ON) with a 4 mm triple-resonance solid probe. The samples were packed into a 4 mm zirconia rotor spun at 13 kHz at room temperature. The spectra were measured at 100.56 MHz for the ^{13}C nuclei with a cross-polarization and magic angle spinning (CP-MAS) pulse sequence. Proton decoupling was performed using a small phase incremental alteration (SPINAL64) decoupling pulse sequence. Using 3012 data points, CP-MAS spectra were acquired with a recycle delay of 5.0 s using a ramped-amplitude pulse sequence with a ^1H - ^{13}C contact time of 2 ms. Either 1024 and 2048 scans were acquired for each spectrum and the spectral width was 30.1 kHz.

I.2 Synthesis of the catalysts

Amounts used for each synthesis are consigned in Table S1. A representative procedure is described for cerium. In a 125 mL Erlenmeyer loaded with a magnetic stirred bar, 0.996 g of sodium dodecyl sulfate were dissolved in 37.5 mL of deionized water at room temperature. Another aqueous solution was prepared by dissolving 0.500 g of Cerium (III) nitrate hexahydrate in 12.5 mL of deionized water, and then added into the Erlenmeyer while stirring. After 3 min of stirring, the solid formed was recovered by Büchner filtration over a paper filter and washed 3 times with 25 mL of deionized water. The solid was then dried in a vacuum oven (50 Torr, 60°C) for 24 hours, giving 1.036 g of a white powder.

Table S1 Amounts used for each syntheses

Lanthanide used	SDS (g)	$\text{Ln}(\text{NO}_3)_3$ (g)	$\text{Ln}(\text{DS})_x$ (g)	Aspect of the solid
La	0.999	0.500	1.055	White
Pr	0.994	0.500	1.037	Greenish
Nd	0.987	0.500	1.036	Pale magenta
Sm	0.973	0.500	1.008	Ivory
Eu	0.970	0.500	1.025	White
Gd	0.961	0.500	1.019	White
Tb	0.955	0.500	0.962	White
Ho	0.981	0.500	0.996	Pale Orange
Er	0.976	0.500	1.017	Pink
Tm	0.934	0.500	0.974	White
Yb	0.963	0.500	1.019	White
Lu	0.922	0.500	1.005	White

I.3 Measurement of gel-time

First, the catalyst and cross-linker were mixed inside a 20 mL vial using an ultrasonic bath with slight heating. Then the epoxy monomer was added to the mixture. Immediately after, the vial was thermostated in a water or sand bath in order to absorb the reaction heat and the mixture was continuously stirred by a wire stirrer (Figure S1) and the gel-time corresponds to the time it takes for the wire to stop stirring. The various formulations used for gel-time measurements are detailed in Table S2 and S3.

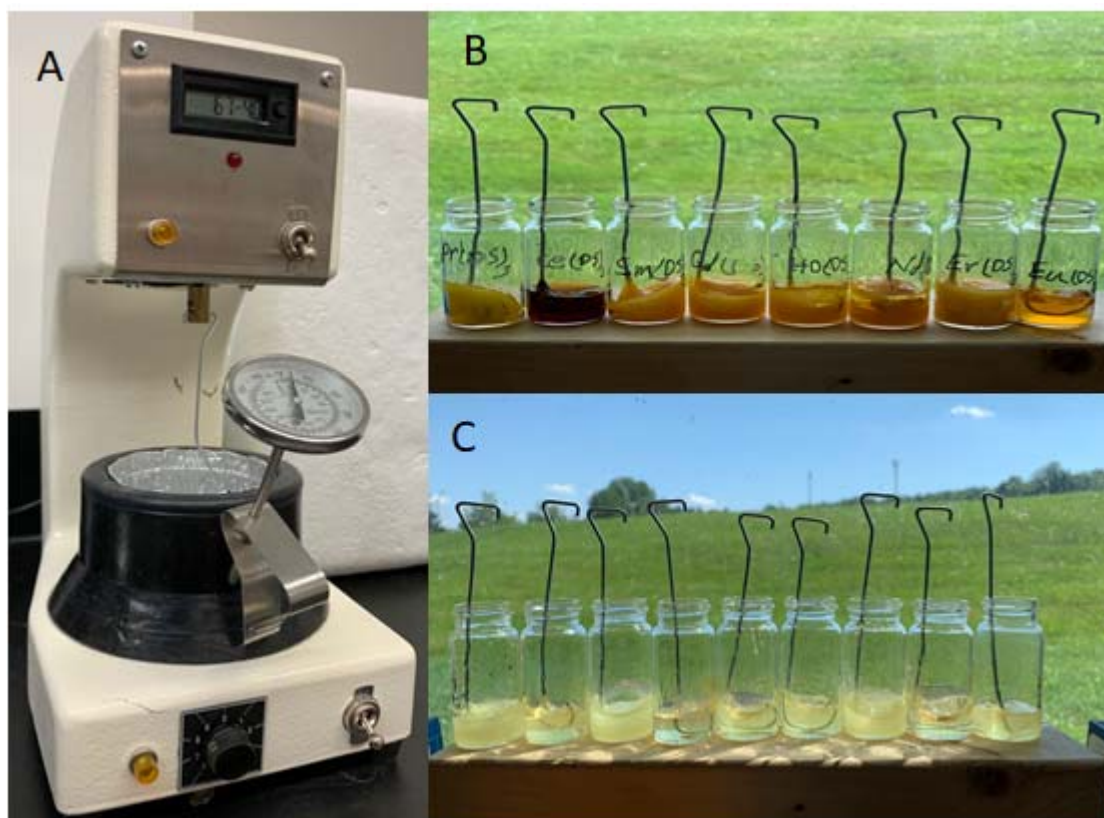


Figure S1 A. gel-time measurement setup. B. Various solid LDO-PEI formulations. C. Various solid BADGE-Epikure formulations.

Table S2 Gel-time for formulations based on BADGE (the reference gel-time for the uncatalyzed reaction was 84 min)

Dodecyl sulfates catalysts	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	Lu
Mass of BADGE (g)							3.40						
Mass of Epikure 3251 (g)							1.52						
Mass of catalyst (g)							0.10						
Gel-time (min) ^a	24	50	44	47	43	57	56	62	62	63	53	51	64

Table S3 Gel-time for formulations based on LDO (the reference gel-time for the uncatalyzed reaction was 48 hours)

Dodecyl sulfates catalysts	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er	Tm	Yb	Lu
Mass of LDO (g)							3.00						
Mass of Polyethylenimine (g)							2.00						
Mass of catalyst (g)							0.92						
Gel-stime (h) ^a	6	10	11	12	12	16	25	12	15	16	18	15	13

I.4 Measurement of the drying time

This procedure was adapted from ASTM D5895. In a 20 mL vial, the catalyst La(DS)_x (0.1 g) was dissolved in Epikure 3251 (3.04g). Then, BADGE (6.81 g) was then added into the vial and quickly mixed with a glass rod for 1 min. The resulting viscous mixture was poured over a glass plate and spread with a universal blade applicator (GARDCO company) set at a nominal 10 mils thickness (250 micrometers). Every 15 min, the film was gently scratch with a needle, and the film was declared dry when the needle did not leave any mark on the film.

I.5 X-ray PhotoElectron Spectroscopy (XPS)

Analyses were performed on a Physical Electronics XPS PHI 5600-ci instrument equipped with an Al anode (1486.6 eV) at 300 W in survey mode, using the charge compensation mode. High resolution analyses were performed at an incident angle of 45 ° on a surface of 0.5 mm². High resolution spectra were performed on C_{1s}, O_{1s} and S_{2p} using 30, 30 et 60 scans respectively.

I.6 Inductive Coupled Plasma (ICP)

ICP-MS measurements were performed on a X series II instrument from ThermoFisher Instrument equipped with a Elemental Scientific PC³ Peltier spray chamber. The nebulizer gaz flow was set at 0.98 L/min, the forward power at 1400 W, the cooling gas at 13 L/min, the auxiliary gas at 0.8 L/min. For each run, 100 sweeps with dwell times of 10 ms were performed. The monitored isotopes were ⁴⁵Sc, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁵Gd, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶¹Dy, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷²Yb and ¹⁷⁵Lu using ¹⁰³Rh as internal standard. ICP-OES measurements were performed an Agilent Technology 5100 ICP-OES instrument. The instrument was calibrated for S, Ce, Pr, Nd, La, Y, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, using ICP-OES standards purchased at Sigma-Aldrich. Samples (analysed both by ICP-MS and ICP-OES) were prepared by dissolving a known amount of catalyst (approx. 10 mg) in 2 mL of of HNO₃ (Tracecert® grade) for 4 h at 65°C. Then, 2 mL of HNO₃ were added to this solution for a second heating step of 2h at 85°C in order to ensure complete dissolution. All sample were analysed as a triplicate

I.7 Single Crystal X-ray Diffraction

A Plate-like specimen of C₄₈H₁₁₀LaNaO₁₈S₄, approximate dimensions 0.025 mm x 0.160 mm x 0.544 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured ($\lambda = 0.71073$ Å). The total exposure time was 4.41 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. Details about sample collection can be found in Table S15. The Ortep representation is found in Figure S15.

I.8 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were performed on a DSC 7 from Mettler-Toledo under nitrogen flux of 20mL/min equipped with an autosampler and a cooler. For each formulation, a sample containing the appropriate mixture of LDO and hardener was vigorously mixed using a vortex for 2 min. The resulting homogeneous and viscous liquid was then immediately placed in a DSC pan, which was hermetically sealed. The sample was then placed on the autosampler and was introduced in the oven which was pre-heated at the requested temperature.

Figure S2 XPS – Survey mode for La(DS)x catalyst

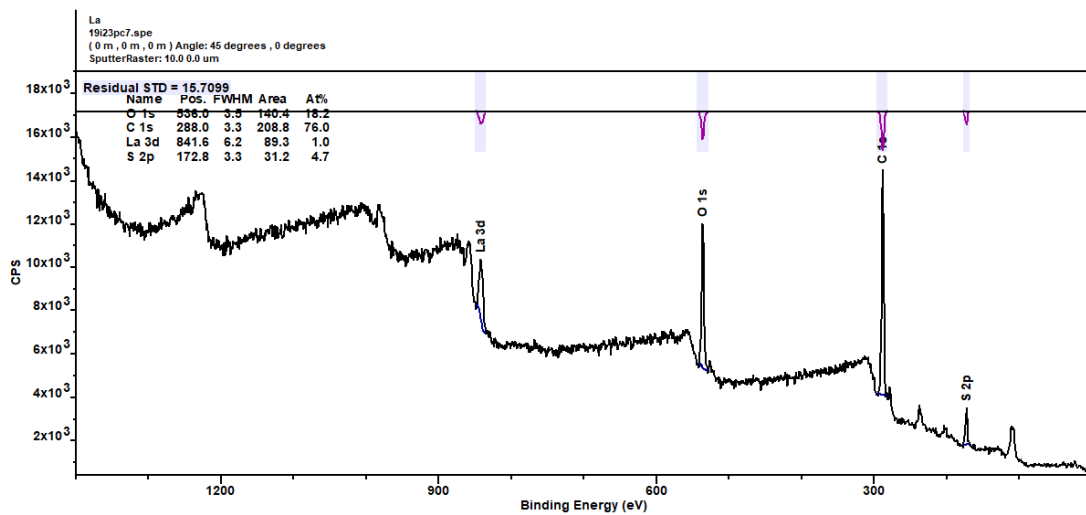


Figure S3 : XPS – Survey mode for Ce(DS)_x catalyst

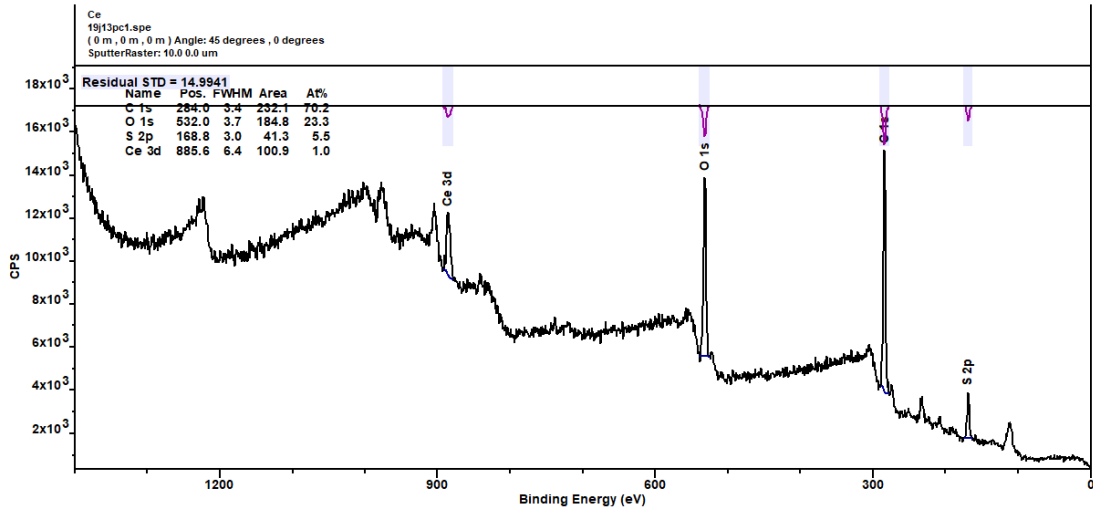


Figure S4 : XPS – Survey mode for Pr(DS)_x catalyst

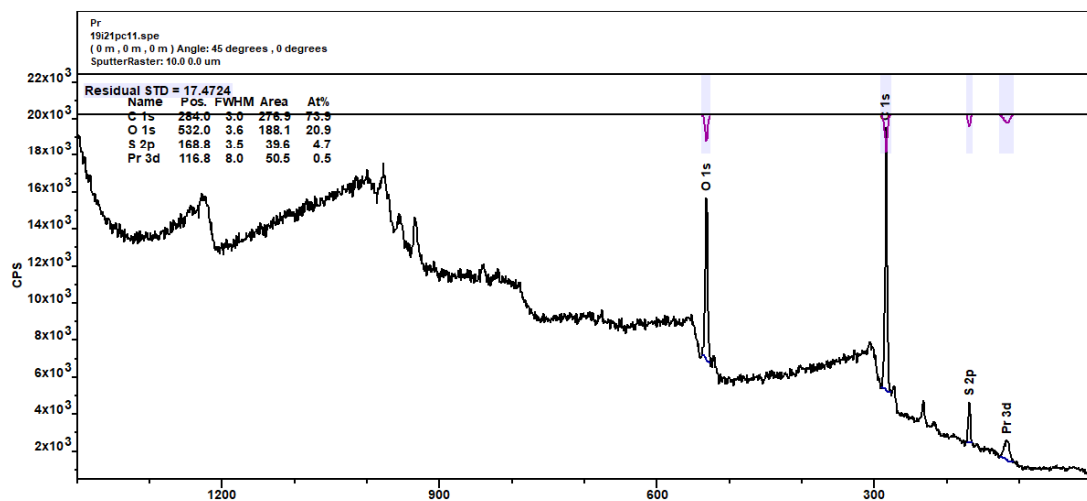


Figure S5 : XPS – Survey mode for $Sm(DS)_x$ catalyst

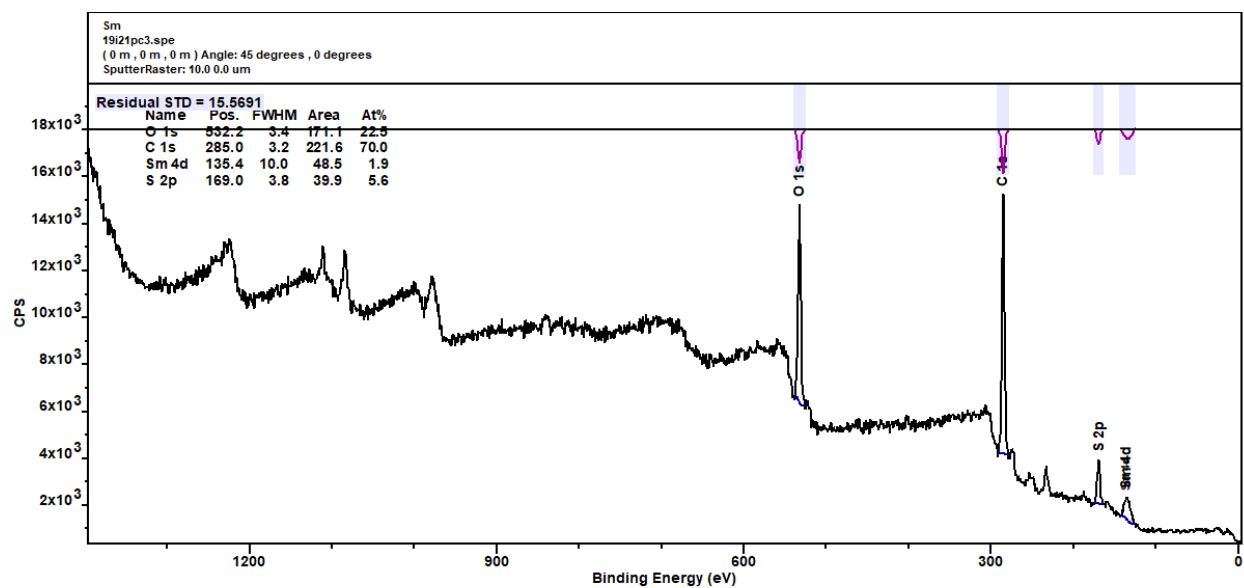


Figure S6 : XPS – Survey mode for Eu(DS)_x catalyst

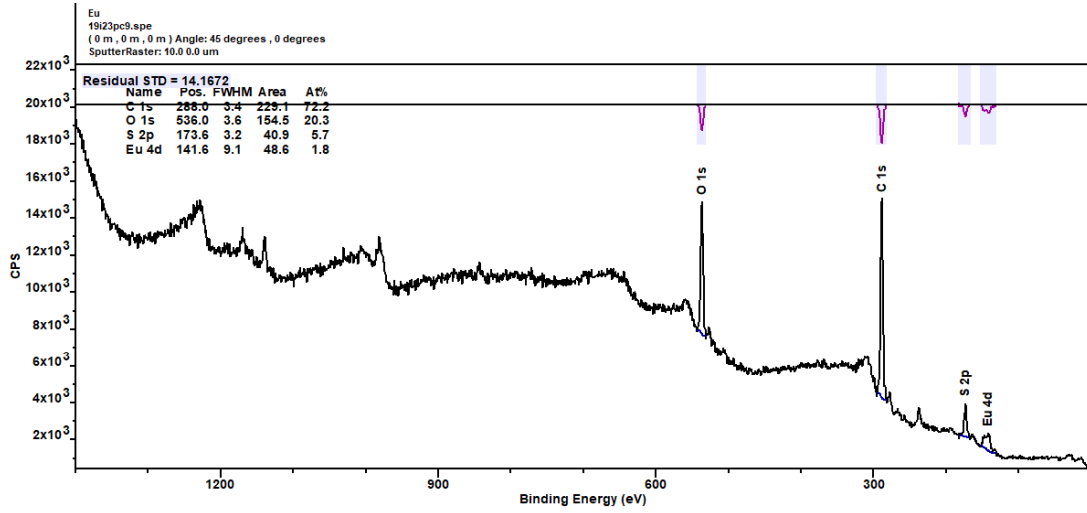


Figure S7 : XPS – Survey mode for Gd(DS)_x catalyst

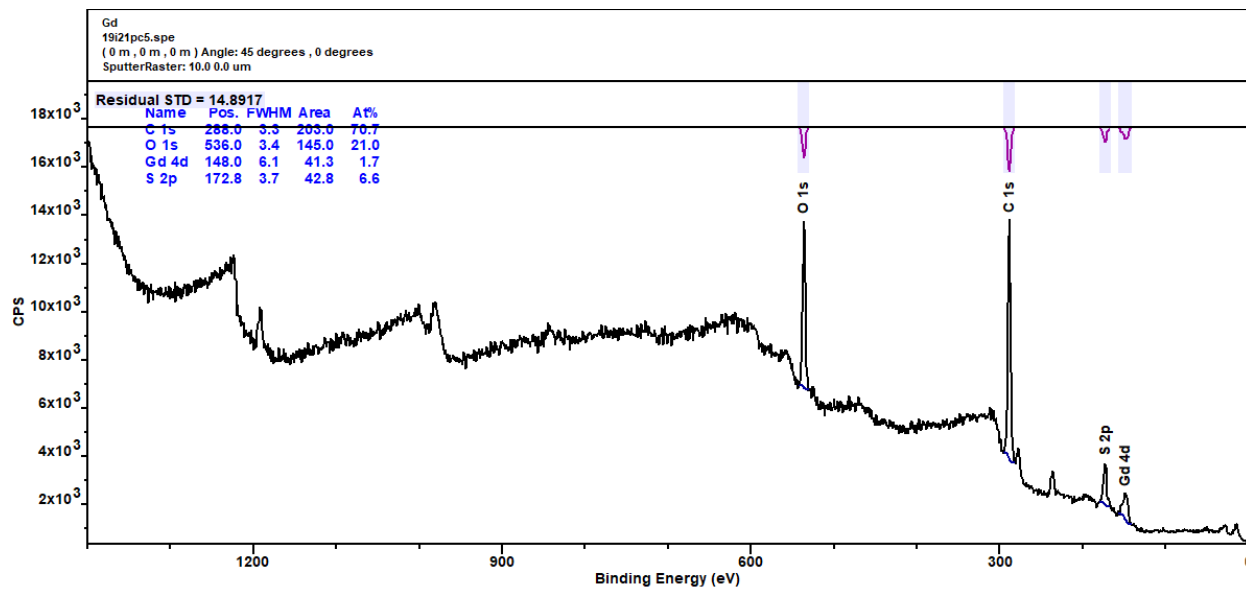


Figure S8 : XPS – Survey mode for Tb(DS)_x catalyst

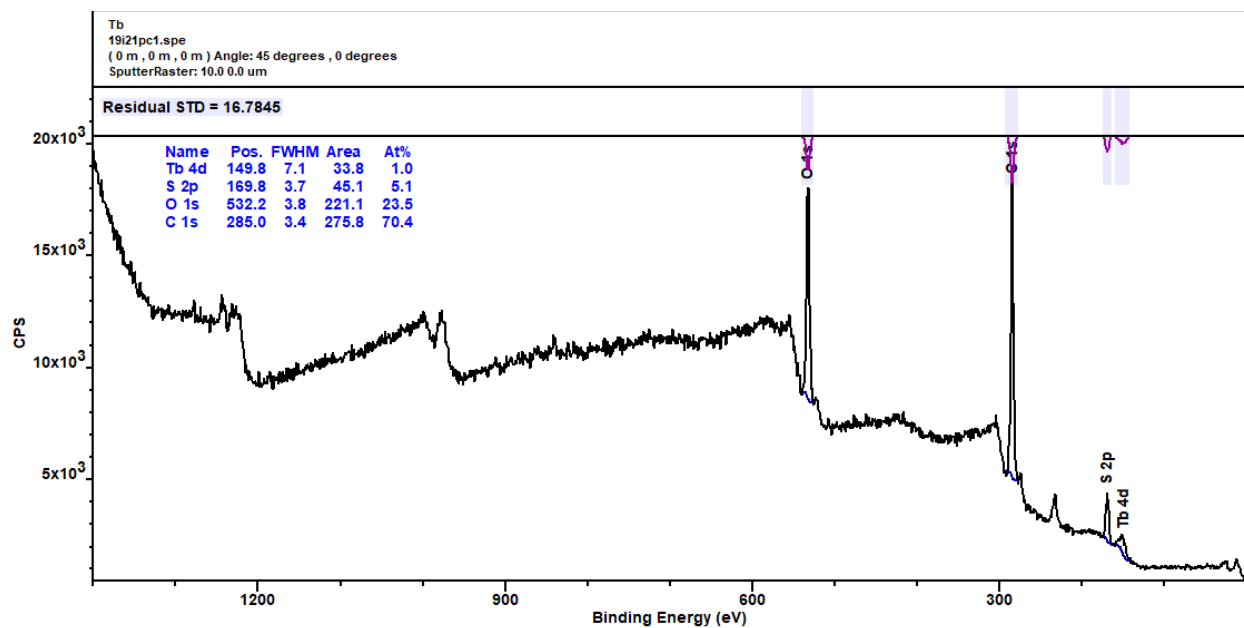


Figure S9 : XPS – Survey mode for Tm(DS)_x catalyst

S

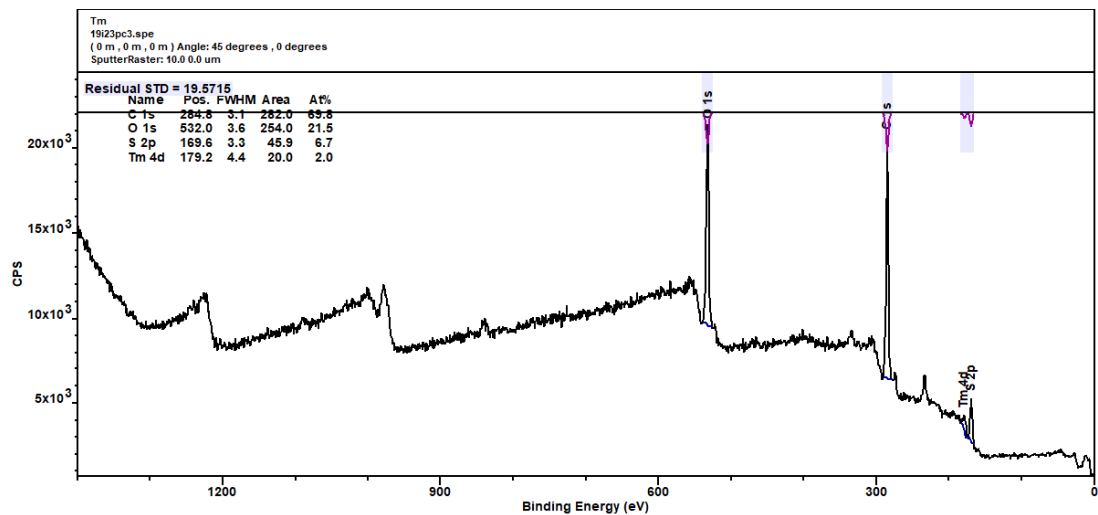


Figure S10 : XPS – Survey mode for Yb(DS)_x catalyst

S

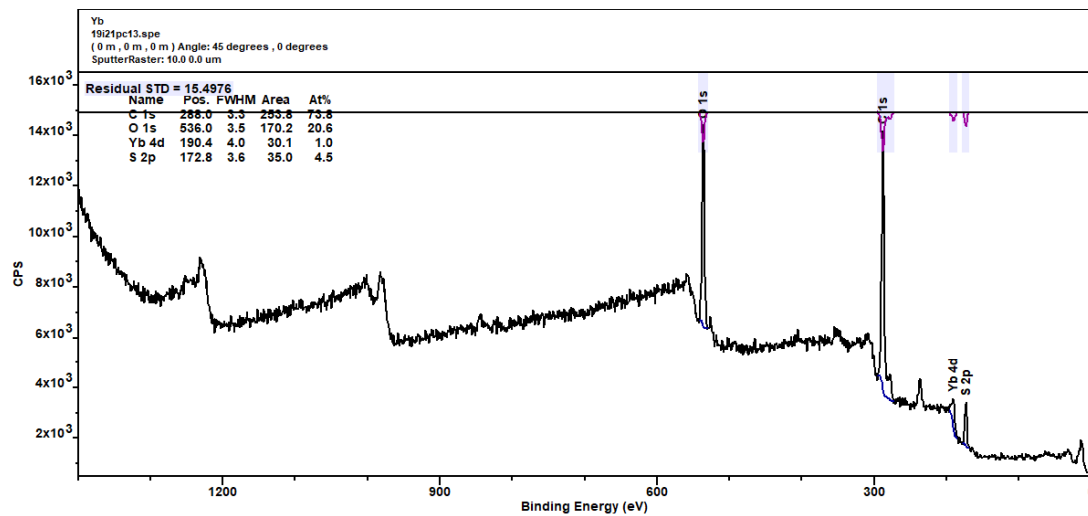


Figure S11 : XPS – Survey mode for Lu(DS)_x catalyst

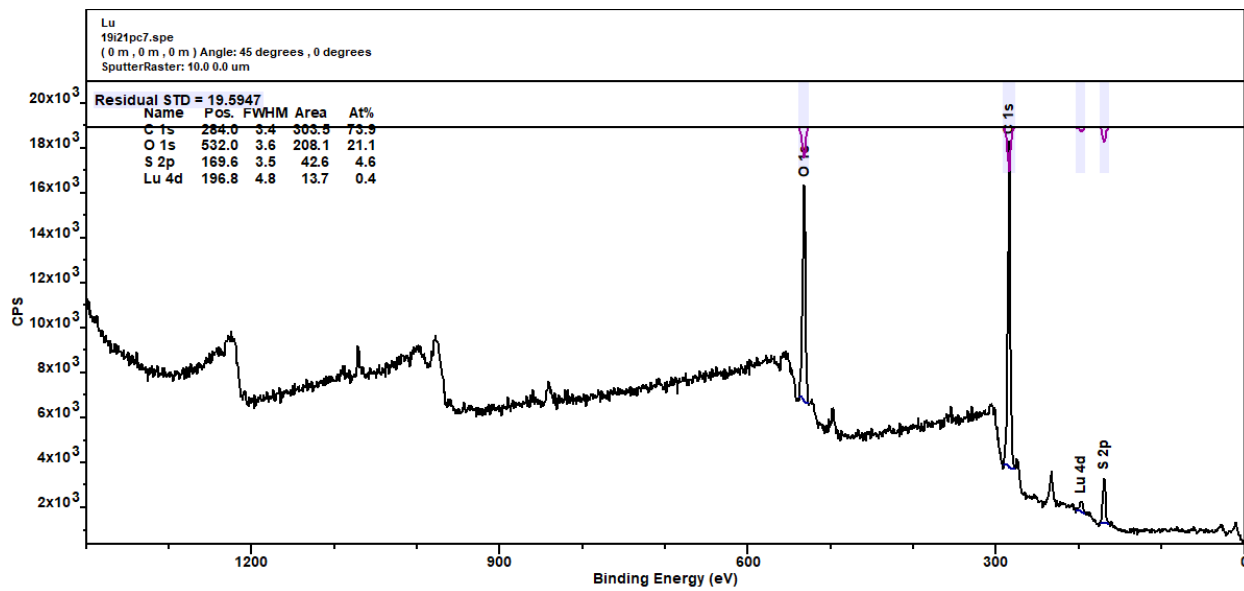
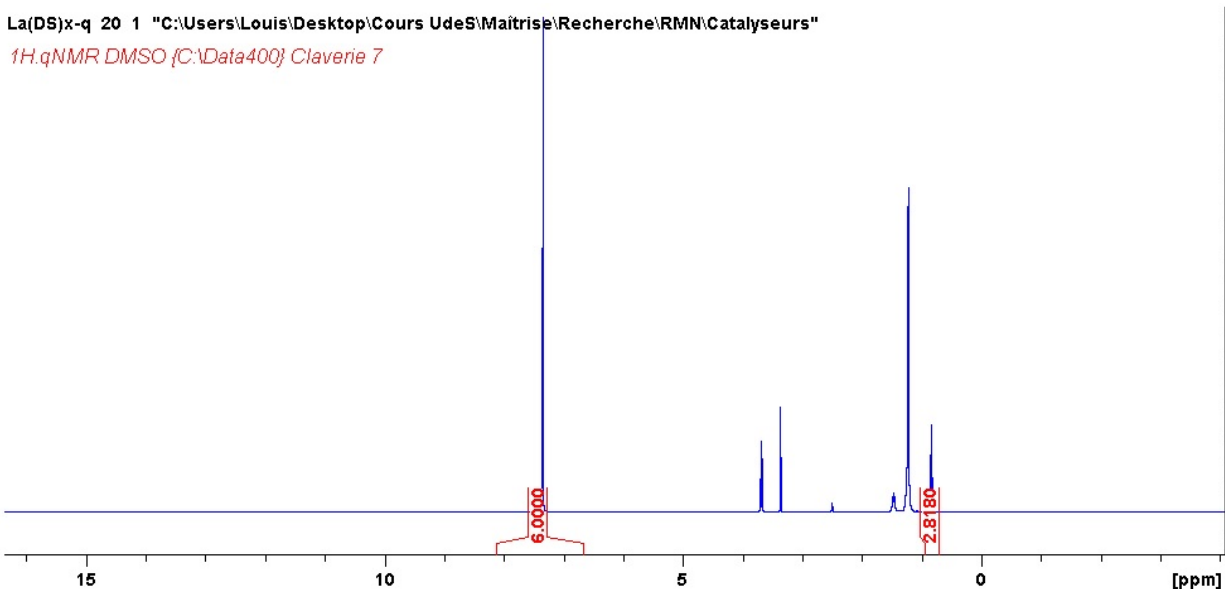


Figure S12 : ^1H NMR (400MHz, DMSO- d_6) of $\text{La}(\text{DS})_x$ and benzene as internal standard



In a clean NMR tube, 48.36 mg of $\text{La}(\text{DS})_x$ catalyst and 12.58 mg of benzene (0.161 mmol) were added to 0.5 mL of DMSO- D_6 . From the benzene integral, it was found that an integral of 1 corresponds to 0.161 mmol of protons. The CH_3 signal of $\text{La}(\text{DS})_x$ has an integral of 2.818. Thus, there are 0.151 mmol of CH_3 groups.

The molecular weight of $\text{La}(\text{DS})_x$ is $138 + 265x + (2-x)18$ (considering that the $\text{La}(\text{DS})_x$ is hydrated and is octa-coordinated). Thus,

$$\frac{x}{138 + 265x + 18 \cdot (2 - x)} = \frac{0.151}{48.36}$$

This leads to $x = 3.85$ (Not taking hydration water in the hydration sphere leads to $x = 2.5$)

Table S4: Summary of the ICP-MS results

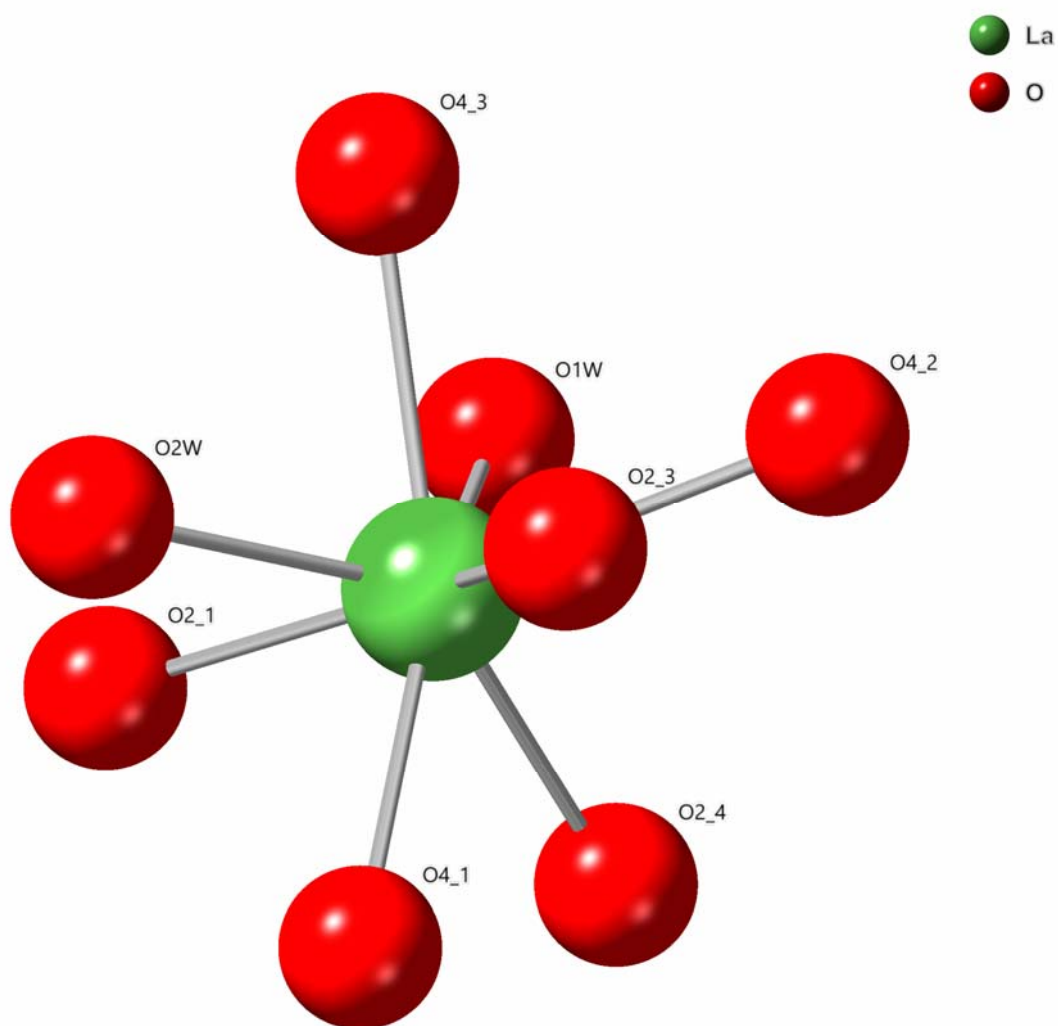
Compounds	% Lanthanide exp	Value of x in $\text{La}(\text{DS})_x\text{Na}_{x-3}(\text{H}_2\text{O})_{x-2}$
Ce(DS)_x	10.78 ± 0,50	4.1
Pr(DS)_x	10.26 ± 0,12	4.3
Nd(DS)_x	11.41 ± 1,04	4.0
Sm(DS)_x	13.63 ± 0,21	4.4
Eu(DS)_x	12.02 ± 0,68	3.4
Gd(DS)_x	13.60 ± 1,12	4.0
Tb(DS)_x	13.13 ± 1,10	3.8
Ho(DS)_x	12.80 ± 0,86	4.0
Er(DS)_x	13.24 ± 0,43	3.9
Tm(DS)_x	14.84 ± 1,49	3.5
Yb(DS)_x	15.63 ± 0,48	3.3
Lu(DS)_x	11.21 ± 0,63	4.5

Table S5: Summary of the ICP-OES results

Compounds	S/Ln	Standard Deviation
La(DS)x	3.8	0.3
Ce(DS)3	3.7	0.2
Pr(DS)3	3.2	0.1
Nd(DS)3	3.2	0.1
Sm(DS)3	3.1	0.3
Eu(DS)3	2.8	0.3
Gd(DS)3	3.0	0.1
Tb(DS)3	3.8	0.7
Ho(DS)3	3.7	0.7
Er(DS)3	3.6	0.1
Tm(DS)3	2.9	0.2
Yb(DS)3	2.3	0.6
Lu(DS)3	3.4	0.8

Figure S13 Environment of the La atom in the crystal cell and corresponding bond distances.

Rank	Bond	From	To	d [Å]
1	La - O	La1	O2_1	2.41711
2	La - O	La1	O2_4	2.42791
3	La - O	La1	O2_3	2.45700
4	La - O	La1	O4_1	2.47316
5	La - O	La1	O4A_1	2.47540
6	La - O	La1	O4_3	2.47808
7	La - O	La1	O2W	2.48243
8	La - O	La1	O4_2	2.50282
9	La - O	La1	O2A_1	2.50894
10	La - O	La1	O1W	2.63201



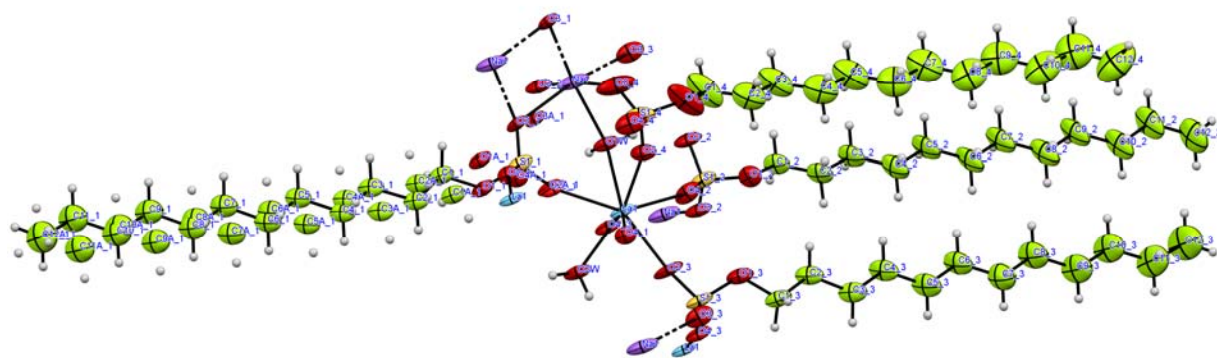


Figure S14 ORTEP diagram of NaLa(DS)₄(H₂O)₂

Table S6 Gel-time of an equimolar formulation of Epikure 3251 and BADGE containing 2 wt% of a commercial catalyst

Catalyst (2%wt)	Gel-time (min)
Without catalyst	84
Benzyl alcohol	67
Nonylphenol	61
Triethanolamine	60
DMP-30	52
La (DS)₃	24

Table S7 Effect of the concentration of $\text{La}(\text{DS})_x$ (equimolar formulation of Epikure 3251 and BADGE)

Catalyst $\text{La}(\text{DS})_3$ (%wt)	Gel-time (min)
0	86
0.5	63
1	42
2	25
3	19

Table S8 Effect of the $\text{La} : \text{NaDS}$ stoichiometry on gel-time (equimolar formulation of Epikure 3251 and BADGE, 2 wt% of catalyst). The catalyst synthesis is performed on 0.5 g of $\text{La}(\text{NO}_3)_3$, with increasing amounts of SDS (0.34, 0.65, 0.99, 1.33 and 2.0 g of SDS)

$\text{La}^{3+} : \text{DS}^-$ Mol: mol	Yield (g)	Gel-time (min)
1:1	0.35	21
1:2	0.69	26
1:3	1.05	28
1:4	1.21	25
1:6	0.87	58

Figure S15 Inverse of the gel time vs $\text{La}(\text{DS})_x$ catalyst concentration (equimolar formulation of Epikure 3251 and BADGE)

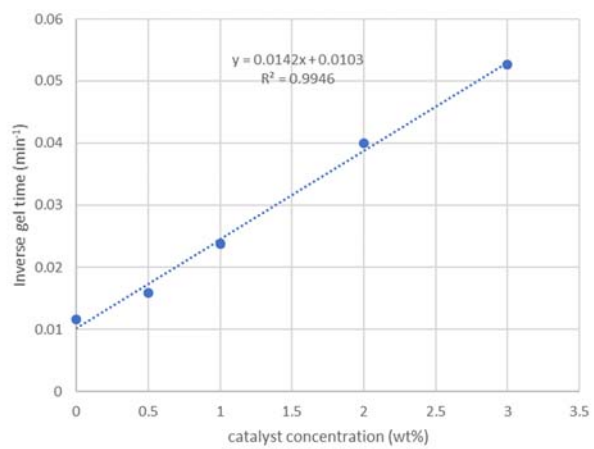


Table S9 The effect of percent La (DS)₃ in Epicure/BADGE (50/50 mol.%) formulation on drying time

Catalyst La (DS) ₃ (%wt)	Dry time (min)
0	120
1	90
2	60

Figure S16 Experimental and fitted curve dx/dt vs conversion (x) at 173°C, 188°C and 203°C (LDO:PEI = 60:40 wt%, no catalyst)

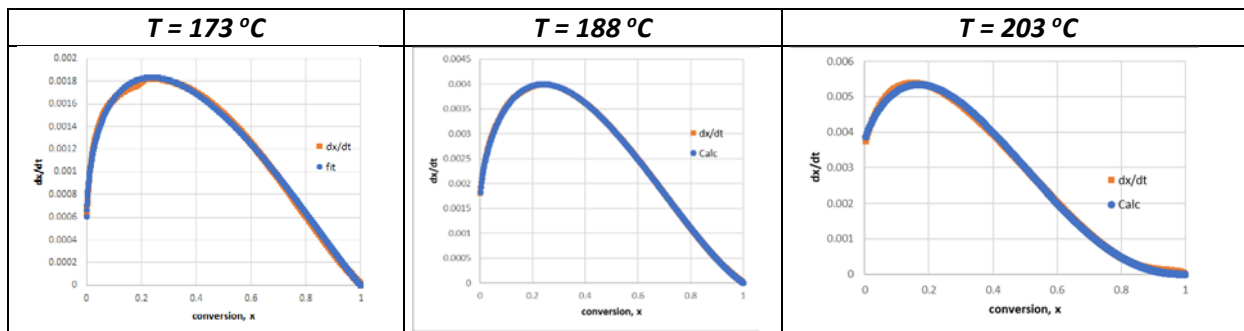


Figure S17 Experimental and fitted curve dx/dt vs conversion (x) at 109°C, 139°C and 169°C (LDO:PEI = 60:40 wt%, 2 wt% of La(DS)x)

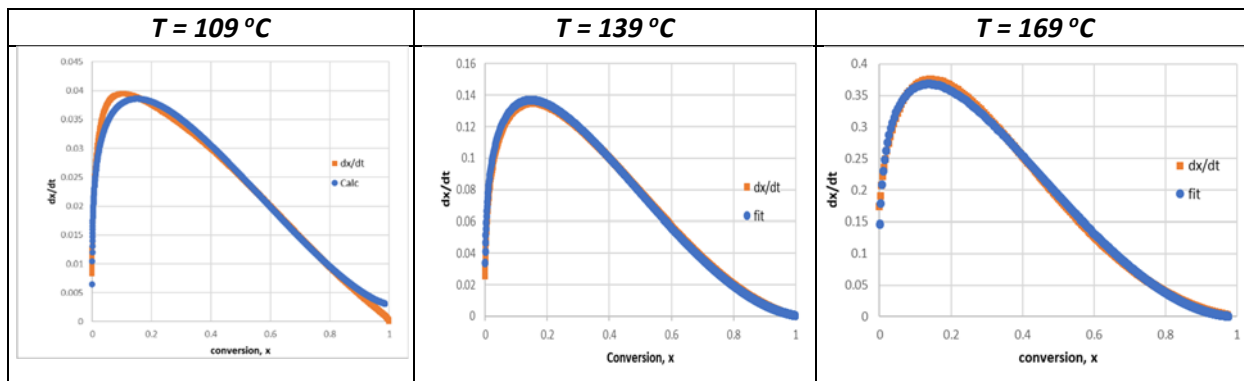


Figure S18 Experimental and fitted curve dx/dt vs conversion (x) at 109°C, 139°C and 169°C (LDO:PEI = 60:40 wt%, 2 wt% of Pr(DS)_x)

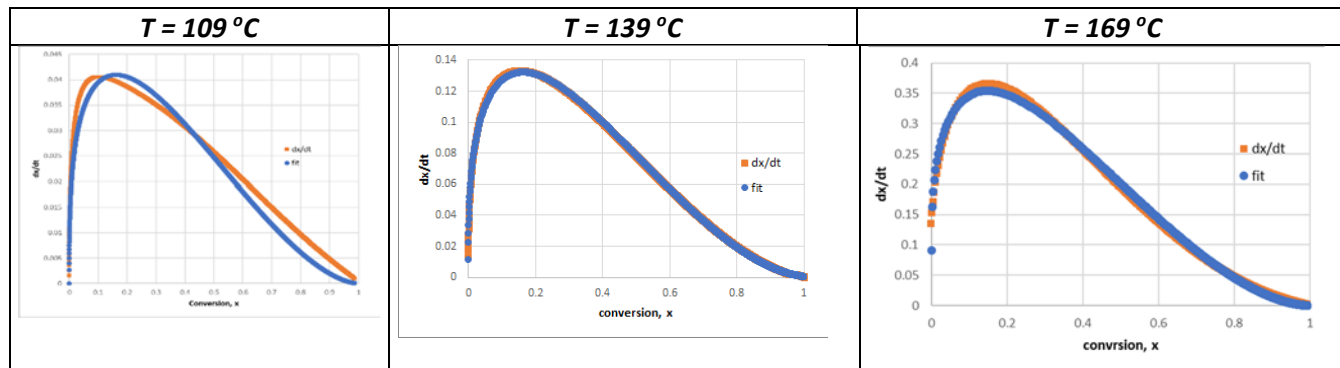


Figure S19 Experimental and fitted curve dx/dt vs conversion (x) at 109°C, 139°C and 169°C (LDO:PEI = 60:40 wt%, 2 wt% of Gd(DS)_x)

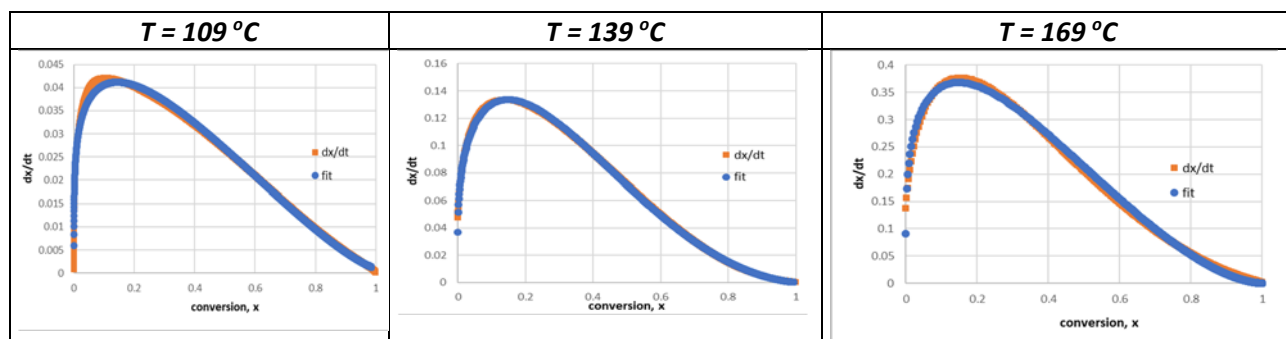


Figure S20 Experimental and fitted curve dx/dt vs conversion (x) at 109°C, 139°C and 169°C (LDO:PEI = 60:40 wt%, 2 wt% of Eu(DS)_x)

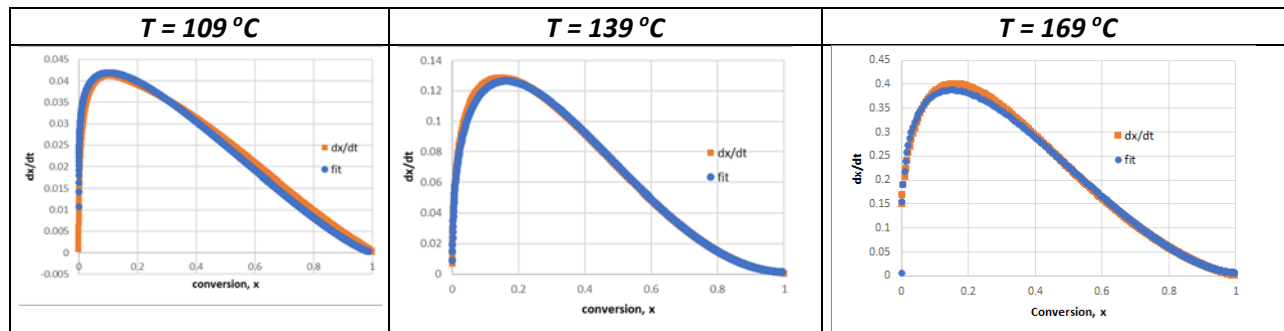


Table S10 Fit parameters corresponding to kinetic curves S13-S17

No catalyst

Parameter	T = 173 °C	T = 188 °C	T = 203 °C
k_1	0.00045	0.0016	0.0037
m_1	1.12	0.84	3.42
k_2	0.0037	0.010	0.025
m_2	0.43	0.630	0.89
n_2	1.12	1.60	2.36

2% La(DS)_x

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0	0.0078	0.087
m_1	1.83	0.51	3.27
k_2	0.099	0.33	0.91
m_2	0.33	0.35	0.39
n_2	1.69	1.82	1.92

2% Pr(DS)_x

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0.00023	0.0032	0.091
m_1	0.90	0.35	3.26
k_2	0.076	0.33	0.87
m_2	0.23	0.35	0.41
n_2	1.43	1.78	1.78

2% Gd(DS)_x

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k_1	0.0015	0.037	0.090
m_1	0.086	1.07	3.27
k_2	0.076	0.34	0.87
m_2	0.23	0.44	0.39
n_2	1.36	2.23	1.70

2% Eu(DS)_x

Parameter	T = 109 °C	T = 139 °C	T = 169 °C
k ₁	0.00060	0.0014	0.0066
m ₁	0.68	0.0028	0.0029
k ₂	0.067	0.36	0.89
m ₂	0.15	0.38	0.30
n ₂	1.30	1.98	1.71

Table S11 Comparison of the gel-time for various catalysts, $La(DS)_x$, $La(OPh)_x$ and $La(DBS)_x$

Formulations	Gel-time of $La(DBS)_x$	Gel-time of $La(OPh)_x$	Gel-time of $La(DS)_x$	Without catalyst
LDO-PEI (60/40 wt%)	39h	42h	33h	>48h
BADGE-Epikure (50/50 mol.%)	43min	55min	24min	84min

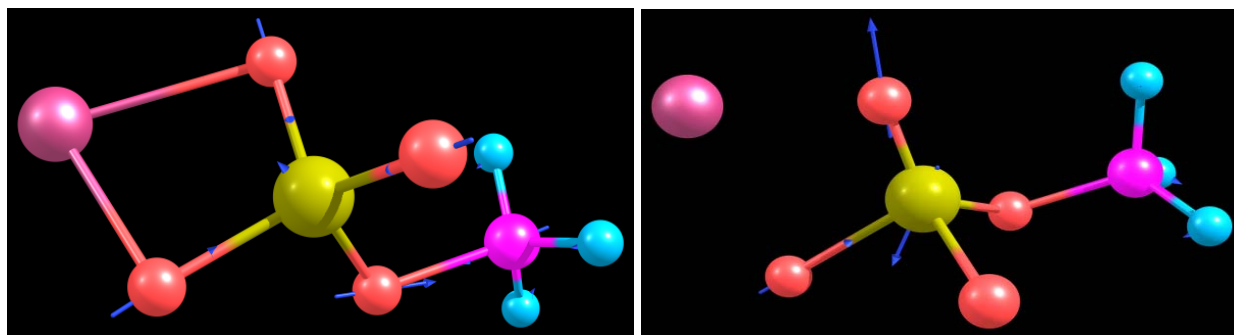
Table S12 Influence of the alkali-metal

Reactants	Gel-time (min)
Lithium dodecyl sulfate + $La(NO_3)_3 \cdot 6H_2O$	27
Sodium dodecyl sulfate + $La(NO_3)_3 \cdot 6H_2O$	28
Potassium dodecyl sulfate + $La(NO_3)_3 \cdot 6H_2O$	30

Table S13 Wavenumbers of the S-O vibrations in Ln(DS)_x complexes

IR Peak Material	Peak of asymmetric stretching S-O (cm-1)	Peak of asymmetric stretching S-O(cm-1)	Peak of symmetric stretching S-O(cm-1)	Peak of symmetric stretching S-O(cm-1)
SDS	1218		1081	
La(DS) ₃	1194	1158	1103	1082
Ce(DS) ₃	1195	1159	1103	1082
Pr(DS) ₃	1196	1161	1102	1084
Nd(DS) ₃	1196	1161	1103	1084
Sm(DS) ₃	1177	1166	1102	1091
Eu(DS) ₃	1179	1169	1102	1096
Gd(DS) ₃	1179	1170	1104	1099
Tb(DS) ₃	1182	Lost	1106	Lost
Ho(DS) ₃	1184	Lost	1107	1096
Er(DS) ₃	1207	1193	1108	1093+1071
Tm(DS) ₃	1193	Lost	1110	1096 +1077
Yb(DS) ₃	1210	1193	1108	1096+ 1071
Lu(DS) ₃	1212	1196	1111	1095+1079

Figure S21 Calculated vibrations for NaSO_4CH_3 at 1076 cm^{-1} and 1225 cm^{-1} (the vectors indicate the direction of displacement)



The molecule was optimized using the def2tzvpp basis set and the MO6 DFT method.

Table S14 Comparison of catalytic activity and SO₂ stretching wavenumber

fastest to slowest LDO curing	fastest to slowest conventional epoxy curing	lowest to highest asym stretching (cm ⁻¹)	lowest to highest sym stretching (cm ⁻¹)
La	La	La	La
Ce	Sm	Ce	Ce
Pr	Pr	Pr	Pr
Nd	Nd	Nd	Nd
Sm	Ce	Sm	Er
Tb	Yb	Eu	Eu
Lu	Tm	Gd	Tm
Ho	Gd		Yb
Yb	Eu		Ho
Eu	Er	Er	
Er	Ho	Yb	
Tm	Tb	Lu	Lu
Gd	Lu	Tm	Gd

Figure S22 ^{13}C Solid-state NMR of epoxy polymer prepared with (top) and without (bottom) catalyst (see Table S2 for amounts of each components)

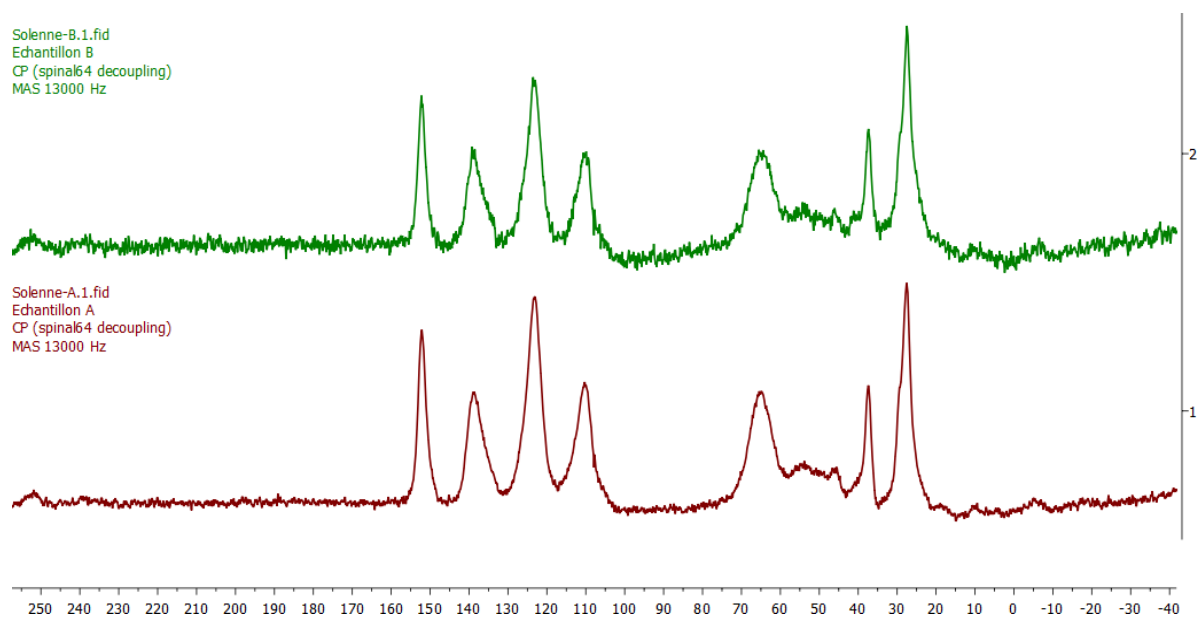


Table S15 Crystal data and data collection details for NaLa(DS)₄(H₂O)₂

Crystal data	
Chemical formula	<u>C₄₈H₁₀₄LaNaO₁₈S₄</u>
<i>M_r</i>	<u>1259.45</u>
Crystal system, space group	<u>Triclinic, <i>P</i></u>
Temperature (K)	<u>173</u>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	<u>9.5203 (9), 10.7677 (10), 31.980 (3)</u>
α, β, γ (°)	<u>81.246 (5), 84.947 (4), 72.957 (3)</u>
<i>V</i> (Å ³)	<u>3094.6 (5)</u>
<i>Z</i>	<u>2</u>
Radiation type	<u>Mo <i>K</i>α</u>
μ (mm ⁻¹)	<u>0.90</u>
Crystal size (mm)	<u>0.54 × 0.16 × 0.03</u>
Data collection	
Diffractometer	<u>Apex II CCD</u>
Absorption correction	<u>Numerical SADABS2016/2 (Bruker,2016) was used for absorption correction. wR2(int) was 0.1058 before and 0.0911 after correction. The Ratio of minimum to maximum transmission is 0.7725. The λ/2 correction factor is Not present.</u>
<i>T_{min}</i> , <i>T_{max}</i>	<u>0.573, 0.742</u>
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	<u>37181, 10627, 7063</u>
<i>R_{int}</i>	<u>0.110</u>
(sin θ/λ) _{max} (Å ⁻¹)	<u>0.595</u>
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	<u>0.069, 0.192, 1.04</u>
No. of reflections	<u>10627</u>
No. of parameters	<u>701</u>
No. of restraints	<u>1669</u>
H-atom treatment	<u>H-atom parameters constrained</u>
Δρ _{max} , Δρ _{min} (e Å ⁻³)	<u>2.13, -1.71</u>

Computer programs: S_AI_NT V8.27B (Bruker, 2012), SHELXT (Sheldrick, 2015), XL (Sheldrick, 2008), Olex2 1.3 (Dolomanov *et al.*, 2009).