

Supporting Information for

Chemical reactivity and the influence of initiators on the epoxidized vegetable oil-dicarboxylic acid system

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Materials and Methods

Materials

Epoxidized linseed oil (ELO; average molecular weight = 980 Da; average functionality = 5.5 epoxides per triglyceride, viscosity ~ 1200 Pa.s) was supplied by Valtris Specialty Chemicals. 2,2'-Dithiodibenzoic acid (DTBA, ≥ 95 %), imidazole (IM, ≥ 99 %), 1-methyl imidazole (1-MI, ≥ 99 %), 2-methyl imidazole (2-MI, ≥ 99 %), 1,2-dimethyl-imidazole (1,2-DMI, ≥ 98 %), 1-methyl-piperazine (1-MP, ≥ 95 %), 2-ethyl-4-methyl-imidazole (2E4MI, ≥ 95 %), N, N'-dimethyl benzamine (DMBA, ≥ 99 %), dimethylaminopyridine (DMAP, ≥ 99 %), 2,4,6-Tris(dimethylaminomethyl)phenol (DMP30, ≥ 95 %), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, ≥ 98%) were purchased from Sigma Aldrich. DMSO-*d*₆ (99.8 % D) solvent was purchased from Eurisotop. All chemicals compounds were used as received without any further purification. The specification of 10 initiators, epoxy monomer and hardener are presented in Table 1.

Samples preparation

The ELO/DTBA copolymerizations were carried out in absence or in presence of 1% (w/w) of initiator. ELO/DTBA mixtures were prepared using ratio R= 1, where R was defined as the ratio of carboxylic acid groups and epoxy groups which are present in all mixes (R = carboxylic acid groups/epoxy groups) according to the literature.

The selected amount of initiator was firstly dissolved in ELO at around 80 °C and mix together for several minutes. Then, at room temperature, DTBA was added and mixed till the complete homogenization. The freshly prepared samples were analysed by FTIR and DSC to follow the copolymerization reaction.

Fourier Transform Infrared Spectroscopy (FT-IR)

The crosslinking reaction kinetic was monitored *in situ* with a Thermo Scientific Nicolet iS50 FT-IR spectrometer with a deuterated L-alanine doped triglycine sulfate (DLaTGS) detector in attenuated total reflectance (ATR) mode. To prepare the formulations, all components were pre-mixed at room temperature, then heated *in situ* from 30 °C to 180 °C at a heating rate of 10 °C·min⁻¹. The FT-IR spectra were taken each minute during heating. The absorption bands were recorded in the range of 600 – 4000 cm⁻¹ with 32 scans and a resolution of 2 cm⁻¹. The data were analyzed using the OMIC software. The conversion of functional groups at time (*t*) is denoted as % and defined by the Equation (1). A comparison of the FT-IR spectra of reactants including ELO, DTBA and each initiator was performed. These data enabled to verify that the addition of DTBA, as well as of the initiator in ELO matrix do not cover the functional bands used for the conversion calculation.

$$\% = \frac{\left(\frac{A \text{ functional groups}}{A1586} \right)_0 - \left(\frac{A \text{ functional groups}}{A1586} \right)_t}{\left(\frac{A \text{ functional groups}}{A1586} \right)_0} * 100 \quad \text{Equation (1)}$$

The area absorbance peaks were calculated and reported at the initial time (A_0) and at different times (A_t). In the region of 823 cm^{-1} corresponds to the oxirane C-O groups, at 895 cm^{-1} corresponds to carboxylic groups and 1586 cm^{-1} is the reference band which belongs to the $\delta_{C=C}$ of the aromatic signal.

Nuclear magnetic resonance (NMR) analysis

^1H -NMR and ^{13}C -NMR spectra were respectively recorded at 400 and 100.6 MHz on a Bruker AVANCE I instrument. ^1H NMR spectral measurements were also performed in the same thermodynamic curing conditions. As NMR solvent, the DMSO- d_6 was particularly chosen because it is the best solvent to solubilize the DTBA. The concentration of ELO was kept constant at 0.05 M in DMSO- d_6 for all NMR analyses. The chemical shifts (δ) are expressed in part per million (ppm). The residual solvent signal at 2.50 ppm was used as a standard reference.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on a Mettler-Toledo DSC 3 apparatus controlled by STARE Software developed by Mettler-Toledo. The instrument heat flow and temperature were calibrated in 3 points using water, indium and zinc standards. The ELO/DTBA copolymerization reactions were directly performed in DSC pans, by simple heating. Samples of 10–15 mg were placed into 100 μL aluminium crucibles. The different mixtures were reacted under non-isothermal conditions at a heating rate β of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ over a temperature range $25\text{--}250\text{ }^\circ\text{C}$. The DSC technique was used also to study the second-order phase transitions on the obtained resins.

Quantum-chemical modelling

All structures were optimized using the Gaussian 16 software¹ at the B3LYP²⁻³ level of density functional theory (DFT). The structures were optimized and characterized with zero imaginary frequencies obtained from vibrational analysis. Atoms were described by the 6-31+G(d,p) basis set. The charge values presented herein are derived from electrostatic potentials at points selected according to the CHelp scheme.⁴

Supplementary Data

I. DSC data

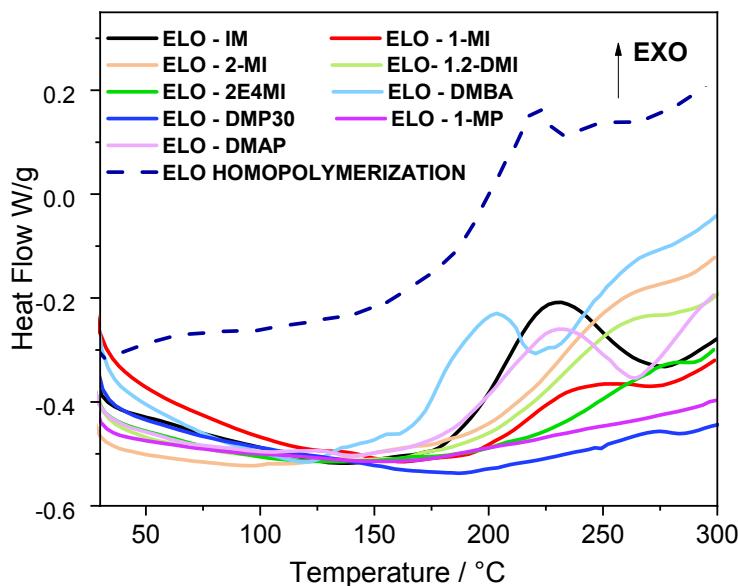


Figure S1. Dynamic DSC thermograms comparing ELO's homopolymerization in presence and absence of initiator during heating at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

Table S1. Temperatures and enthalpies of ELO's homopolymerization reactions in presence of different initiators obtained *via* dynamic DSC studies.

System	T _{on} (°C)	T _{peak} (°C)	T _{end} (°C)	ΔH (J.g ⁻¹)
ELO	205	219	230	14
ELO / IM	187	227	268	66
ELO / 1-MI	200	236	287	28
ELO / 2-MI	197	253	292	18
ELO / 1,2-DMI	197	255	292	15
ELO / 2E4MI	245	275	292	10
ELO / DMBA	168	200	219	20
ELO / DMP30	247	269	292	5
ELO / 1-MP	-	-	-	-
ELO / DMAP	185	230	262	54

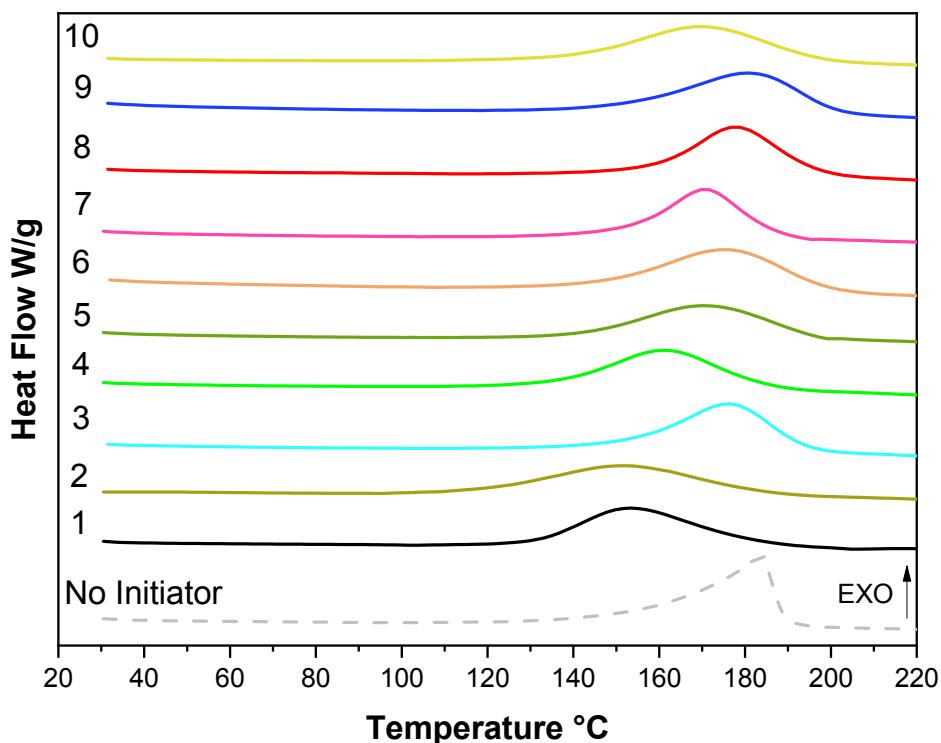


Figure S2. Dynamic DSC thermograms during heating at $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$ of ELO/DTBA systems without initiator and with 1 wt. % of initiator: (1) IM; (2) 1-MI; (3) 2-MI; (4) 1,2-DMI; (5) 2E4MI; (6) DMBA; (7) DMP30; (8) 1-MP; (9) DMAP and (10) TBD.

Table S2. Evaluation of DSC dynamic heating at $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$ of ELO/DTBA systems without and with 1 wt. % of initiator and glass transition temperatures of the obtained resins.

	Initiators	T_{on} ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)	T_{end} ($^{\circ}\text{C}$)	ΔH ($\text{J}.\text{g}^{-1}$)	T_g ($^{\circ}\text{C}$)
0	No initiator	167	184	189	248	13
1	IM	130	154	184	214	76
2	1-MI	117	152	184	206	74
3	2-MI	151	177	195	240	46
4	1,2-DMI	135	162	186	208	70
5	2E4MI	142	171	197	186	64
6	DMBA	145	176	200	260	37
7	DMP 30	158	178	197	220	55
8	1-MP	152	181	202	244	65
9	DMAP	150	171	188	206	64
10	TBD	141	170	198	189	61

II. FTIR-NMR data

1. Characterization of starting material

➤ ELO

The FT-IR spectrum of ELO is shown in Figure S3. The characteristic band of the oxirane ring is detected at 823 cm^{-1} and the carbonyl group stretching from the ester functionality in the triglycerides is observed at 1740 cm^{-1} . The characteristic bands of ELO are summarised in Table S3.

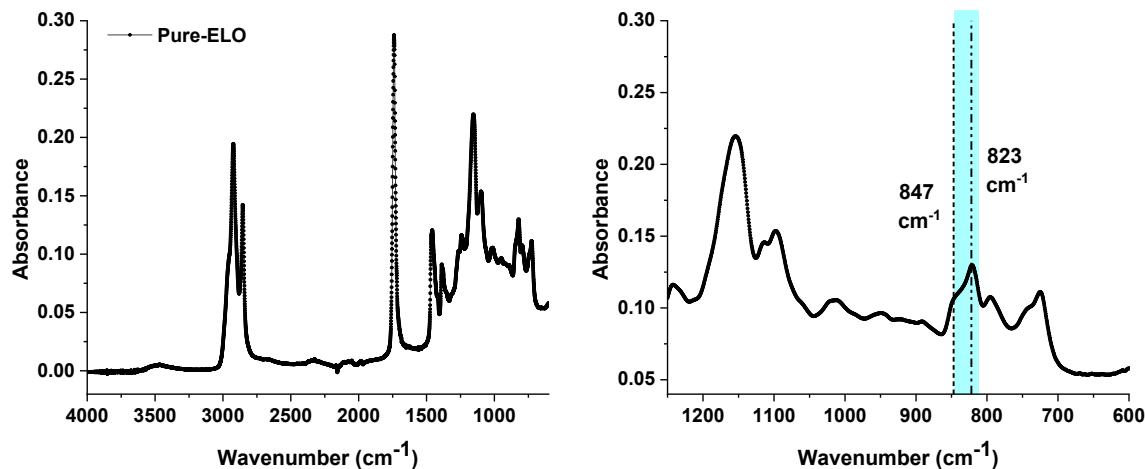


Figure S3. FT-IR Spectrum of ELO, **Left:** Whole spectrum, **Right:** Zoom in the region of $1200\text{-}600\text{cm}^{-1}$.

Table S3. FT-IR assignments characteristic bands of ELO ⁵⁻⁶.

Wavenumber (cm^{-1})	Appearance of peak	Assignments of ELO
3478	Broad (w)	-O-H stretching
2927	s	-C-H asymmetric stretching of CH_2, CH_3
2849	s	-C-H symmetric stretching of CH_2, CH_3
1740	s	-C=O stretching of ester groups
1459	m	Scissoring of CH_2 , asymmetric bending of CH_3
1389	w	$-\text{CH}_3$ symmetric deformational
1243	m	C-O-C stretching of epoxy groups
1155	s	C-O asymmetric of ester groups ($\text{O}=\text{C}-\text{O}$)
1098	w	C-O stretching of $\text{O}-\text{CH}_2$
847 & 823	w	C-O or C-H wagging of epoxy groups
725	w	In phase rocking of $(\text{CH}_2)_n, n>3$

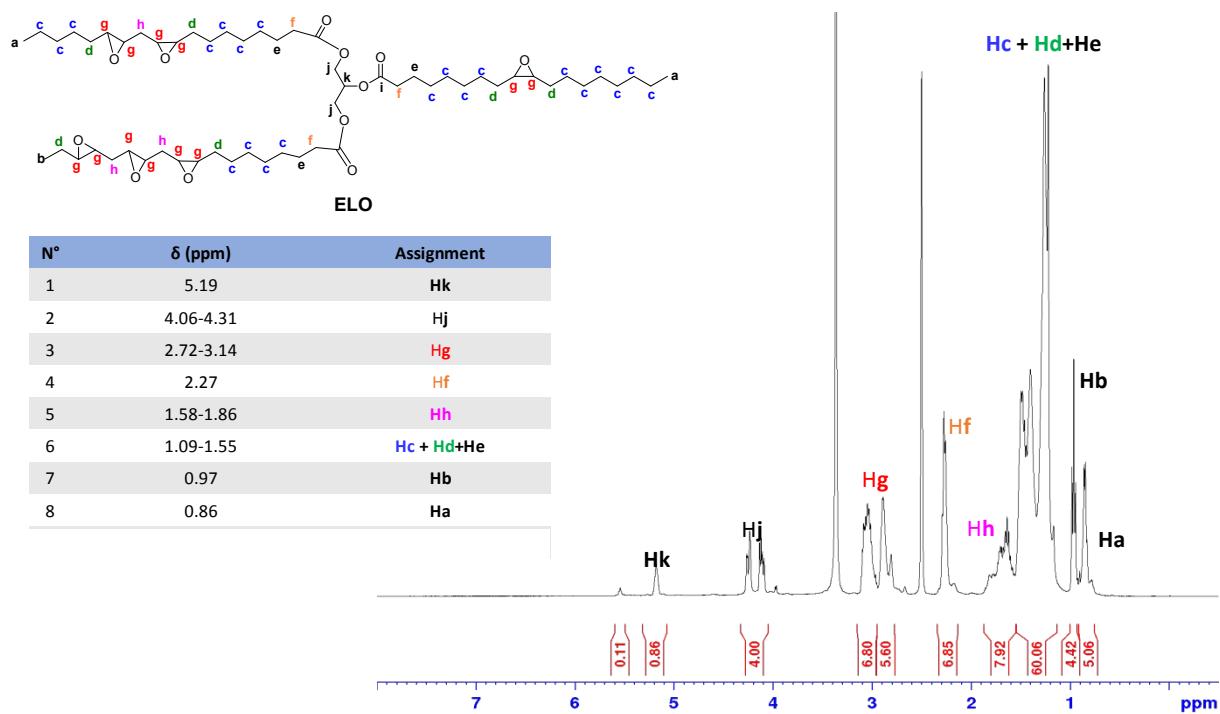


Figure S4. ¹H NMR Spectrum of ELO with corresponding assignments of each proton.

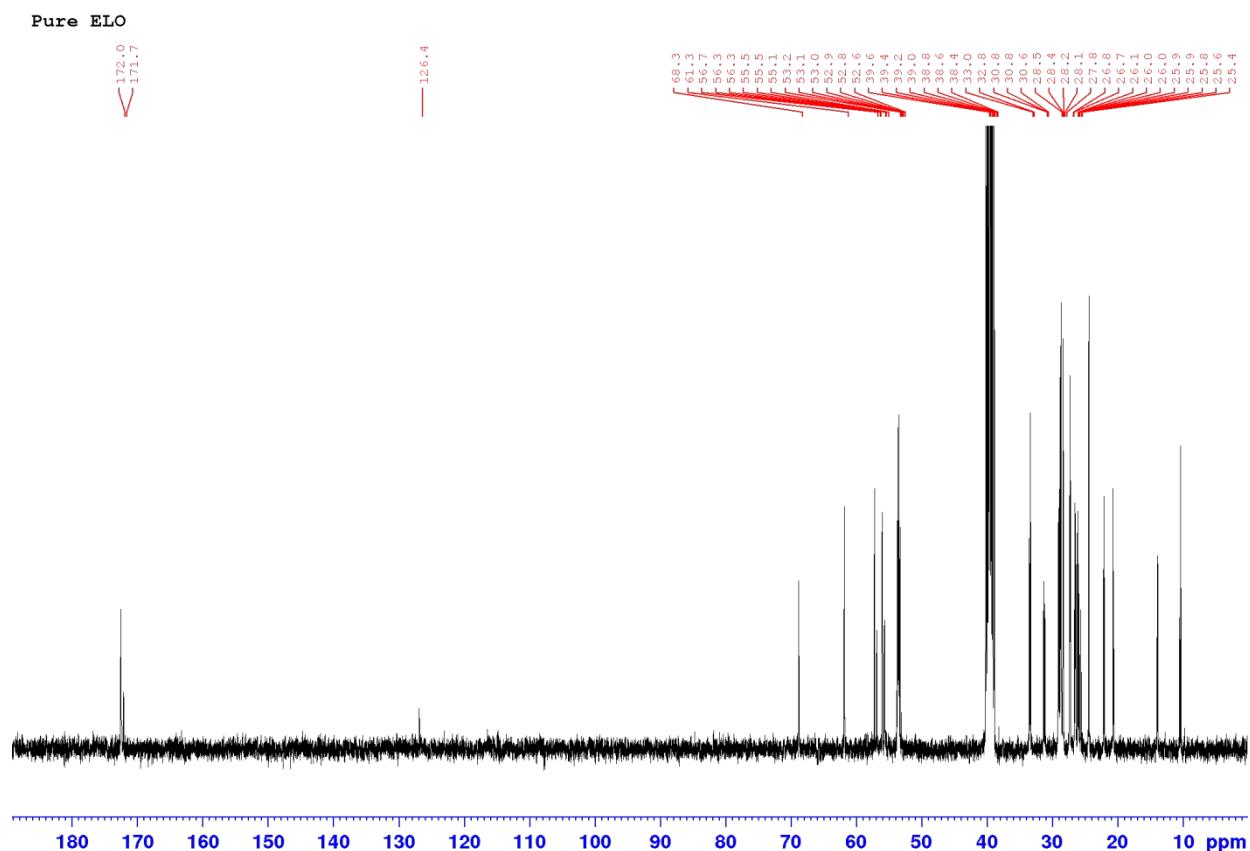


Figure S5. ¹³C NMR Spectrum of ELO, in DMSO-*d*₆.

➤ DTBA

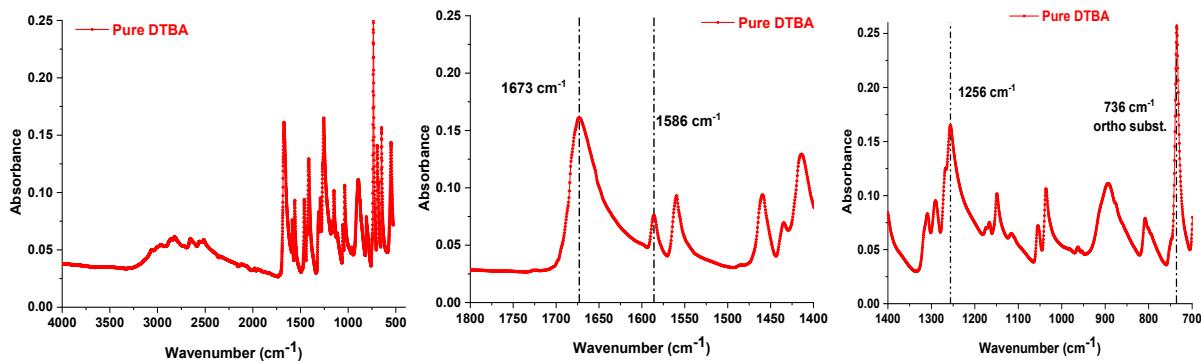


Figure S6. FT-IR spectrum of DTBA, **Left:** Whole spectrum, **Middle:** Zoom in the region of 1800-1400 cm^{-1} **Right:** Zoom in the region of 1400-700 cm^{-1} .

Table S4. FT-IR assignments of characteristic peaks of DTBA.

Wavenumber (cm^{-1})	Appearance of peak	Assignments of DTBA
3200-2300	Broad (w)	O-H stretching, partially obscure with C-H stretching
1673	s	-C=O stretching of acid group
1586 and 1560	m	C=C and -C-C aromatic stretching
1256	m	C-O-C stretching of acid group
1148	s	C-O asymmetric stretching
895	w	O-H out of plane bending
736	w	C-H out of plane bending, <i>ortho</i> -substituted ring

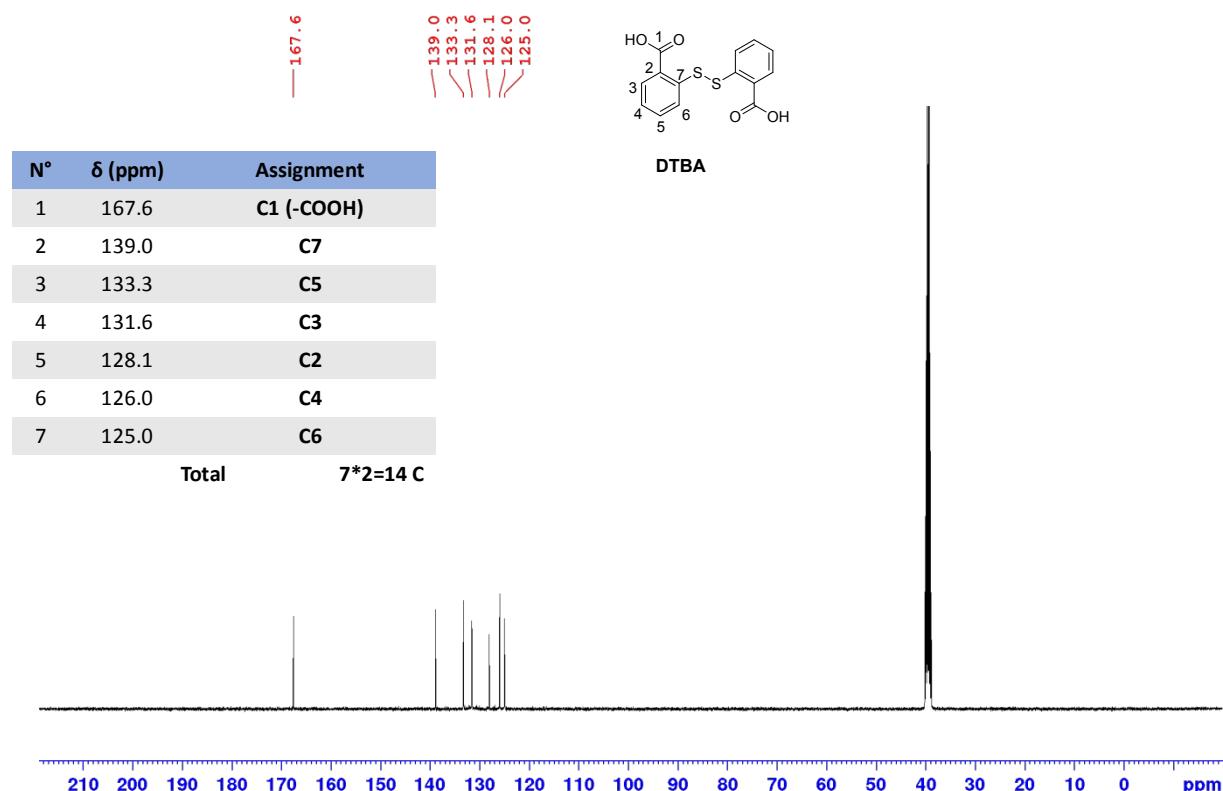
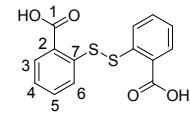


Figure S7. ^1H NMR Spectrum of DTBA with corresponding assignments of each proton.

N°	δ (ppm)	App	Assignment	Total of proton
1	8.02	d	H3	2H
2	7.65-7.01	m	H5+H6	4H
3	7.33	t	H4	2H

Total **8H of DTBA**



DTBA

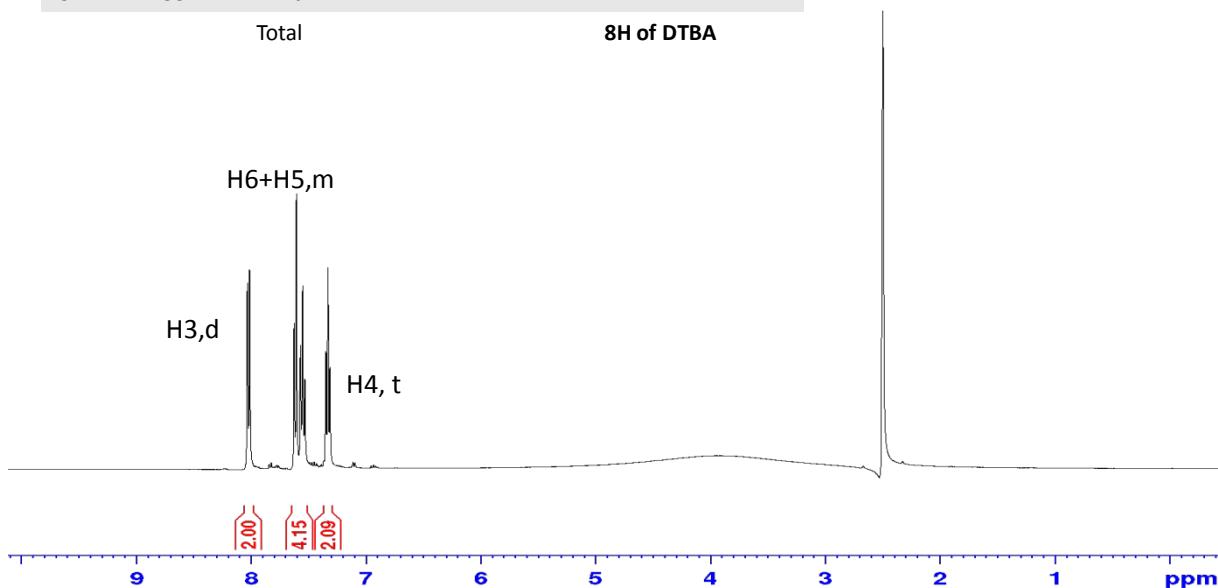


Figure S8. ^{13}C NMR Spectrum of DTBA.

2. Characterization of ELO + initiator mixture

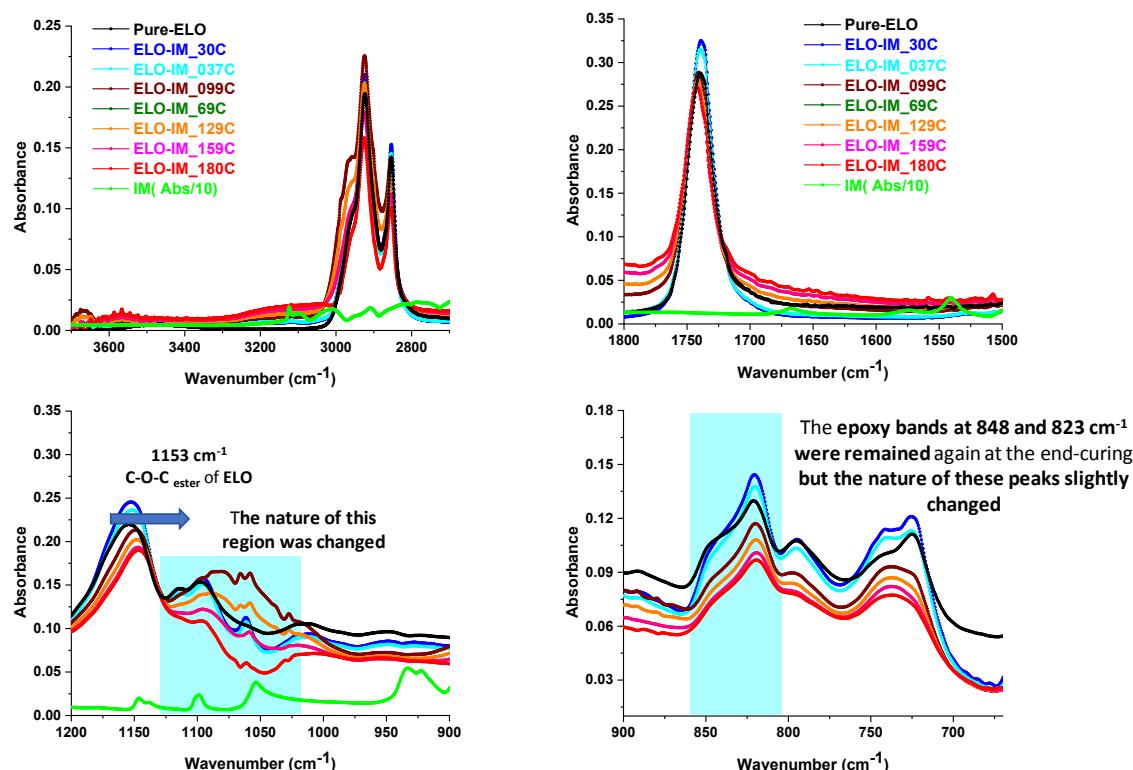


Figure S9. Evolution of FT-IR spectra of the mixture ELO+IM_{1%} during heating from 30°C to 180°C. Interaction ELO-IM detected.

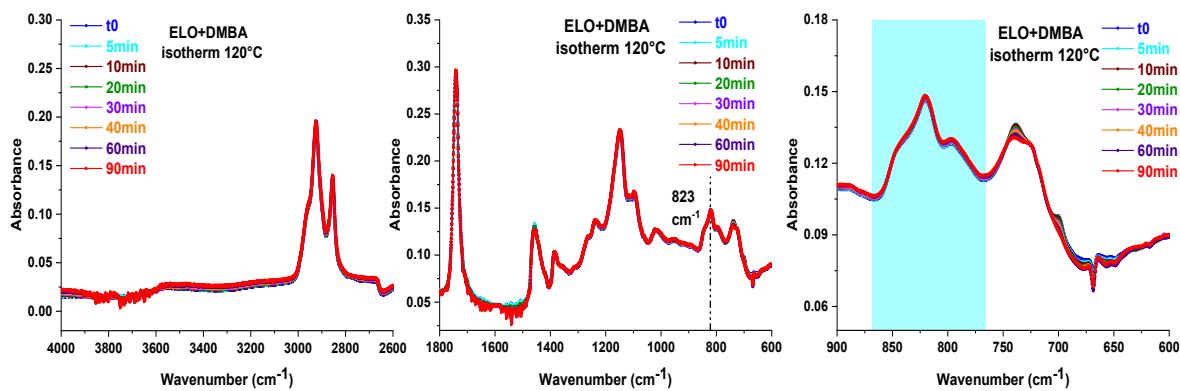


Figure S10. Evolution of FT-IR spectra of the mixture ELO+IM_{1%} during isothermal study at 120°C for 90 min.

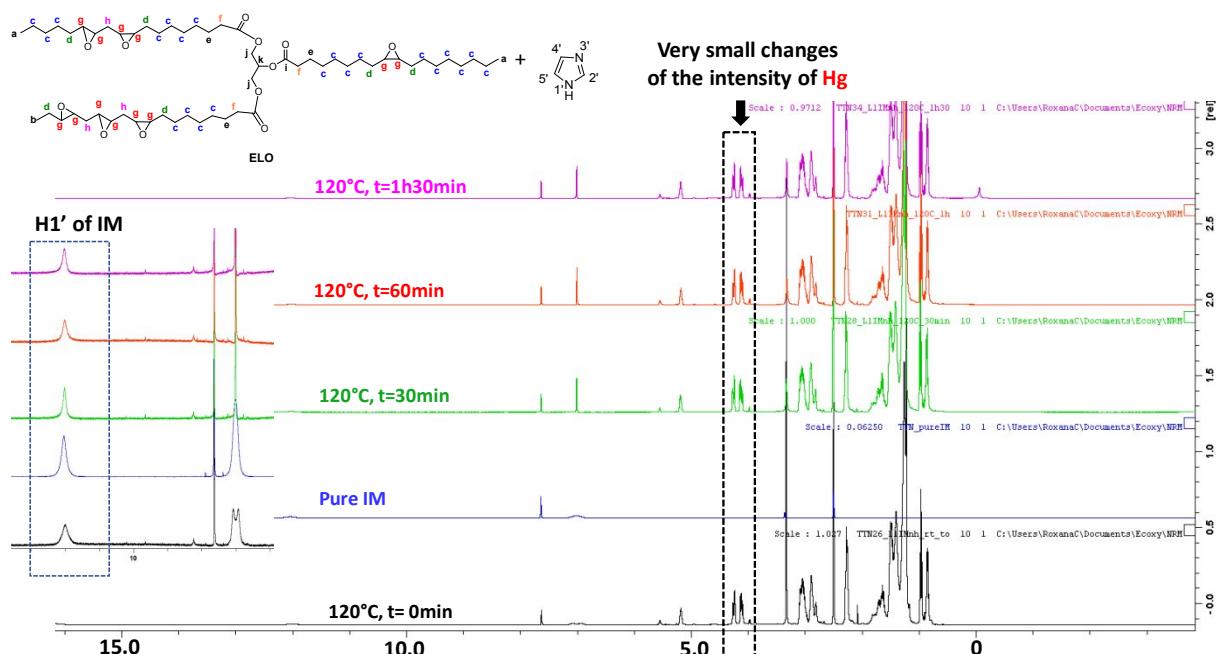


Figure S11. Evolution of NMR spectra of the mixture ELO+IM_{1%} in solution of DMSO-*d*₆, during isothermal study at 120°C at different times.

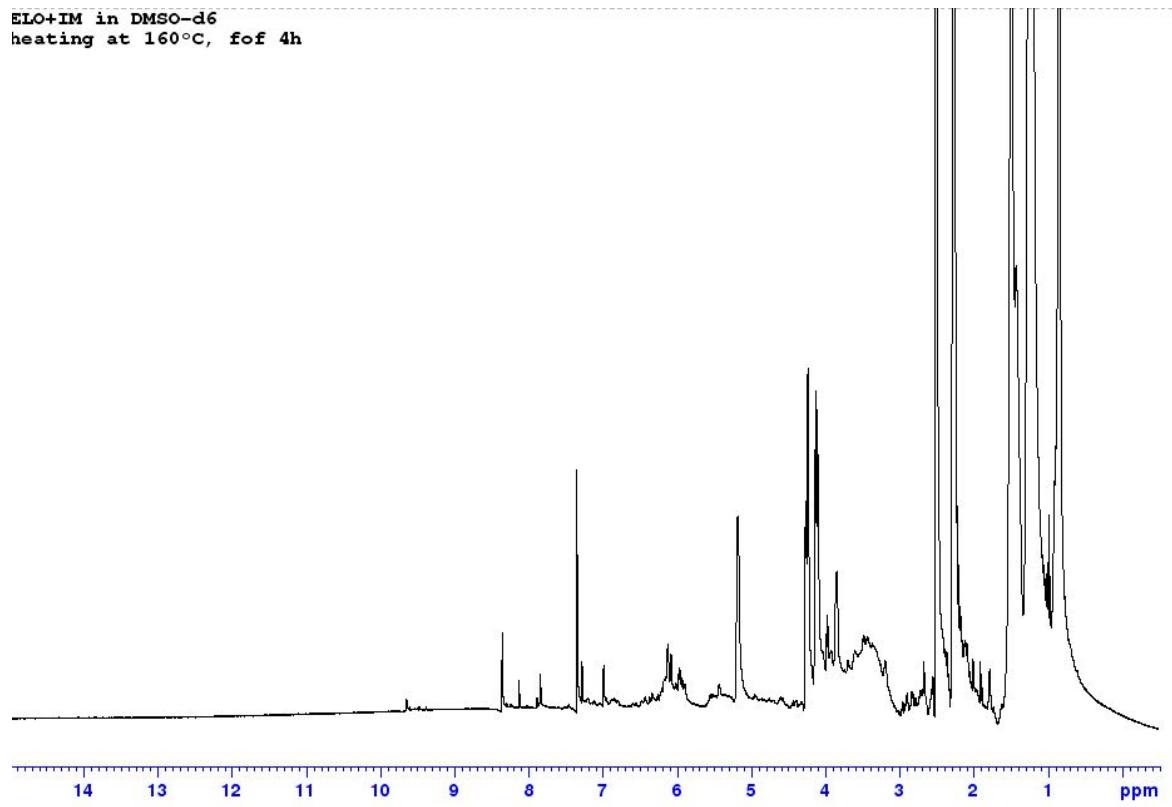


Figure S12. ¹H NMR spectra of the mixture ELO+IM_{1%} in solution of DMSO-d₆, isotherm at 160°C for 4h.

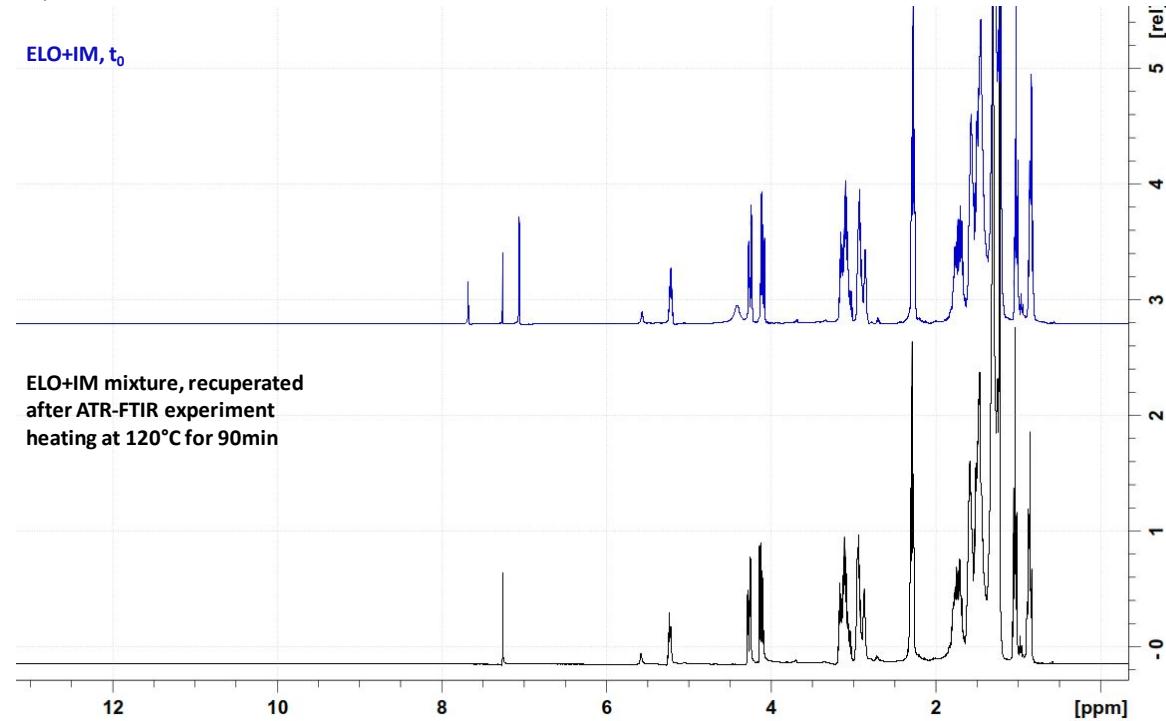


Figure S13. ¹H NMR spectra of the mixture ELO+IM_{1%}, recuperated after isotherm FT-IR experiment at 120 °C, for 90min, dissolved in CDCl₃, compared with that at t_0 . A small change is observed in epoxy region. All chemical shifts were slightly shifted, compared to that at t_0 . The disappearance of protons of IM molecule was detected.

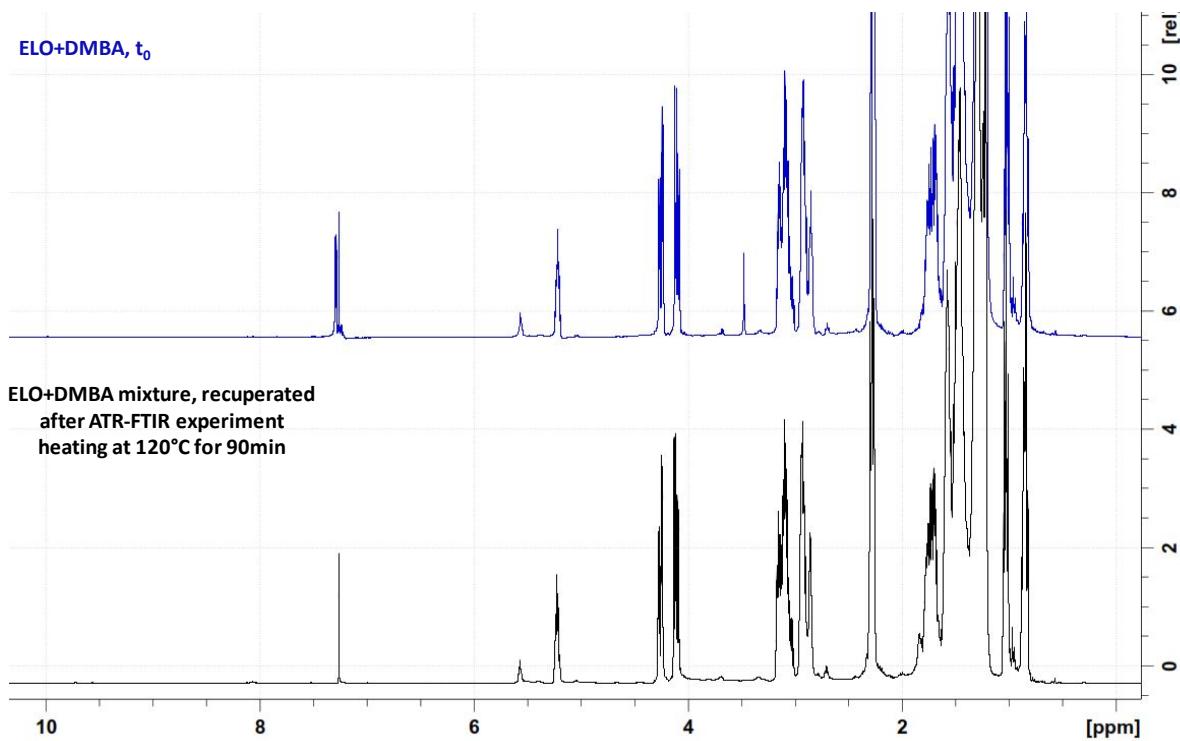


Figure S14. ¹H NMR spectra of the mixture ELO+DMBA_{1%}, recuperated after FT-IR experiment at 120 °C, for 90 min, dissolved in CDCl₃ in comparison with that at t₀. A small change is observed in epoxy region. All chemical shifts were slightly shifted, compared to that at t₀. The disappearance of protons of DMBA molecule were detected.

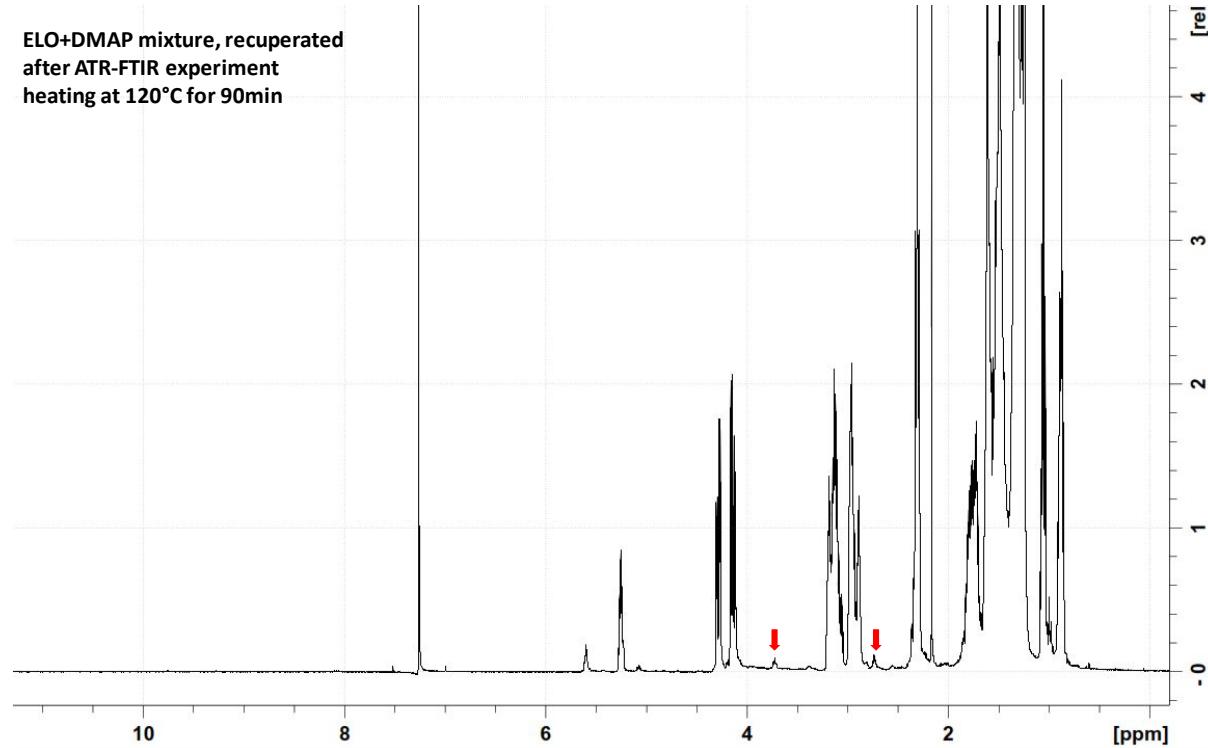


Figure S15. ¹H NMR spectra of the mixture ELO+DMAP_{1%}, recuperated after FT-IR experiment at 120 °C, for 90 min, dissolved in CDCl₃. A small change is observed in epoxy region, following by the appearance of new signal. It indicates that an attack of DMAP on epoxy ring was carried out.

3. Characterization of DTBA+IM mixture

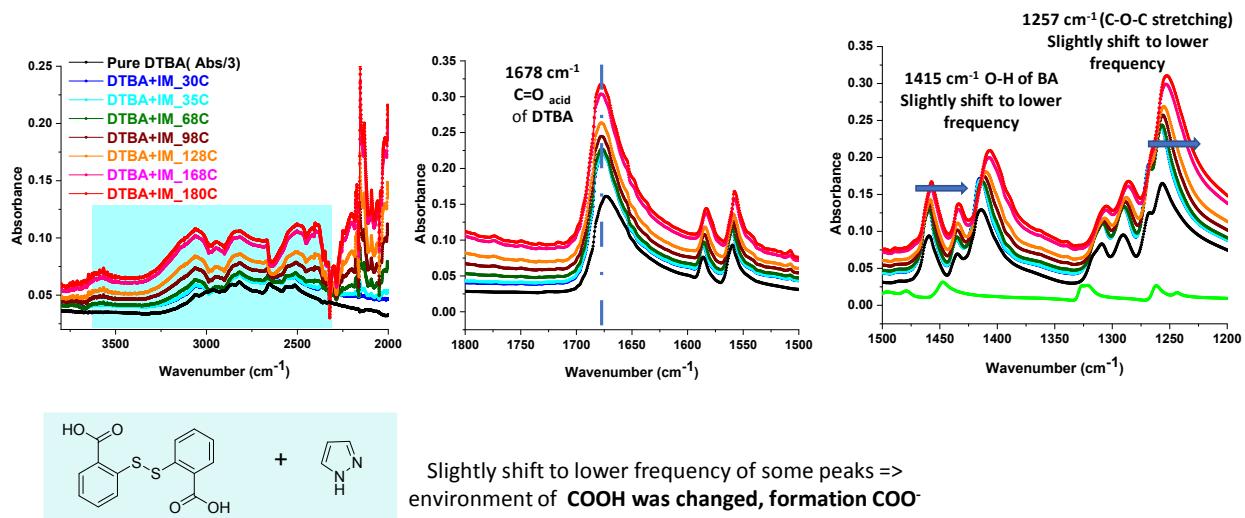


Figure S16. Evolution of FT-IR spectra of the mixture DTBA+IM_{1%} during heating from 30 °C to 180 °C.

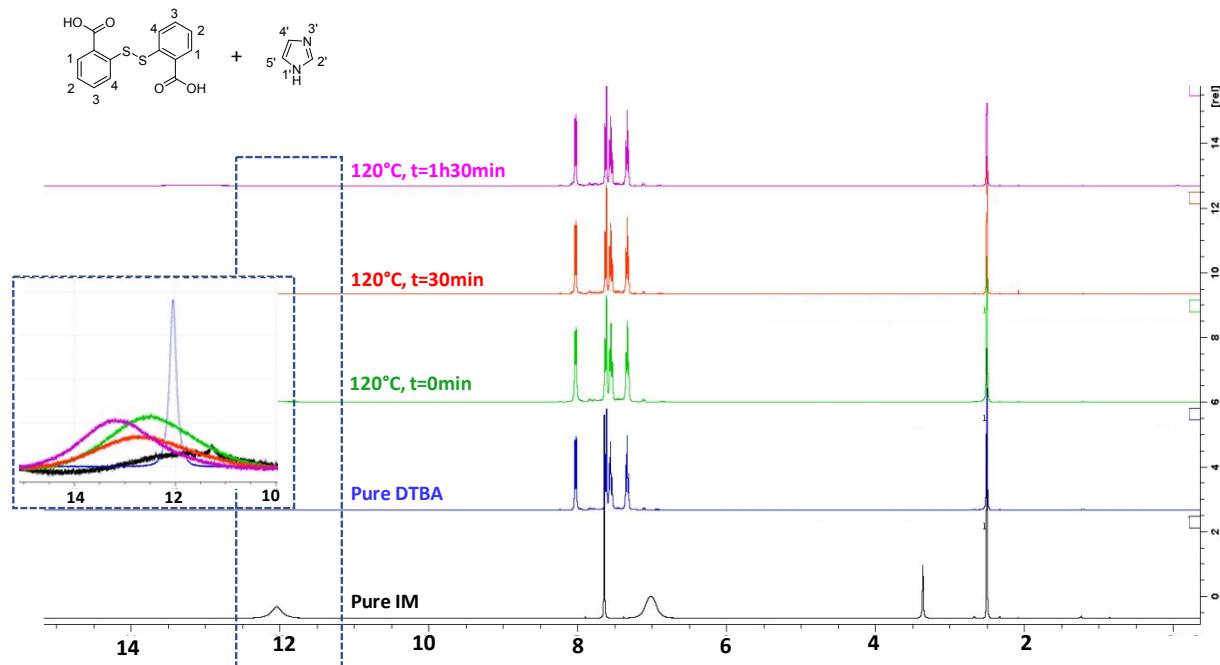


Figure S17. Evolution of NMR spectra of the mixture DTBA+IM_{1%}, isothermal heating at 120 °C at different times.

4. Characterization of ELO+ DTBA+ Initiator mixture

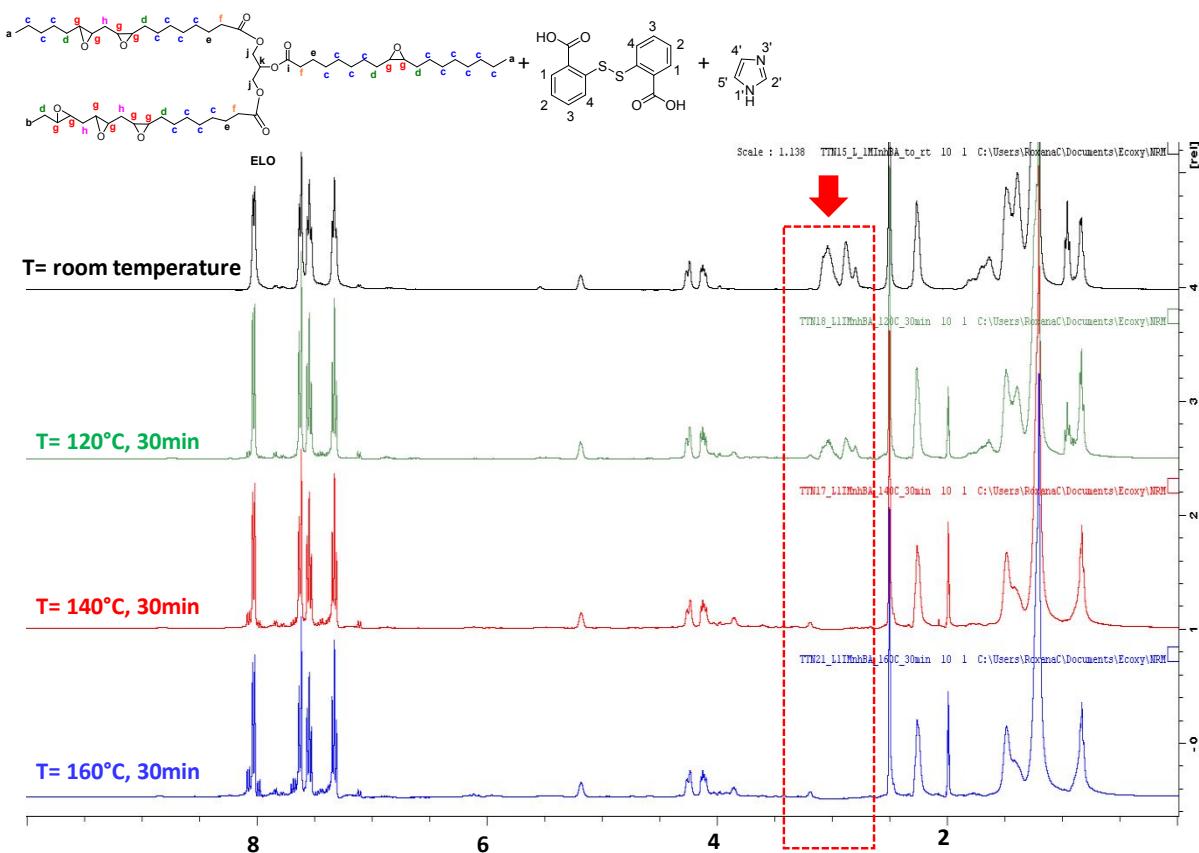


Figure S18. ^1H NMR spectra evolution at different temperature for ELO+DTBA+IM_{1%} mixture in DMSO- d_6 solution.

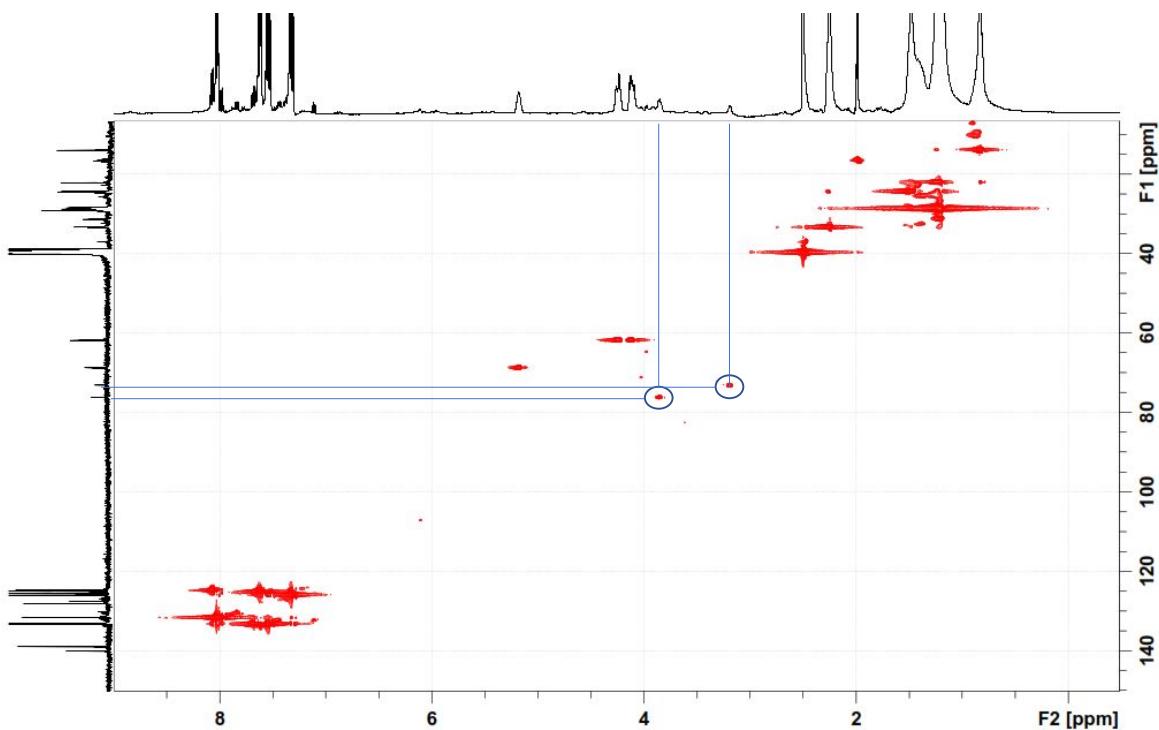


Figure S19. ^1H - ^{13}C HSQC NMR of ELO+DTBA+IM_{1%} mixture in DMSO- d_6 solution, heating at 120 °C for 90 min.

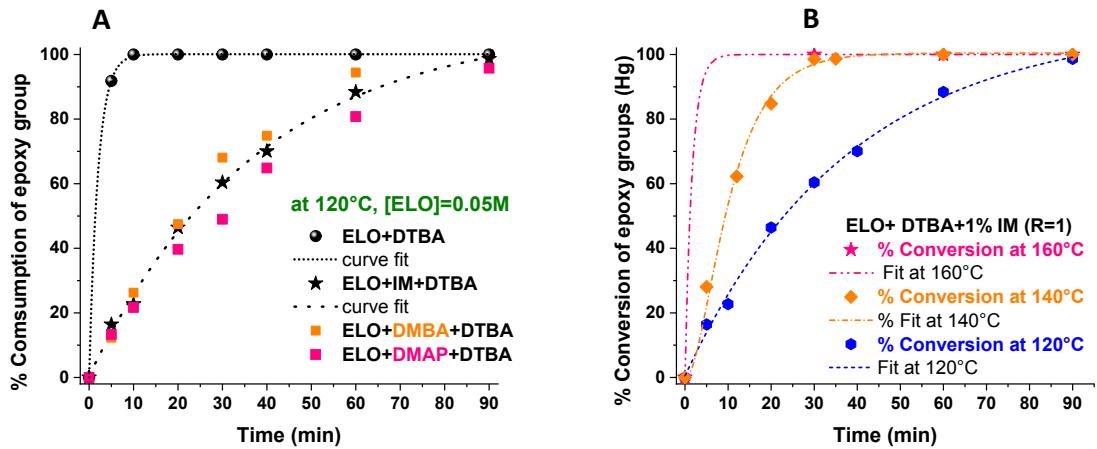


Figure S20. Conversion of epoxy functions, determined by ^1H NMR analysis, the concentration of ELO was kept constant at 0.05 M in $\text{DMSO}-d_6$ for all NMR analyses (A): at 120 °C; (B): at different temperatures.

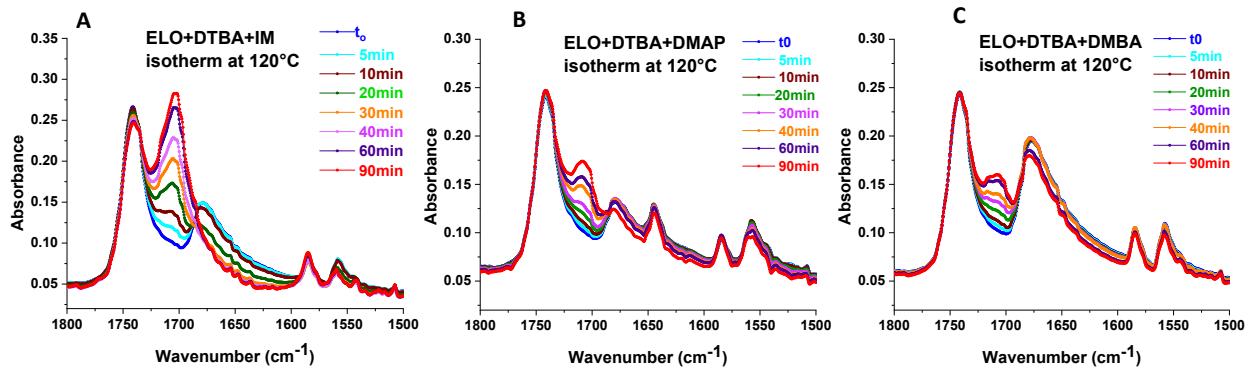


Figure S21. FT-IR spectra evolution of ELO+DTBA+1 wt.% of initiator during 90 min of heating at 120 °C: (A) Imidazole; (B) DMAP; (C) DMBA.

Table S5. Comparison between ELO homopolymerizations in presence of 1 wt.% imidazoles initiators.

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