Electronic Supplementary Material (ESI) for Polymer Chemistry.

ELECTRONIC SUPPORTING INFORMATION

Unveiling the reactivity of epoxides in carbonated epoxidized soybean oil and application to the stepwise synthesis of hybrid poly(hydroxyurethane) thermosets

P. Helbling[1,2], F. Hermant[2], M. Petit[2], T. Tassaing[3], T. Vidil[1*] and H. Cramail[1*]
[1]Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, 16 avenue Pey-Berland 33600 Pessac, France

[2]Saint-Gobain Recherche Paris, 39 Quai Lucien Lefranc 93300 Aubervilliers, France

[3]Univ. Bordeaux, CNRS, ISM, 351 cours de la Libération 33400 Talence, France

TABLE OF CONTENTS

Characterization

Nuclear Magnetic Resonance (NMR): ^{1}H NMR spectra were recorded on a Bruker Advance 400 spectrometer (400.20 MHz) at room temperature. DMSO-d_6 and CD_2Cl_2 were used as deuterated solvents and 1,2,4-trichlorobenzene was used as an internal reference.

Infrared spectroscopy: Fourier transform infrared (FTIR) spectra were recorded on a Bruker-VERTEX 70 instrument (400 to 4000 cm^{-1}, 4 cm^{-1} resolution, 32 scans, DLaTGS MIR) equipped with a Pike GladiATR optical design (diamond crystal) for attenuated total reflectance (ATR). In the case of *in-situ* monitoring, the spectrometer was equipped with a thermally controlled diamond plate surrounded by a metallic piece creating a leak-proof cavity in order to proceed to the crosslinking reaction directly on the plate.

Raman spectroscopy: Raman measurements were performed with a XploRA spectrometer from Horiba using a laser source operating at 30 mW output power with a 785 nm excitation wavelength (260 to 2600 cm^{-1}, 6 cm^{-1} resolution, 600 lines mm^{-1}). In order to obtain a good signal to noise ratio, each spectrum resulted from the average of 12 or 24 accumulated scans with an integration time for each scan of about 10 seconds. A homemade stainless-steel cell equipped with a sapphire window was used to collect the Raman spectra during the crosslinking reactions, the laser beam being focused at the sample/sapphire window interface with the confocal microscope (X10 objective).

Rheological analyses: Rheological monitoring of the crosslinking reactions was performed using an Anton Paar MCR 302 rheometer equipped with disposable parallel plates (Ø = 25 mm) and operating in the multiwave mode using Fourier transform mechanical spectroscopy (FTMS).[41] A multiwave strain signal of 1 % amplitude for the 1 rad s^{-1} component was applied in order to collect G' and G'' data every 5 minutes for the 7 following frequencies: 1, 3, 6, 10, 30, 60 and 100 rad s^{-1}.

Thermogravimetric analysis (TGA): The thermal decomposition of the polymer networks was studied using a TA Instruments Q50. The samples were, in a first time, heated from 20 to 600 °C under a nitrogen atmosphere at a rate of 10 °C min^{-1} and then heated until 700 °C under air atmosphere.

Differential scanning calorimetry (DSC): Differential scanning calorimetry thermograms were recorded on a TA instrument DSC Q100. The samples, whose mass is comprised between 3 and 9.5 mg, were sealed in aluminium pans and analysed under nitrogen atmosphere. Two cycles were performed: a first one from -75 °C to 180 °C at a rate of 10 °C min^{-1} and a second one from -75 °C to 220 °C. The glass transition temperature (T_g) was measured from the latter.

Size exclusion chromatography (SEC): Polymer molar masses were determined by SEC using dimethylformamide (DMF + lithium bromide LiBr 1 g L^{-1}) as the eluent. Measurements were performed on an Ultimate 3000 system from Thermoscientific equipped with a diode array detector (DAD). A multi-angles laser light scattering detector (MALLS) and differential refractive index detector (dRI) from Wyatt technology are also included. Species were separated on two Shodex Asahipack gel columns GF310 and GF510 (300 x 7.5 mm - exclusion limits from 500 Da to 300000 Da) at a flowrate of 0.5 mL min^{-1}. The temperature of the columns was held at 50 °C. Easivial Polystyrene kit from Agilent was used for the standards (M_n from 162 to 364 000 Da).

Synthesis of partially carbonated ESBO: CSBOX

A first range of experiments was carried out in order to optimize the parameters for the carbonation reactions. To this end the influence of the temperature, the initial pressure of CO_2, the amount of catalyst, and the stirring mode was studied by measuring the conversion of epoxides into carbonates X – in other words the carbonate ratio – after a reaction time of 24 or 72 hours. Figure S1 represents the evolution of X as a function of the various parameters of the reaction. For each experiment, X is measured at the end of the reaction according to ^1H NMR analyses (see Figure S3). The temperature as well as the amount of catalyst have a significant impact on X, as already illustrated by different authors.[1,2] Increasing the temperature from 80 °C to 120 °C results in an increase of X from 34 % to 99 % (Figure S1a). The use of the catalyst TBABr is necessary as the catalyst-free reaction does not proceed (Figure S1b). Furthermore, an increase of the catalyst content from 1.5 to 3 wt% fostered the conversion from 50 % up to 80 %. Increasing the stirring from 250 to 500 rpm (Figure S1c) or the initial pressure of CO_2 from 25 to 45 bar (Figure S1d) has no significant impact on X.

In the end, after taking into account the influence of each parameter, the carbonation reactions were carried out at 120 °C under a 250 rpm magnetic stirring with an initial pressure of CO_2 of 45 bar and a catalyst content of 3 wt%.

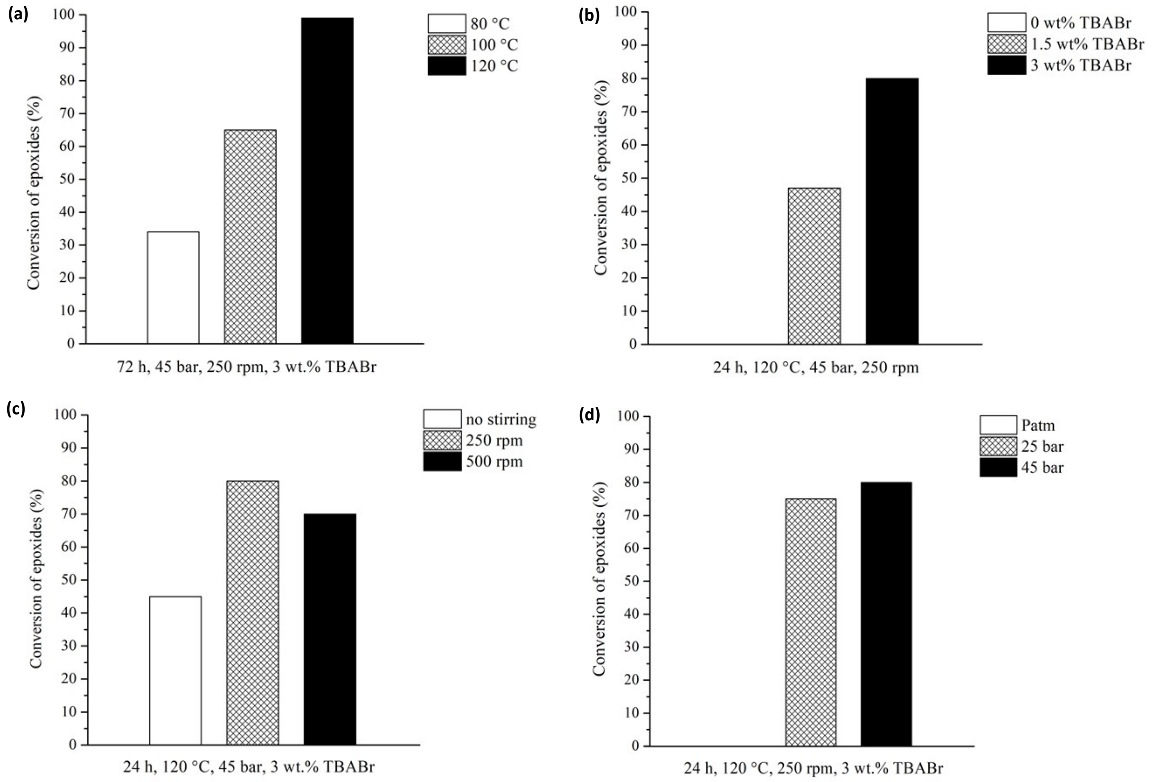

Figure S1: Conversion of epoxides, X, during carbonation reactions depending on the parameters: a) temperature, b) amount of catalyst, c) stirring mode and d) initial pressure of CO2

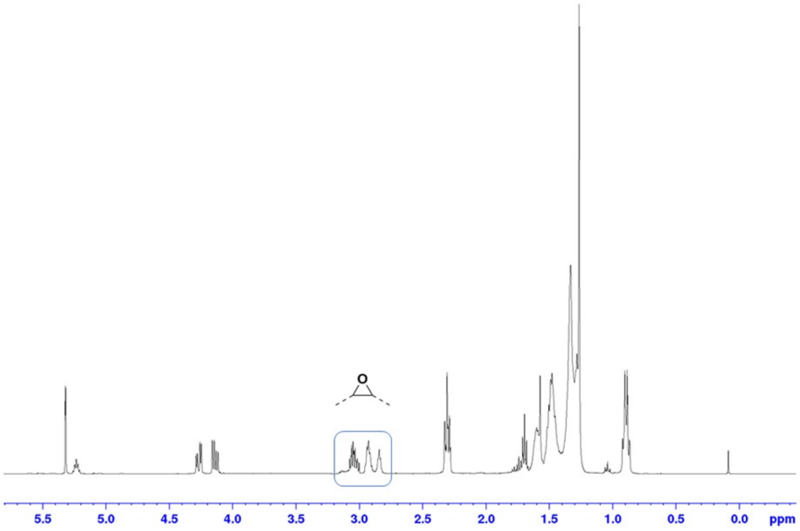

Figure S2: ^{1}H NMR spectrum of ESBO in CD_2Cl_2

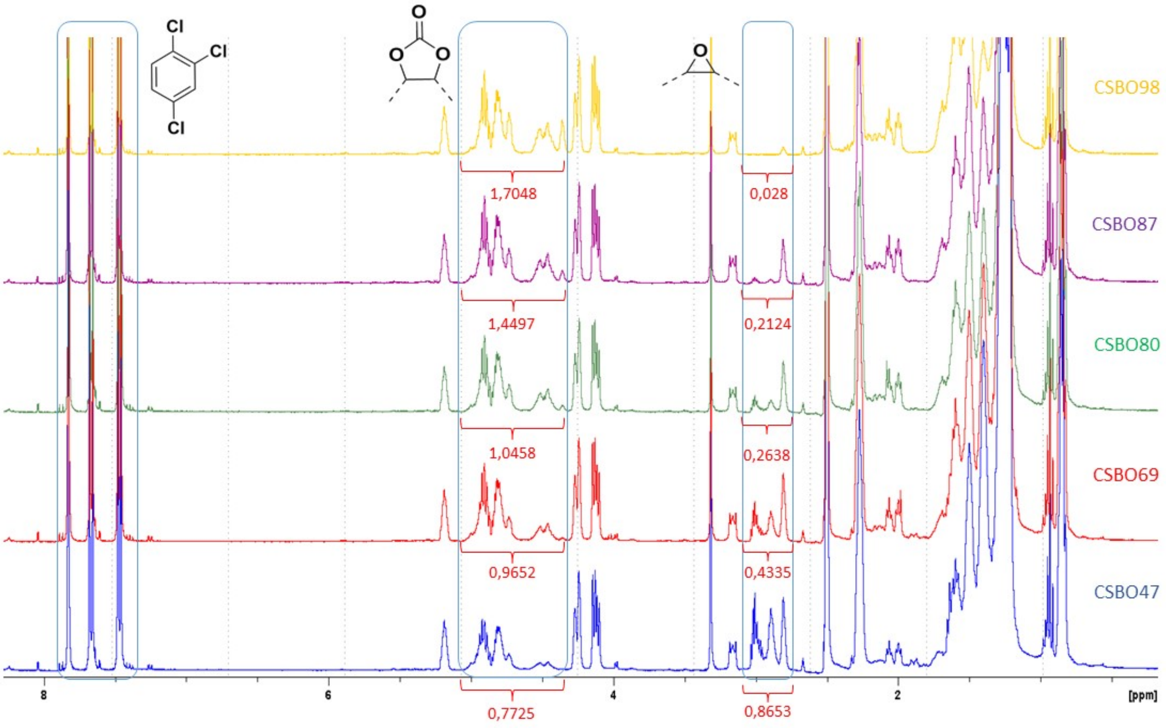

Figure S3: Overlay of ^{1}H NMR spectra in DMSO-d_6 of partially carbonated epoxidised soybean oils which X is comprised between 47 and 98 %

Method for NMR integration:

The signal associated with the reference protons of 1,2,4-trichlorobenzene are integrated as 3 protons.

Considering the conversion of epoxides into carbonate as the only reaction occurring, (**Eq. S*1*** was used to calculate the conversion of epoxides into carbonates, X, for each carbonation reaction:

$$X\,(\%) = \frac{\int H_{carbonate}}{\int H_{carbonate} + \int H_{epoxide}} \qquad \textbf{(Eq. S1)}$$

with $\int H_{epoxide}$ and $\int H_{carbonate}$ the integrals of the peaks associated with the 2 protons of epoxide and carbonate functions respectively.

(**Eq. S*2*** was then used to calculate $C_{carbonate}$ as the number of moles of cyclic carbonate per kilogram of a partially carbonated soybean oil CSBOX :

$$C_{carbonate}\left(\text{mol kg}^{-1}\right) = \frac{\int H_{carbonate}}{2} \times n_{REF} \times \frac{1000}{m_{CSBOx}} \qquad \textbf{(Eq. S2)}$$

with $\int H_{carbonate}$ the integral of the peaks associated with the 2 protons of carbonate functions, n_{ref} the number of moles of internal reference and m_{CSBOx} the mass of partially carbonated soybean oil used for the analysis.

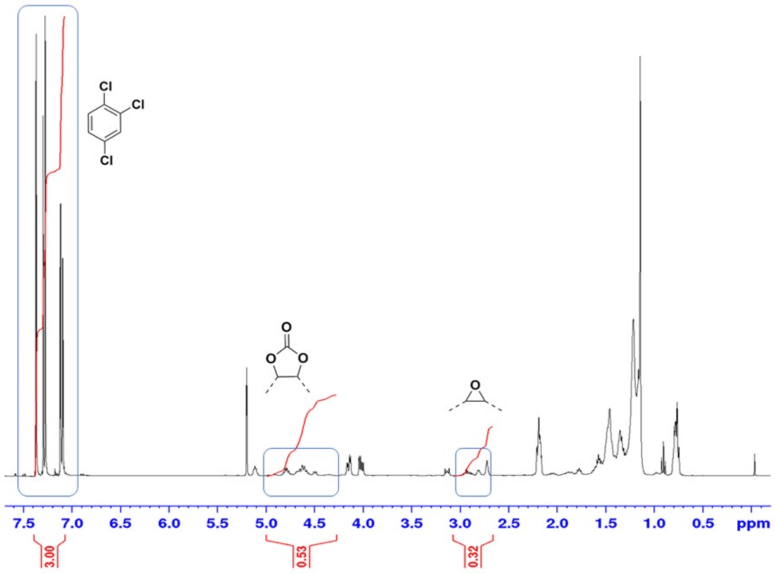

Figure S4: ^{1}H NMR spectrum of CSBO45 in CD_2Cl_2

Dual-spectroscopic investigation of the crosslinking reaction of CSBO45

Methods used to follow the conversion of reactive functions of CSBO45:

In the case of *in-situ* IR spectroscopy monitoring, the conversion of the carbonate and ester functions was followed thanks to the disappearance of their carbonyl related absorbance bands, respectively at 1808 and 1744 cm^{-1}. The absorbance band at 2920 cm^{-1}, related to the C-H of the aliphatic chains, was chosen as an internal standard. Conversions α_{function} (%) of either carbonates or esters were determined thanks to Equation S(**Eq. S***3* following the Beer-Lambert law from the change of normalized absorbance at 1808 and 1744 cm^{-1}:

$$\alpha_{\text{function}}(\%) = \left(1 - \frac{\bar{A}^{\,t}_{\text{function}}}{\bar{A}^{\,0}_{\text{function}}}\right) \times 100$$

(Eq. S3)

where $\bar{A}^{\,0}_{\text{function}} = \frac{A^{0}_{\text{function}}}{A^{0}_{2920}}$ and $\bar{A}^{\,t}_{\text{function}} = \frac{A^{t}_{\text{function}}}{A^{t}_{2920}}$ are the normalized absorbance of the function studied before curing and after the reaction time t respectively.

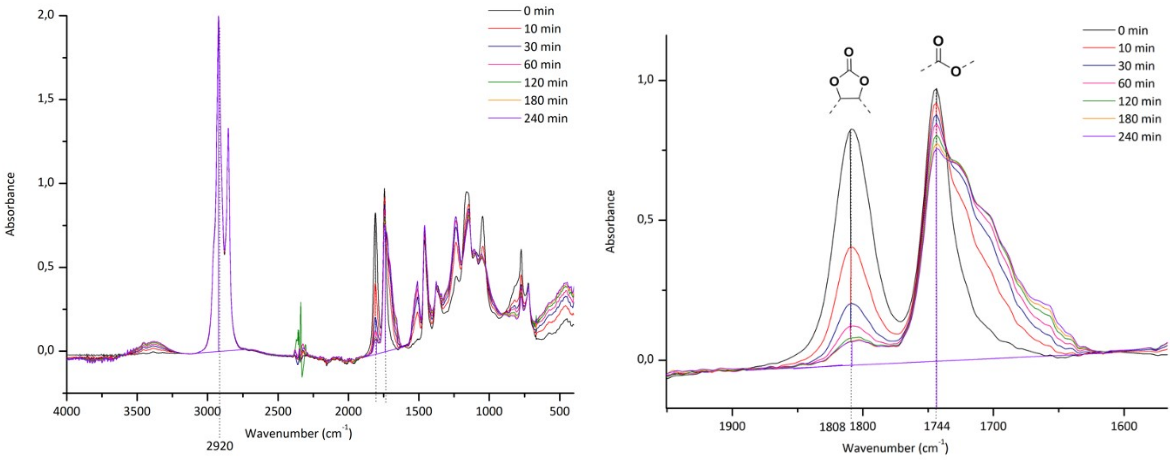

Figure S5: Overlay of IR spectra and zoom on the 1650-1950 cm^{-1} window from the monitoring of the 4 h curing at 120 °C of CSBO45-Priamine 1075 system

In the case of in-situ Raman spectroscopy monitoring, the sample was poured into a closed cell adapted to the spectrometer and then heated to the desired temperature. The conversion of the epoxide functions was determined thanks to the disappearance of the band at 1267 cm^{-1} comparatively to the band at 1440 cm^{-1}, chosen as an internal standard. In this case, the conversion of epoxides was determined by Equation S(**Eq. S**4 :

$$\alpha_{\text{epoxide}}(\%) = \left(1 - \frac{\bar{A}^{\,t}_{\text{epoxide}}}{\bar{A}^{\,0}_{\text{epoxide}}}\right) \times 100$$

(Eq. S)

where $\bar{A}^{0}_{epoxide} = \frac{A^{0}_{epoxide}}{A^{0}_{1440}}$ and $\bar{A}^{t}_{function} = \frac{A^{t}_{epoxide}}{A^{t}_{1440}}$ are the normalized absorbance of the function studied before curing and after the reaction time t respectively.

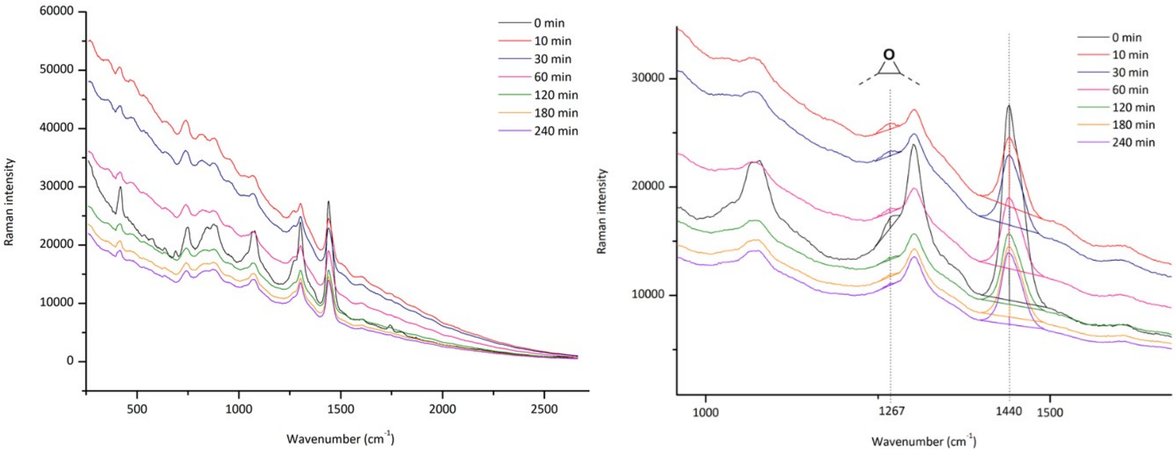

Figure S6: Overlay of Raman spectra and zoom on the 1000-1600 cm^{-1} zone from the monitoring of the 4 h curing at 120 °C of CSBO45-Priamine 1075 system

Methods used to follow the gelation of the polymers by rheology:

The gel point, t_{gel}, was defined as the moment when Winter and Chambon criterion was met, that is to say:

$$G'(\omega) \sim G''(\omega) \sim \omega^{n}$$

where G’ and G’’ are the storage and loss modulus, respectively, and ω the angular frequency.

More precisely, t_{gel} was the moment when G’ and G’’ curves as function of ω were linear and parallel in logarithmic scale with a slope equal to n. In the end, t_{gel} can also be determined thanks to the loss factor tan(δ) plotted as a function of time. t_{gel} would be the moment when all the representative curves of tan(δ) for various ω meet.

Conversion of reactive functions for CSBO45 – Priamine 1075 reactions:

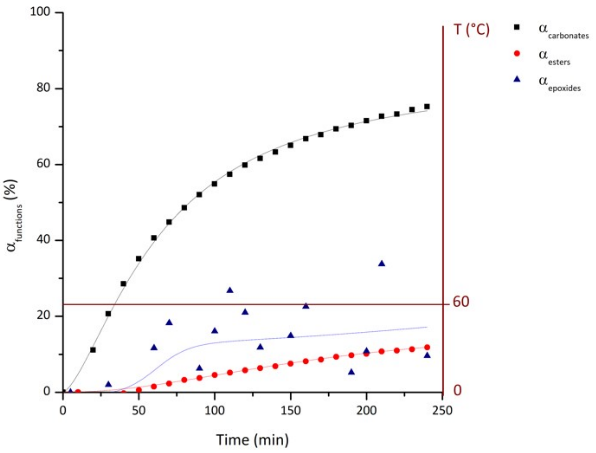

Figure S7: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 60 °C of CSBO45-Priamine 1075

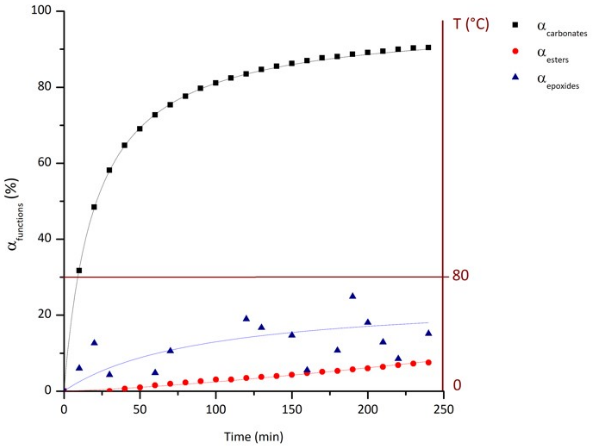

Figure S8: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 80 °C of CSBO45-Priamine 1075

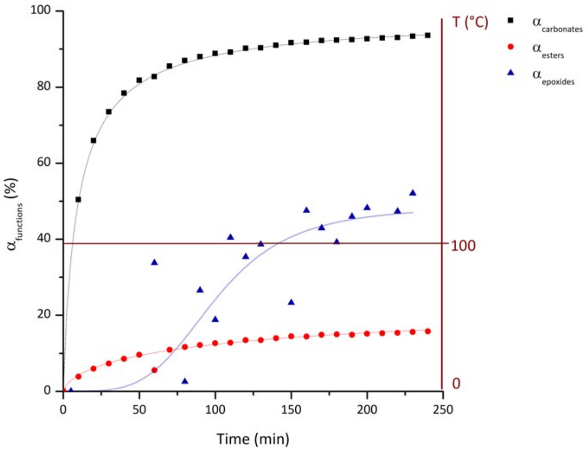

Figure S9: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 100 °C of CSBO45-Priamine 1075

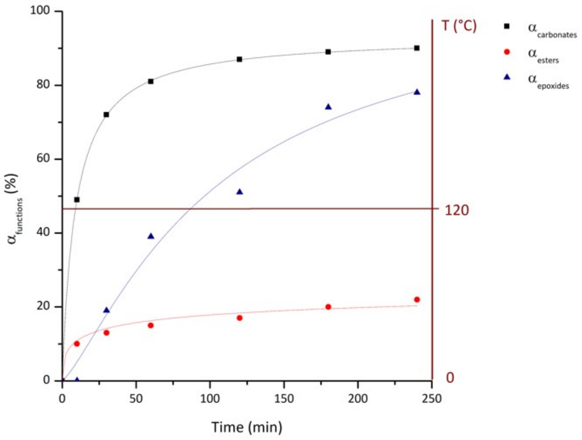

Figure S10: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 120 °C of CSBO45-Priamine 1075

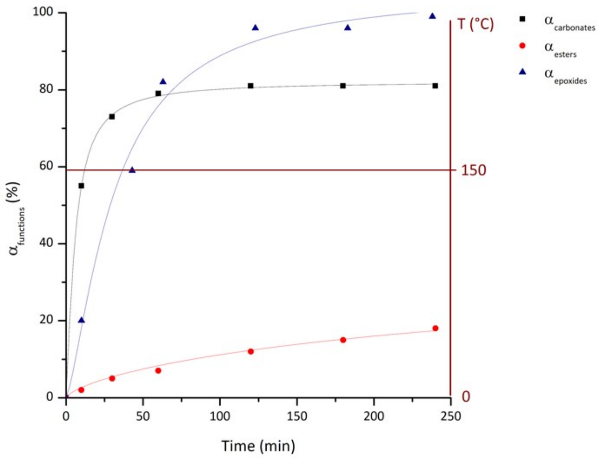

Figure S11: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 150 °C of CSBO45-Priamine 1075

Conversion of reactive functions for CSBO45 – 8DA reactions:

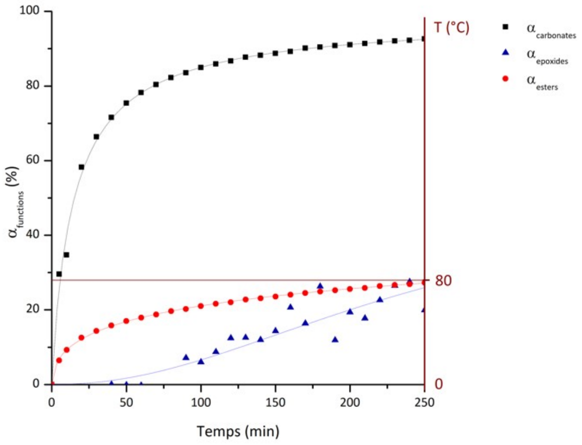

Figure S12: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 80 °C of CSBO45-8DA

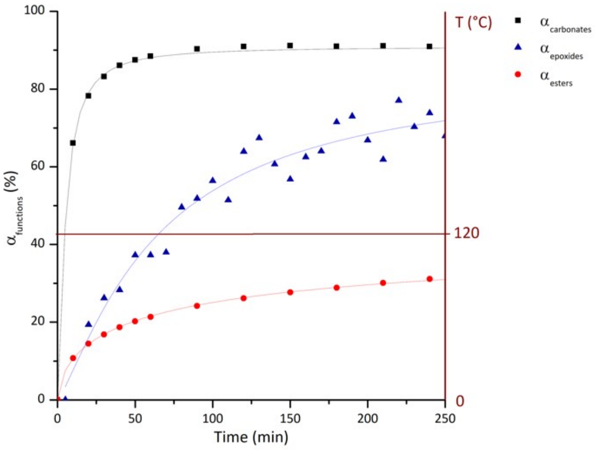

Figure S13: Conversion curves of carbonates (black), esters (red) and epoxides (blue) as a function of time for the 4 h curing at T = 120 °C of CSBO45-8DA

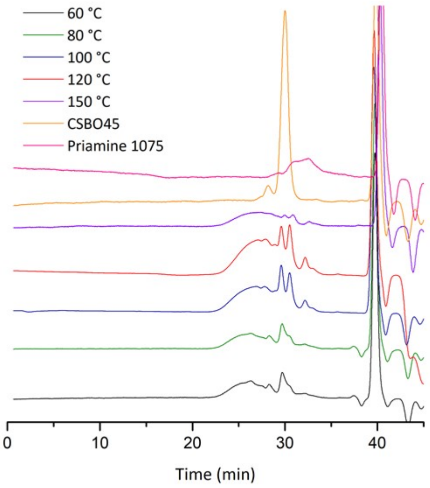

Figure S14: Overlay of SEC traces of the soluble fraction of CSBO45+Priamine 1075-based polymers cured for 4 h at 60, 80, 100, 120 and 150 °C respectively and of both reactants

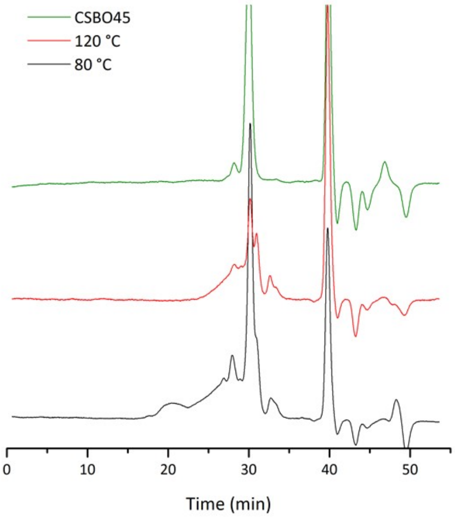

Figure S15: Overlay of SEC traces of the soluble fraction of CSBO45+8DA-based polymers cured for 4 h at 80 and 120 °C respectively and of CSBO45

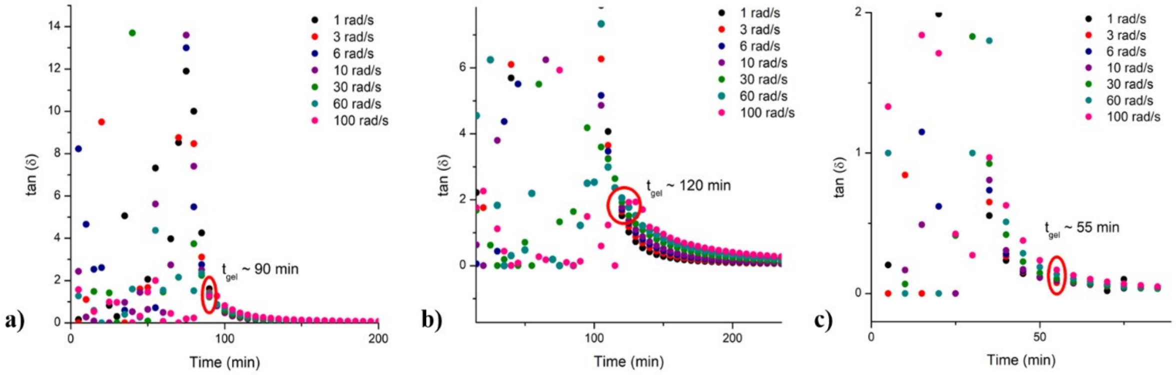

Figure S16: Tan(δ) curves as a function of time recorded at various angular frequencies during rheological monitoring of a) CSBO45-Priamine 1075 curing at 120 °C ; b) CSBO45-8DA curing at 80 °C ; c) CSBO45-8DA curing at 120 °C - gel points determined *via* the Winter and Chambon criterion

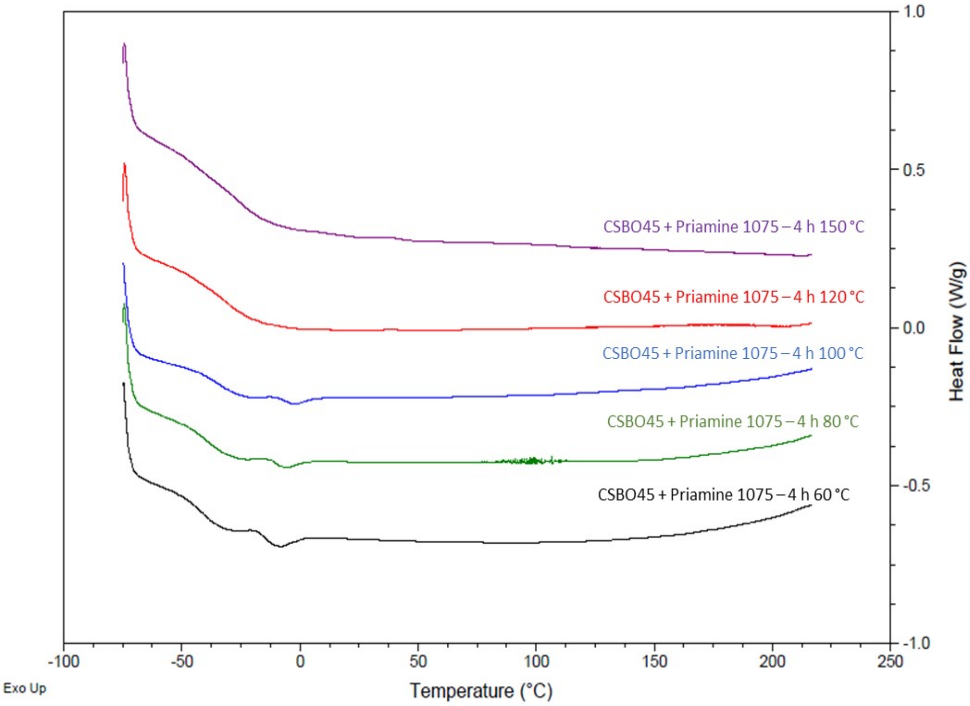

Figure S17: Overlay of DSC traces of CSBO45+Priamine 1075-based polymers cured for 4 h at 60, 80, 100, 120 and 150 °C respectively

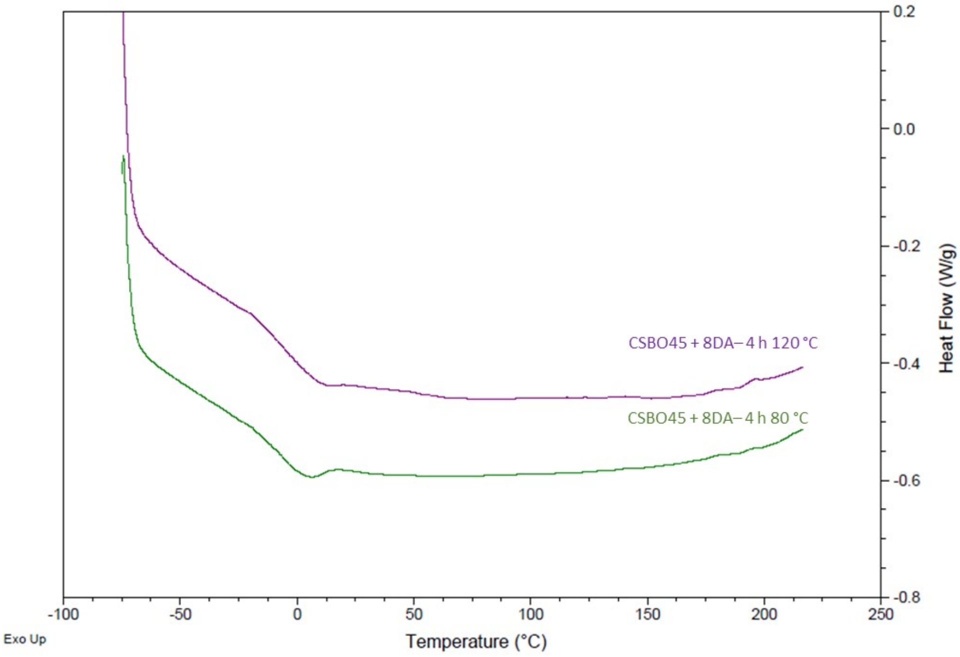

Figure S18: Overlay of DSC traces of CSBO45+8DA-based polymers cured for 4 h at 80 °C and 120 °C respectively

Crosslinking reactions of ESBO with Priamine

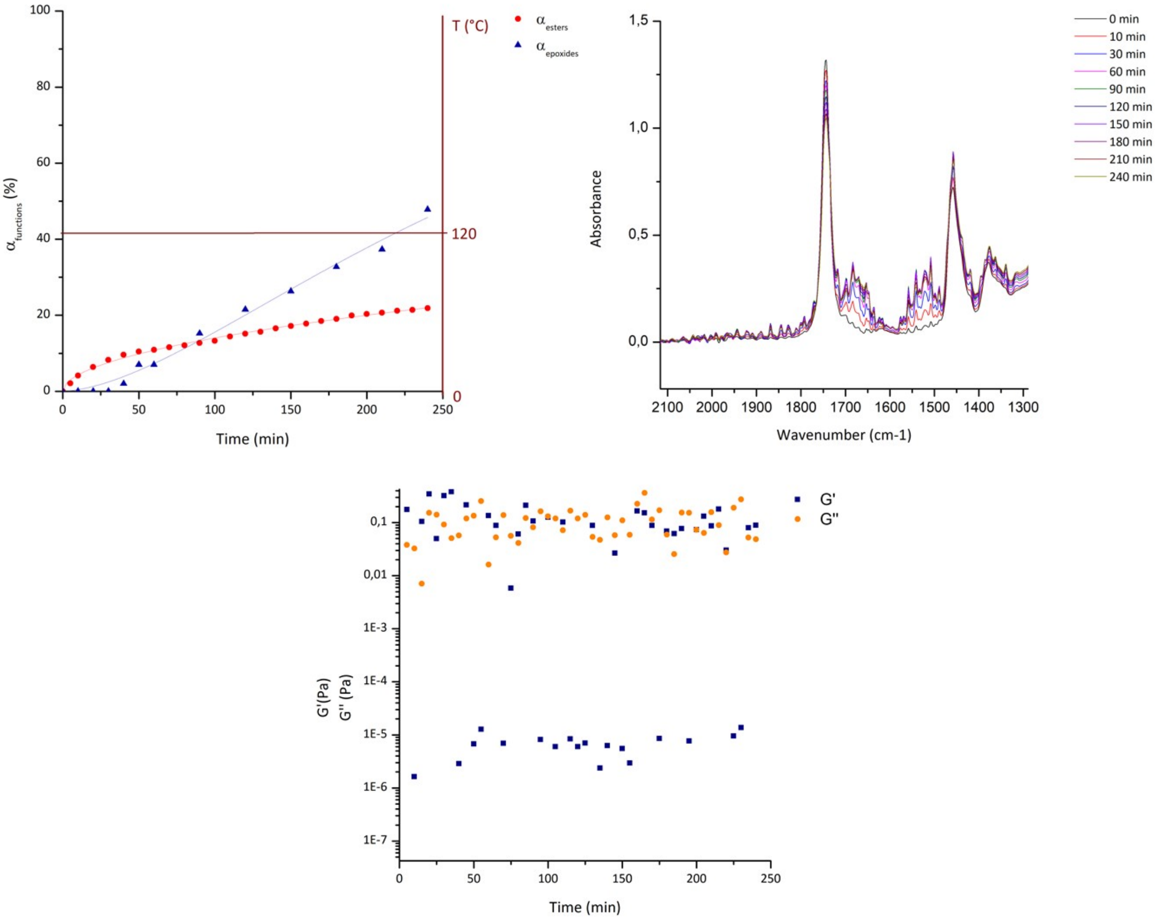

Figure S19: Conversion curves of esters (red) and epoxides (blue), IR spectra overlay and rheological monitoring of the 4 h curing at T = 120 °C of ESBO-Priamine 1075

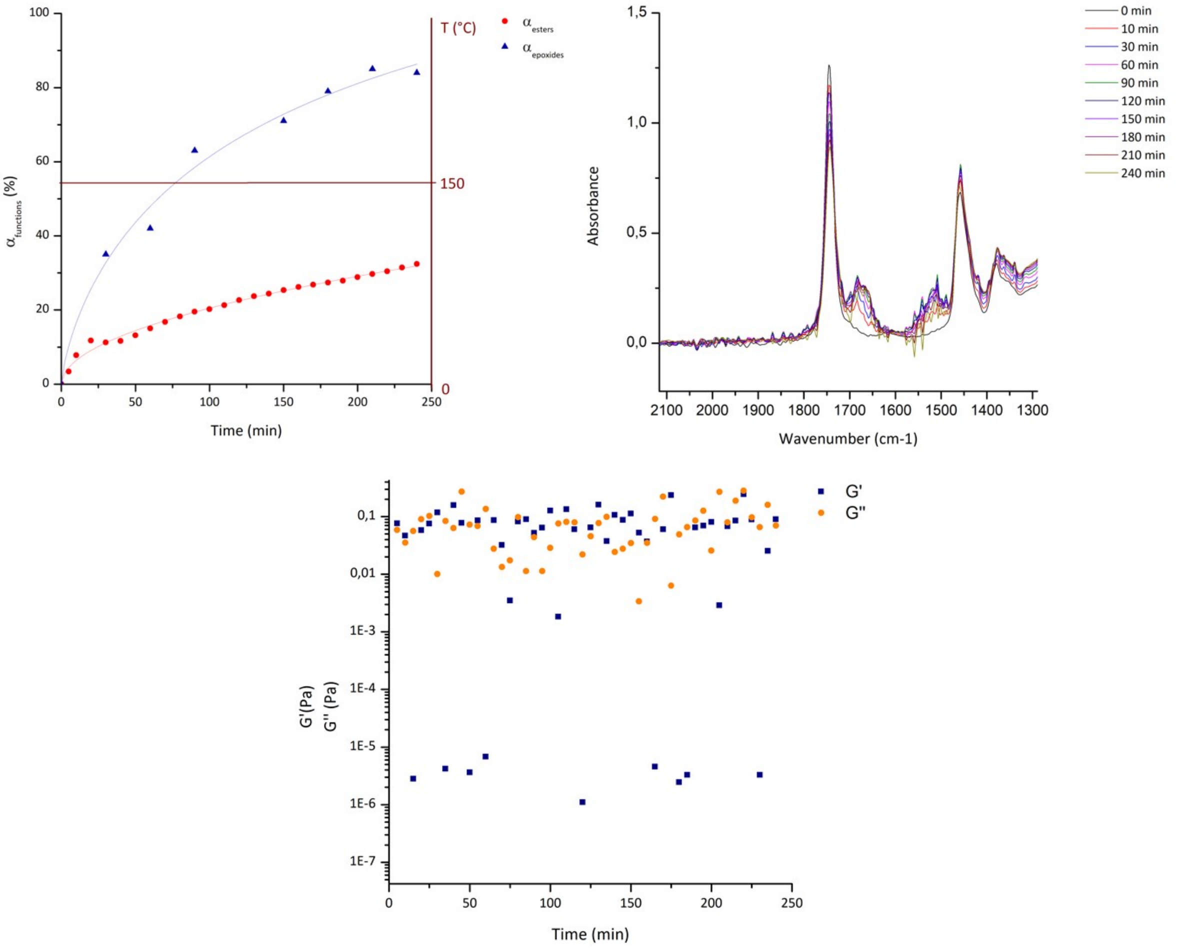

Figure S20: Conversion curves of esters (red) and epoxides (blue), IR spectra overlay and rheological monitoring of the 4 h curing at T = 150 °C of ESBO-Priamine 1075

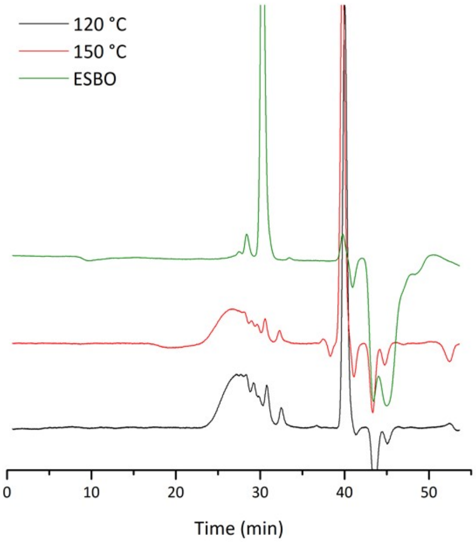

Figure S21: Overlay of SEC traces of ESBO+Priamine 1075-based polymers cured for 4 h at 120 and 150 °C respectively and of ESBO

Thermolatent systems based on CSBOX

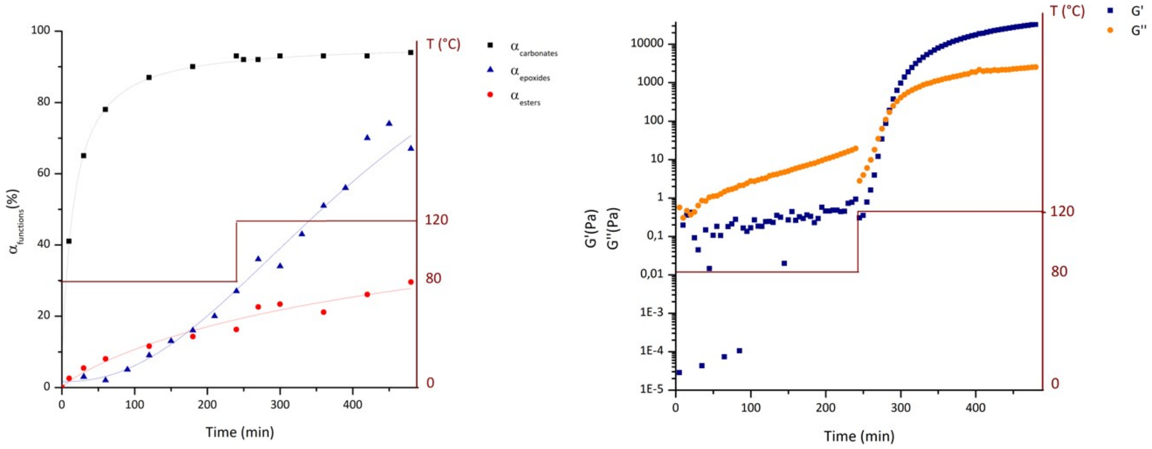

Figure S22: Conversion of carbonates (black), esters (red) and epoxides (blue) and rheological monitoring of the 2-step curing sequence (t_1 = 4 h, T_1 = 80 °C and t_2 = 4 h, T_2 = 120 °C) of CSBO45-Priamine 1075

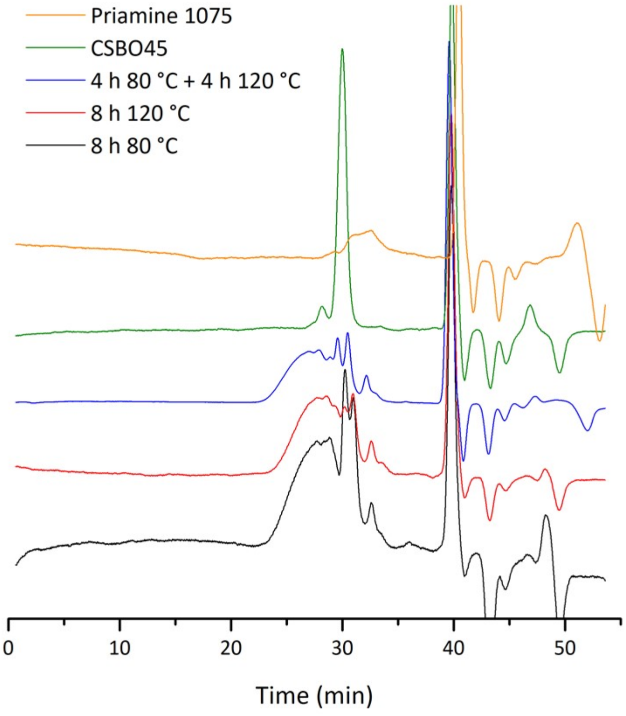

Figure S23: Overlay of SEC traces of the soluble fraction of CSBO45+Priamine 1075-based polymers cured for 8 h at 80 °C (black line) and 120 °C (red line) respectively, 4 h at 80 °C + 4 h at 120 °C (green line) and of both reactants

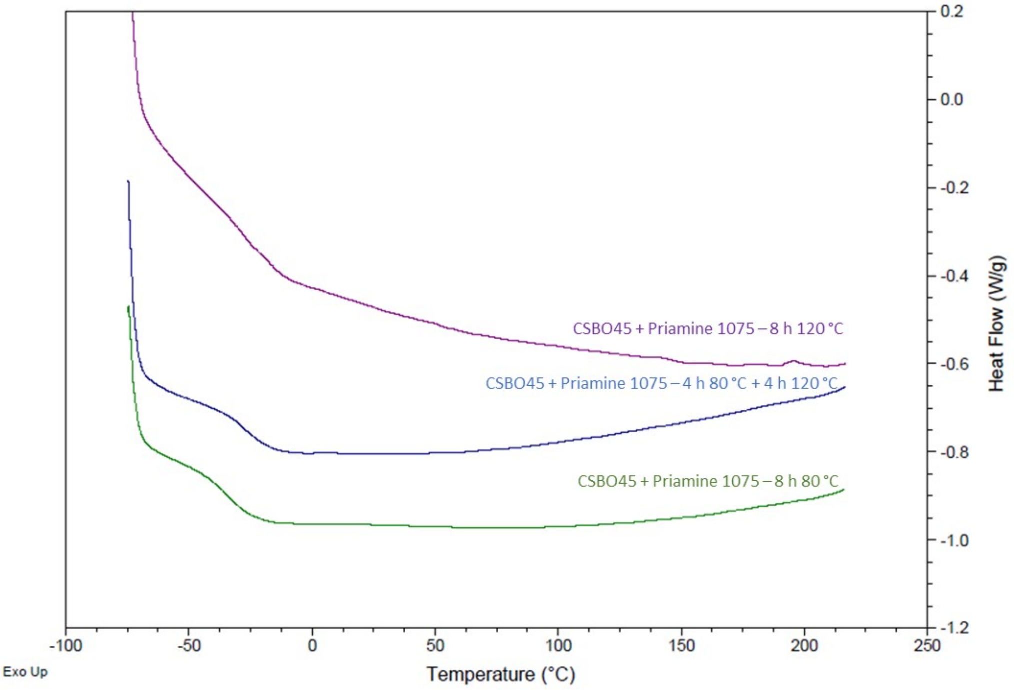

Figure S24: Overlay of DSC traces of CSBO45+Priamine 1075-based polymers cured for 8 h at 80 °C (green line) or 120 °C (purple line) respectively and 4 h at 80 °C + 4 h at 120 °C (blue line)

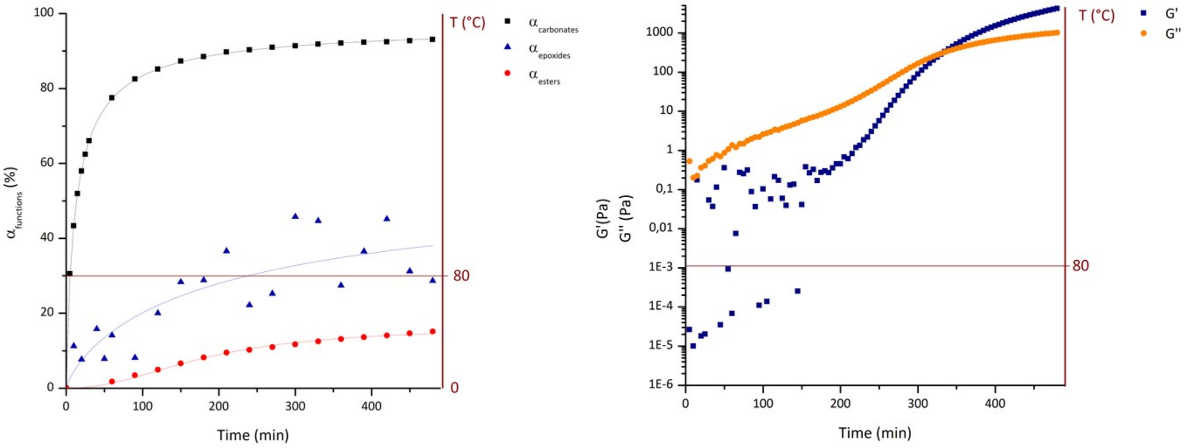

Figure S25: Conversion of carbonates (black), esters (red) and epoxides (blue) and rheological monitoring of the 8 h curing at T = 80 °C of CSBO45-Priamine 1075

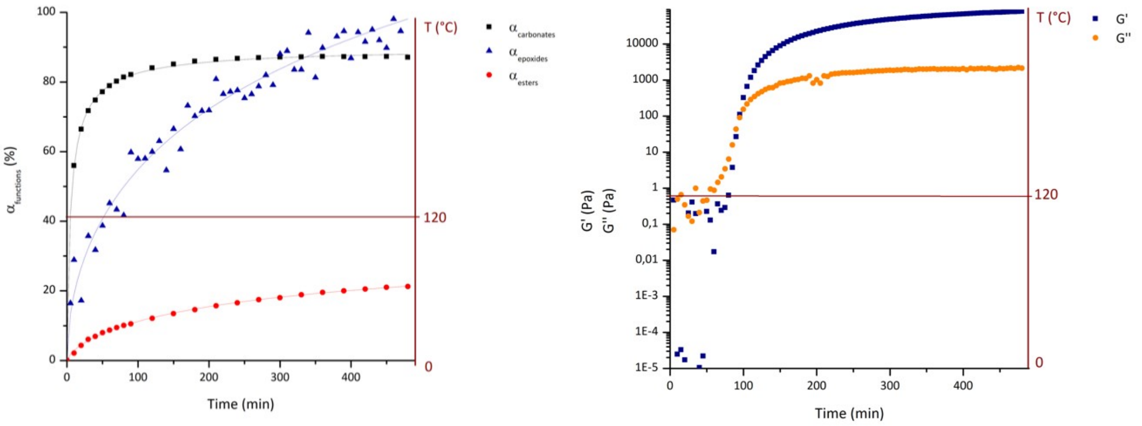

Figure S26: Conversion of carbonates (black), esters (red) and epoxides (blue) and rheological monitoring of the 8 h curing at T = 120 °C of CSBO45-Priamine 1075

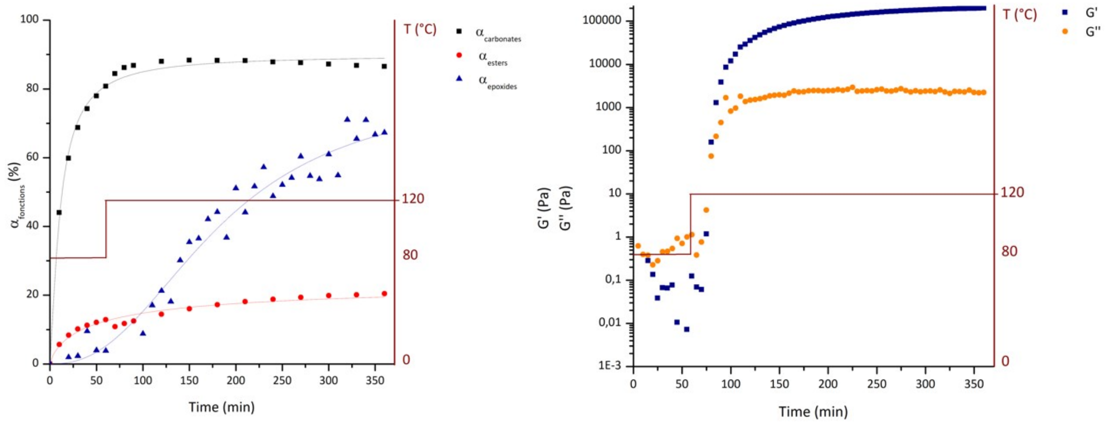

Figure S27: Conversion of carbonates (black), esters (red) and epoxides (blue) and rheological monitoring of the 2-step curing sequence (t_1 = 1 h, T_1 = 80 °C and t_2 = 5 h, T_2 = 120 °C) of CSBO45-8DA

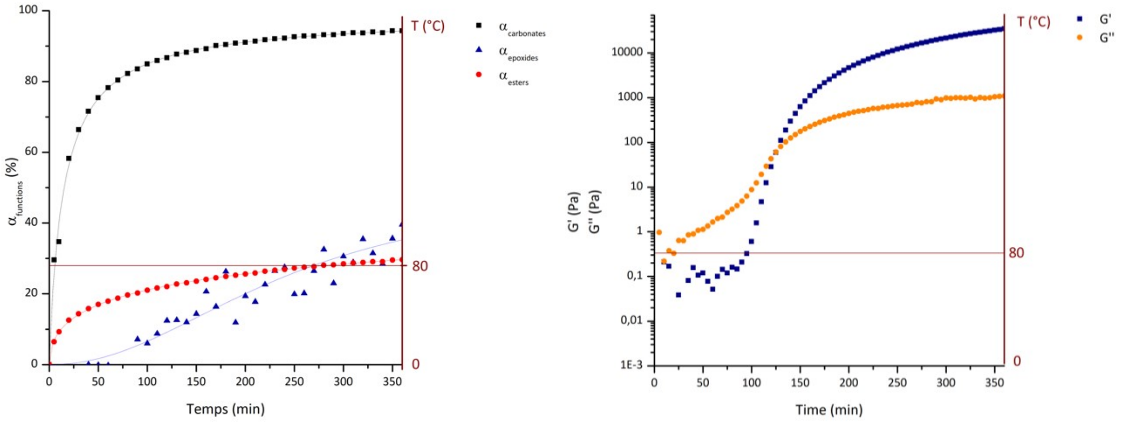

Figure S28: Conversion of carbonates (black), esters (red) and epoxides (blue) and rheological monitoring of the 6 h curing at T = 80 °C of CSBO45-8DA

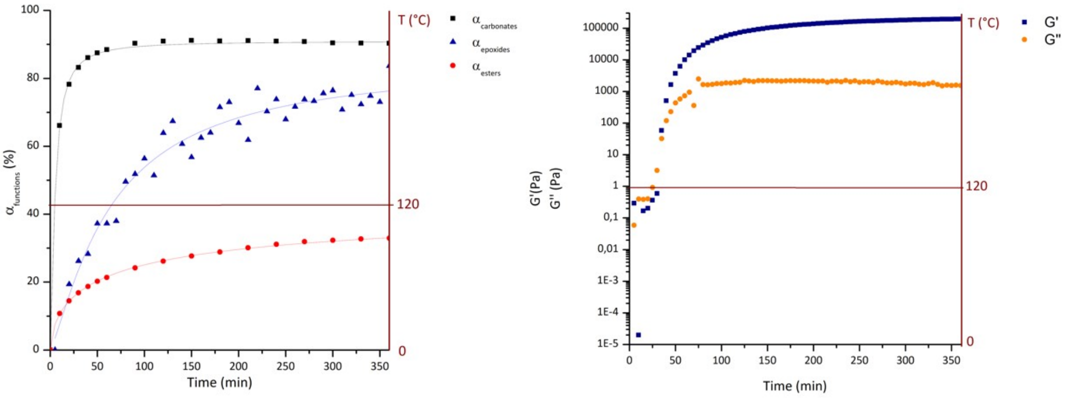

Figure S29: Conversion of carbonates (black), esters (red) and epoxides (blue) and rheological monitoring of the 6 h curing at T = 120 °C of CSBO45-8DA

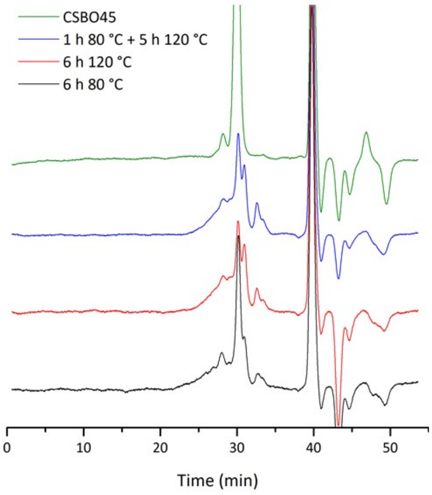

Figure S30: Overlay of SEC traces of the soluble fraction of the CSBO45+8DA-based polymers cured for 6 h at 80 °C (black line) and 120 °C (red line) respectively, 1 h at 80 °C + 5 h at 120 °C (blue line) and of CSBO45 (green line)

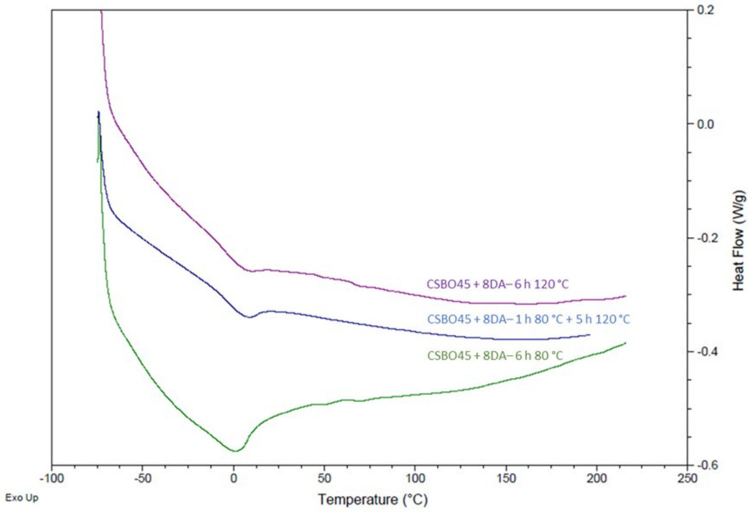

Figure S31: Overlay of DSC traces of CSBO45+8DA-based polymers cured for 6 h at 80 °C (green line) or 120 °C (purple line) respectively and 1 h at 80 °C + 5 h at 120 °C (blue line)

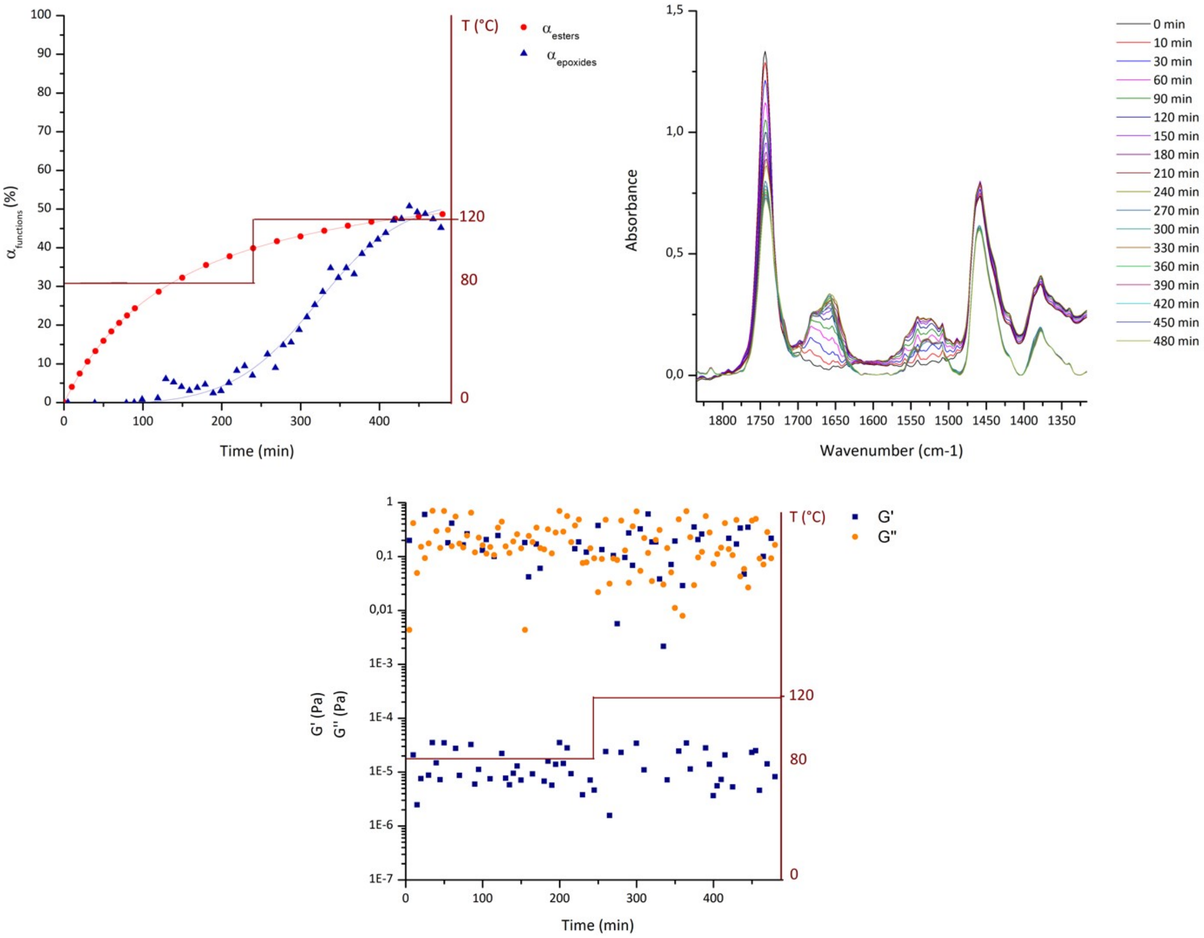

Figure S32: Conversion of esters (red) and epoxides (blue), overlay of IR spectra and rheological monitoring of the 2-step curing sequence ((t_1 = 4 h, T_1 = 80 °C and t_2 = 4 h, T_2 = 120 °C) of ESBO-Priamine 1075

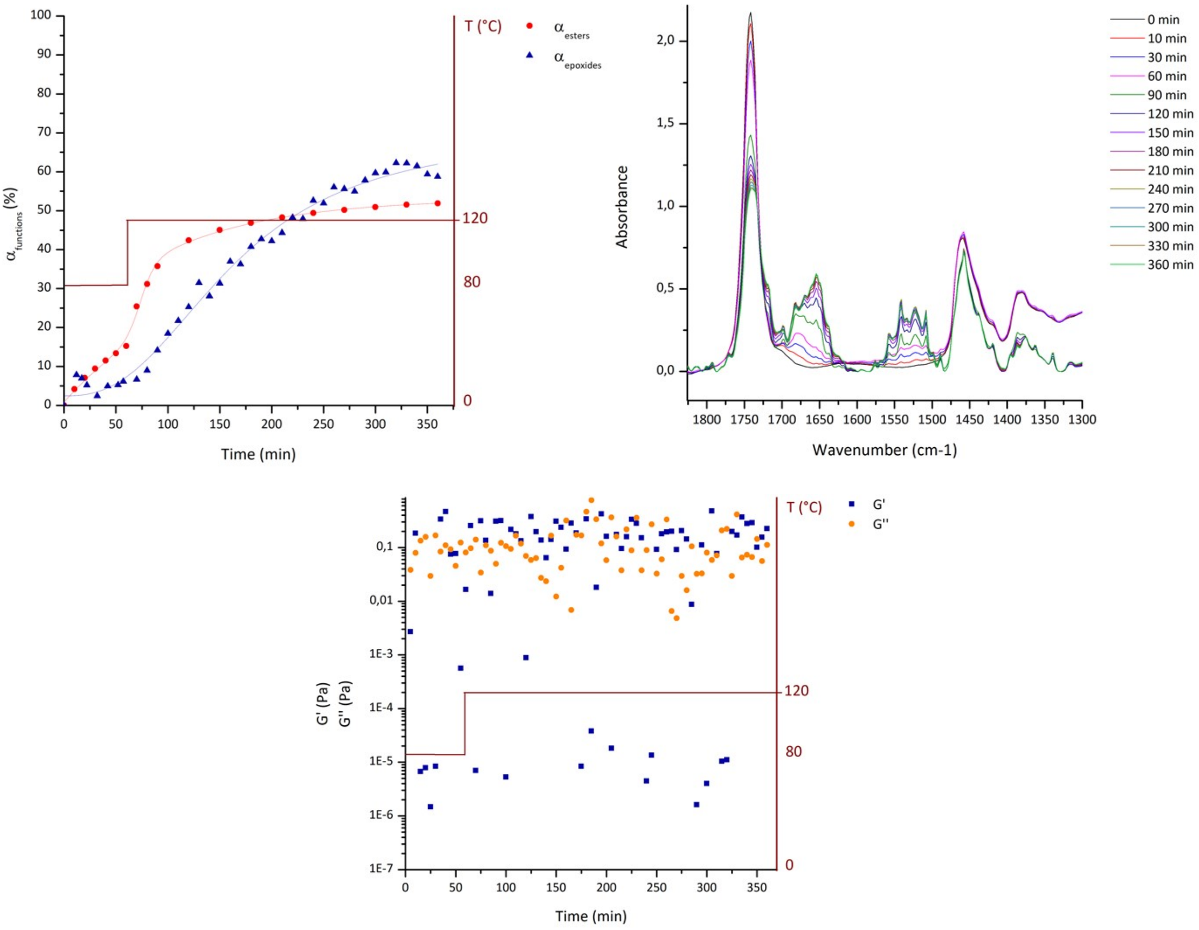

Figure S33: Conversion of esters (red) and epoxides (blue), overlay of IR spectra and rheological monitoring of the 2-step curing sequence (t_1 = 1 h, T_1 = 80 °C and t_2 = 5 h, T_2 = 120 °C) of ESBO-8DA

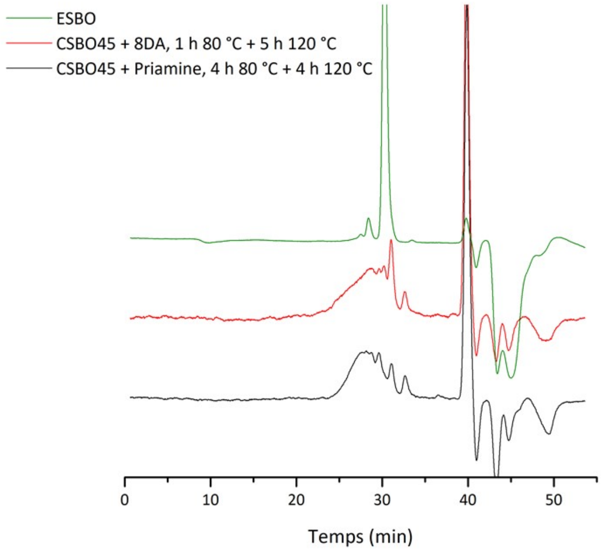

Figure S34: Overlay of SEC traces of ESBO (green line), ESBO-Priamine 1075-based polymer cured 4 h at 80 °C + 4 h at 120 °C (black line) and of ESBO-8DA-based polymer cured 1 h at 80 °C + 5 h at 120 °C (red line)

References

1 M. Bähr and R. Mülhaupt, Linseed and soybean oil-based polyurethanes prepared via the non-isocyanate route and catalytic carbon dioxide conversion, *Green Chem.*, 2012, **14**, 483–489.

2 S. Javni, I., Hong, D. P., Petrovic, Z., Soy-Based Polyurethanes by Nonisocyanate Route, *J. Appl. Polym. Sci.*, 2008, **108**, 3867–3875.