Supporting Informations to Phosphorus acid: an asset for flame-retardant sustainable vitrimers

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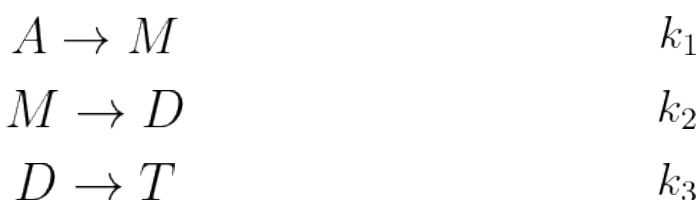
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A. Kinetic model equations of the reactional system

The reactional system can be described as follows:

$$A \to M \qquad\qquad k_1$$
$$M \to D \qquad\qquad k_2$$
$$D \to T \qquad\qquad k_3$$

where A is the acid H_3PO_4, M the monosubstituted RH_2PO_4, D the disubstituted R_2HPO_4 and T the trisubstituted R_3PO_4 ; k_1, k_2 and k_3 are k_{obs} in the case of a pseudo-first order reaction. The kinetics equations of this systems can be written as follows (Equations S1 to S4):

$$\frac{dA}{dt} = -k_1 \cdot A \tag{S1}$$

$$\frac{dM}{dt} = k_1 \cdot A - k_2 \cdot M \tag{S2}$$

$$\frac{dD}{dt} = k_2 \cdot M - k_3 \cdot D \tag{S3}$$

$$\frac{dT}{dt} = k_3 \cdot D \tag{S4}$$

Solving the system of differential equations leads to the following solutions (Equations S5 to S8):

$$A = A_0 \cdot exp^{-k_1 \cdot t} \tag{S5}$$

$$M = \frac{A_0 \cdot k_1}{k_2 - k_1} \cdot (exp^{-k_1 \cdot t} - exp^{-k_2 \cdot t}) \tag{S6}$$

$$D = \frac{A_0 \cdot k_1 \cdot k_2}{k_2 - k_1} \cdot \left(\frac{exp^{-k_1 \cdot t}}{k_3 - k_1} - \frac{exp^{-k_2 \cdot t}}{k_3 - k_2} \right) + \frac{A_0 \cdot k_1 \cdot k_2}{k_3 - k_1} \cdot exp^{-k_3 \cdot t} \tag{S7}$$

$$T = 1 + \frac{A_0}{(k_1 - k_2)(k_1 - k_3)(k_2 - k_3)} \cdot \left[(k_3 - k_2) \left[(k_3 - k_1)(1 - k_1 - k_2) + k_1 \cdot k_2 \right] \cdot exp^{-k_1 \cdot t} + k_1 (k_3 - k_1)(k_2 - k_3 - 1) \cdot exp^{-k_2 \cdot t} + k_1 \cdot k_2 (k_2 - k_1) \cdot exp^{-k_3 \cdot t} \right] \tag{S8}$$

B. General experimental procedure for the determination of epoxy equivalent weights (EEW) by ^{1}H NMR

50 to 70 mg of benzophenone and 50 to 130 mg of epoxy were dissolved in deuterated acetone. ^{1}H NMR spectra were integrated in the 7.87-7.28 ppm range for benzophenone protons (10 H), and in the range of CH oxirane peaks and CH_2 oxirane peaks. EEW for each epoxy resin was calculated as follows :

$$EEW_{CH} = \frac{m_{epoxy} \times \int_{7.28}^{7.87} benzophenone \times M_{benzophenone}}{10 \times m_{benzophenone} \times \int CH\ oxirane}$$

$$EEW_{CH_2} = \frac{2 \times m_{epoxy} \times \int_{7.28}^{7.87} benzophenone \times M_{benzophenone}}{10 \times m_{benzophenone} \times \int CH_2\ oxirane}$$

Material	m $_{epoxy}$ (g)	m $_{phosphoric\ acid}$ (g)[a]	m $_{citric\ acid}$ (g)	m $_{acetone}$ (g)
DGEVAPE	40.0	4.86	-	8.0
ELOPE	40.0	6.84	-	20.0
CEPE	40.0	2.92	-	-
DGEVACE	40.0	-	9.51	-
ELOCE	40.0	-	13.40	-
CECE	40.0	-	5.71	-

Table S1. Compositions of phosphate ester vitrimers and carboxylate ester reference materials

[a] mass of 85 % phosphoric acid solution (d = 1.685)
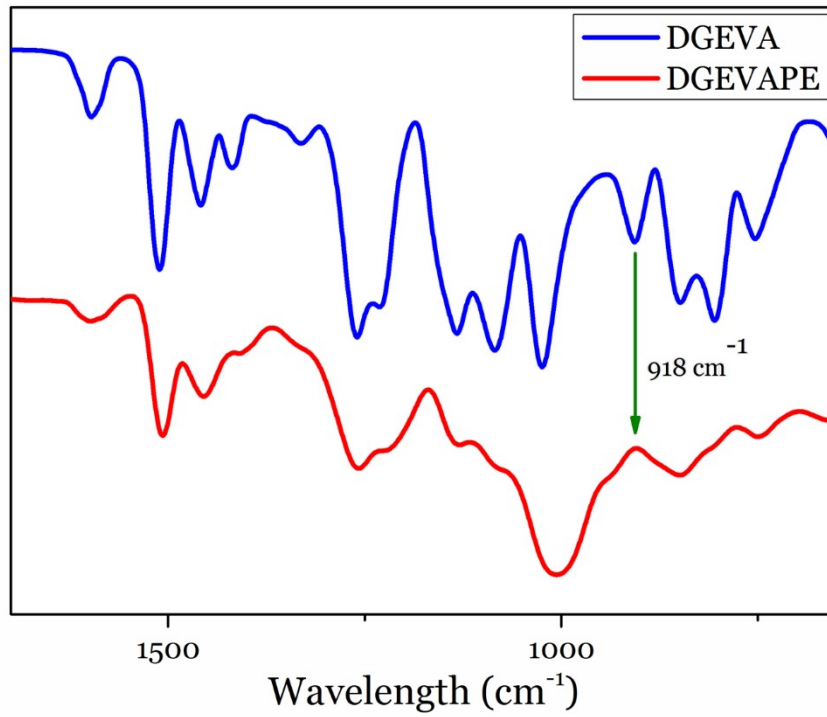
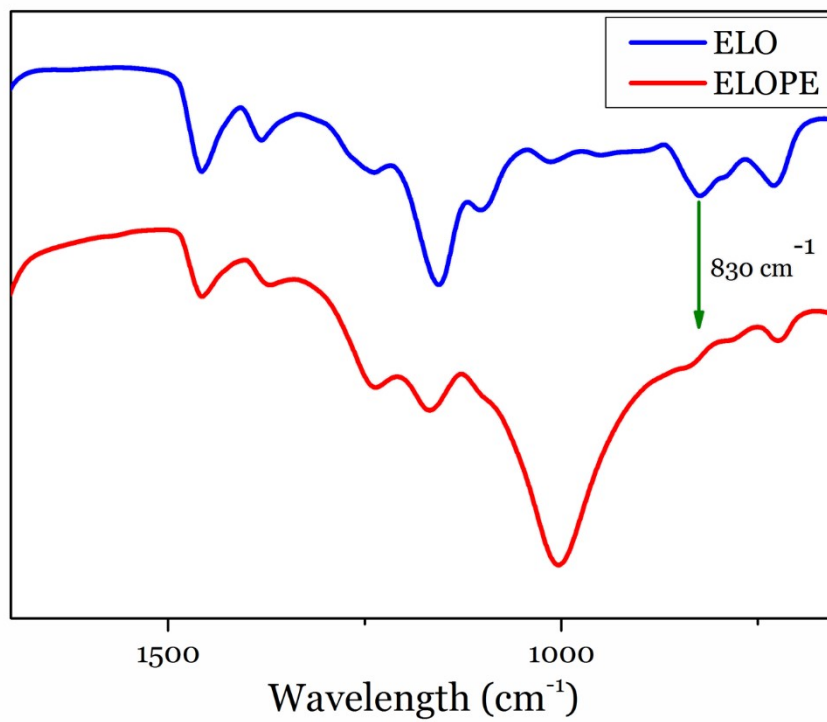*Figure S1. FTIR spectra of DGEVA (epoxy resin) and DGEVAPE (vitrimer)*

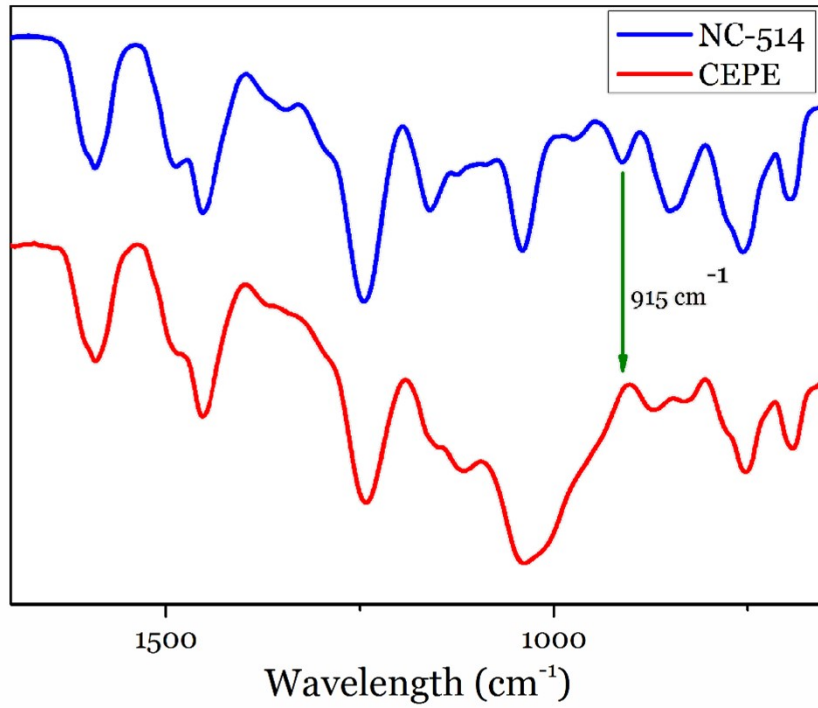*Figure S2. FTIR spectra of ELO (epoxy resin) and ELOPE (vitrimer)*

Figure S3. FTIR spectra of NC-514 (epoxy resin) and CEPE (vitrimer)
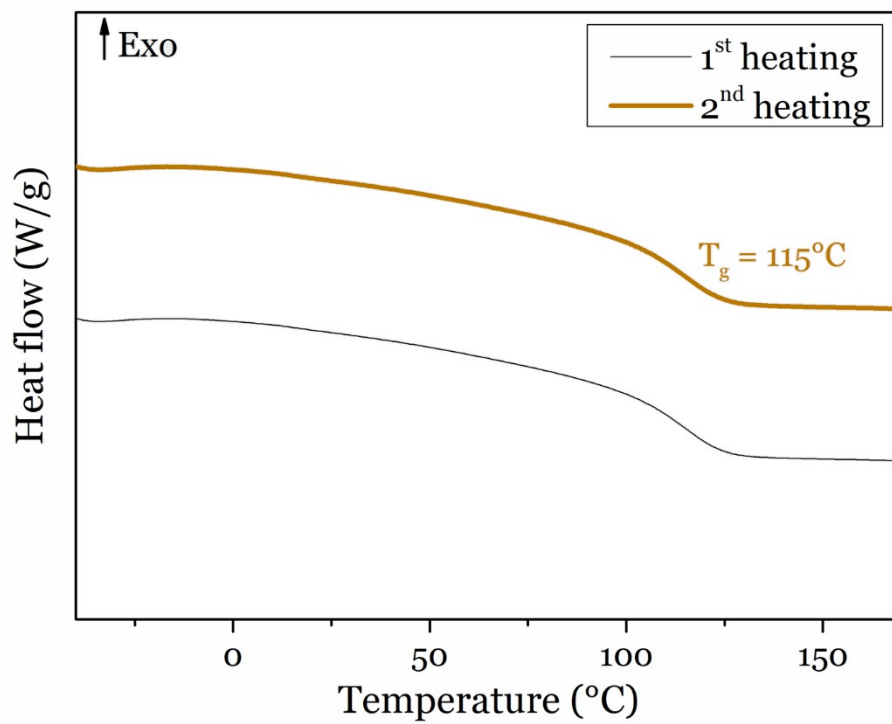
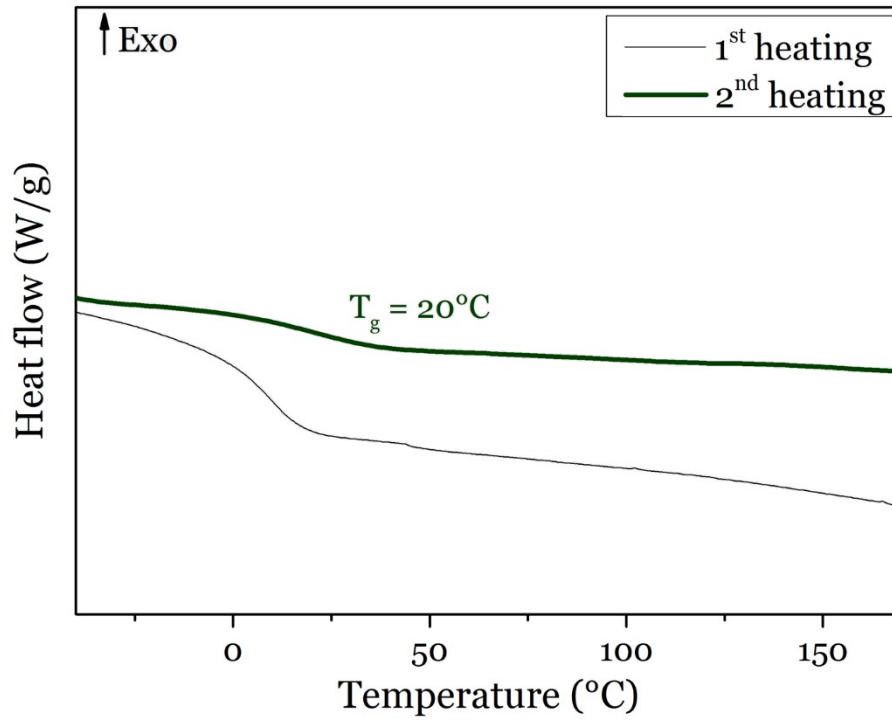

Figure S4. DSC thermograms of DGEVAPE
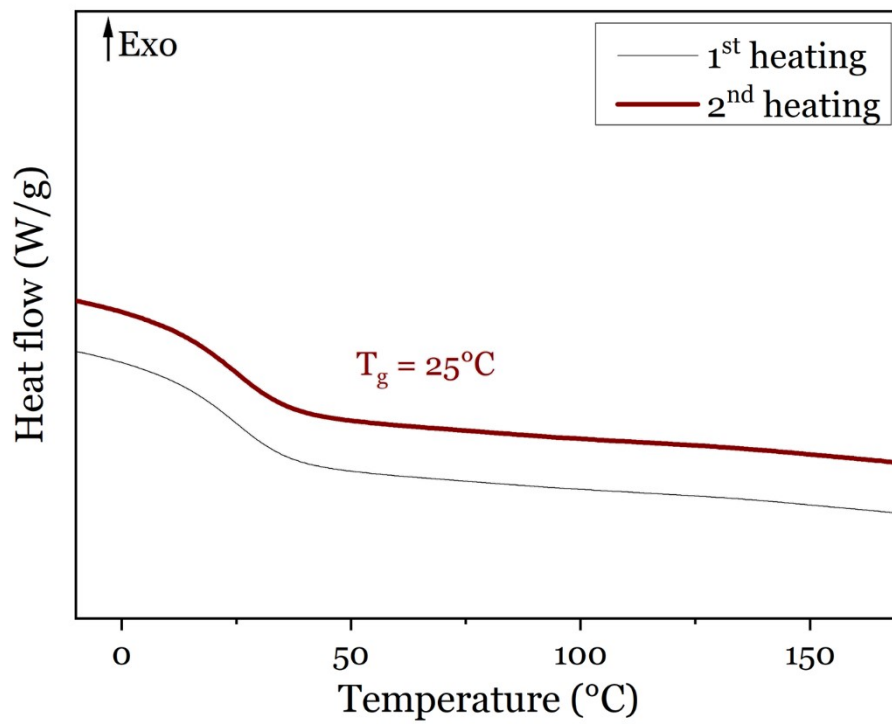
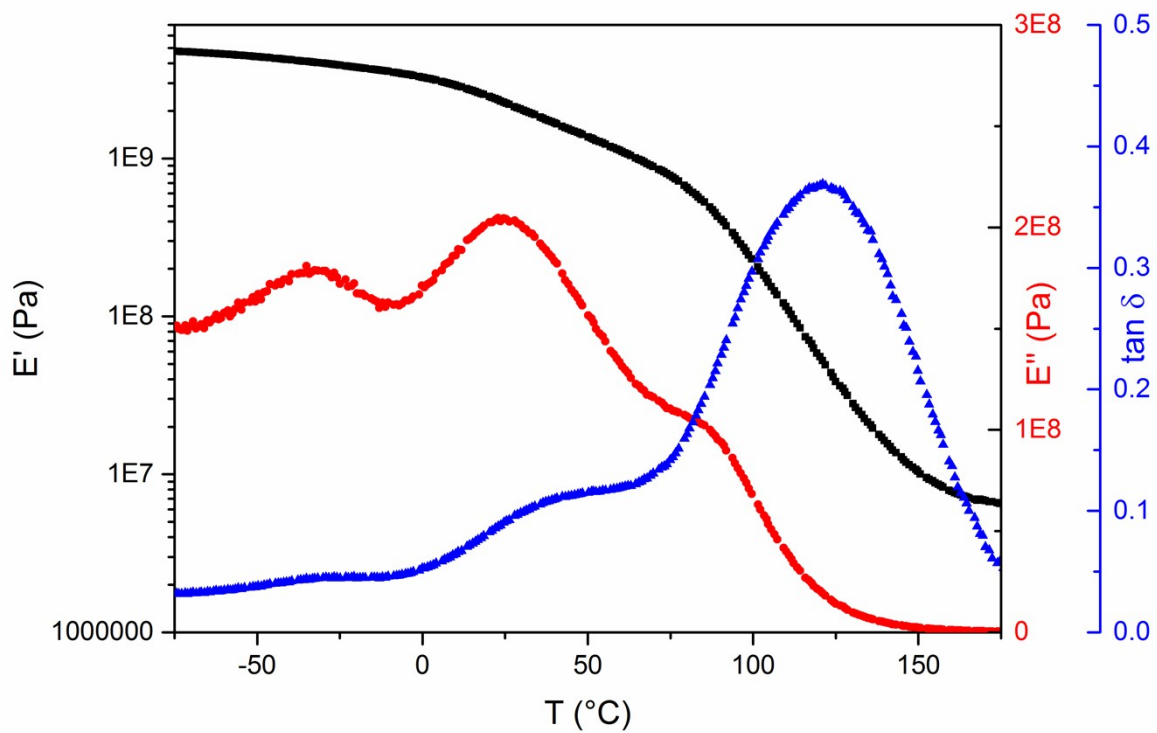*Figure S5. DSC thermograms of ELOPE*

Figure S6. DSC thermograms of CEPE
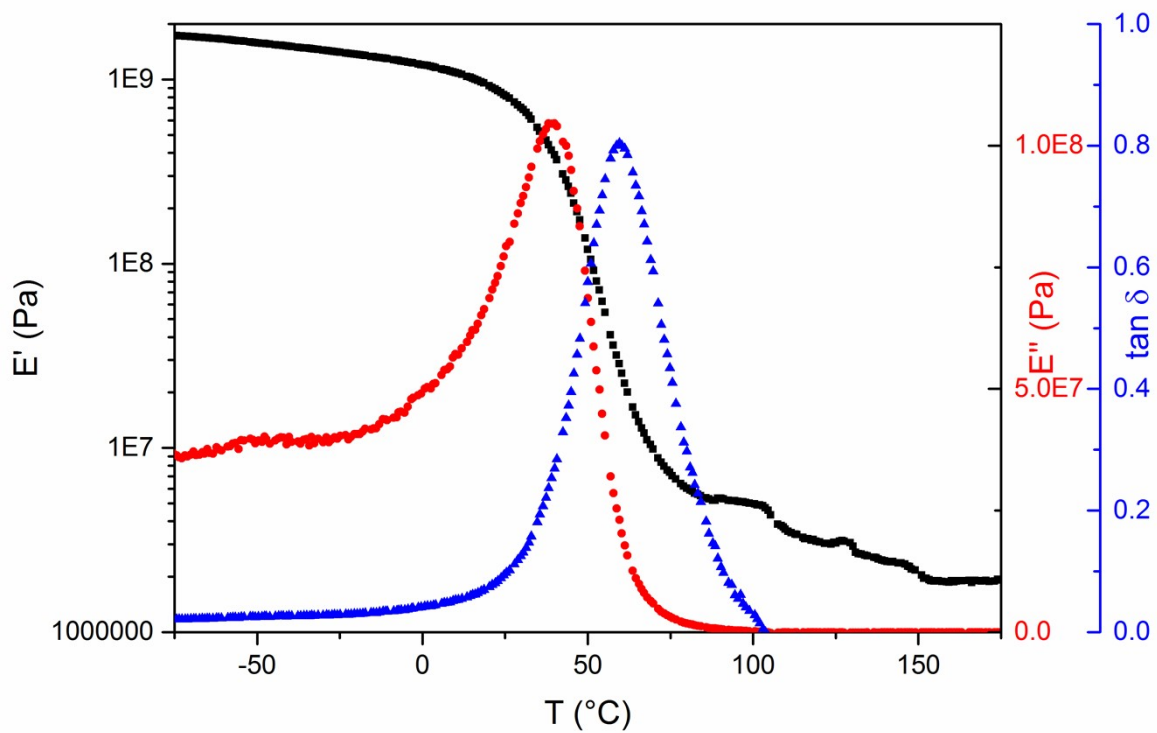
Figure S7. DMA thermograms of DGEVAPE (1 Hz, 3 °C/min)
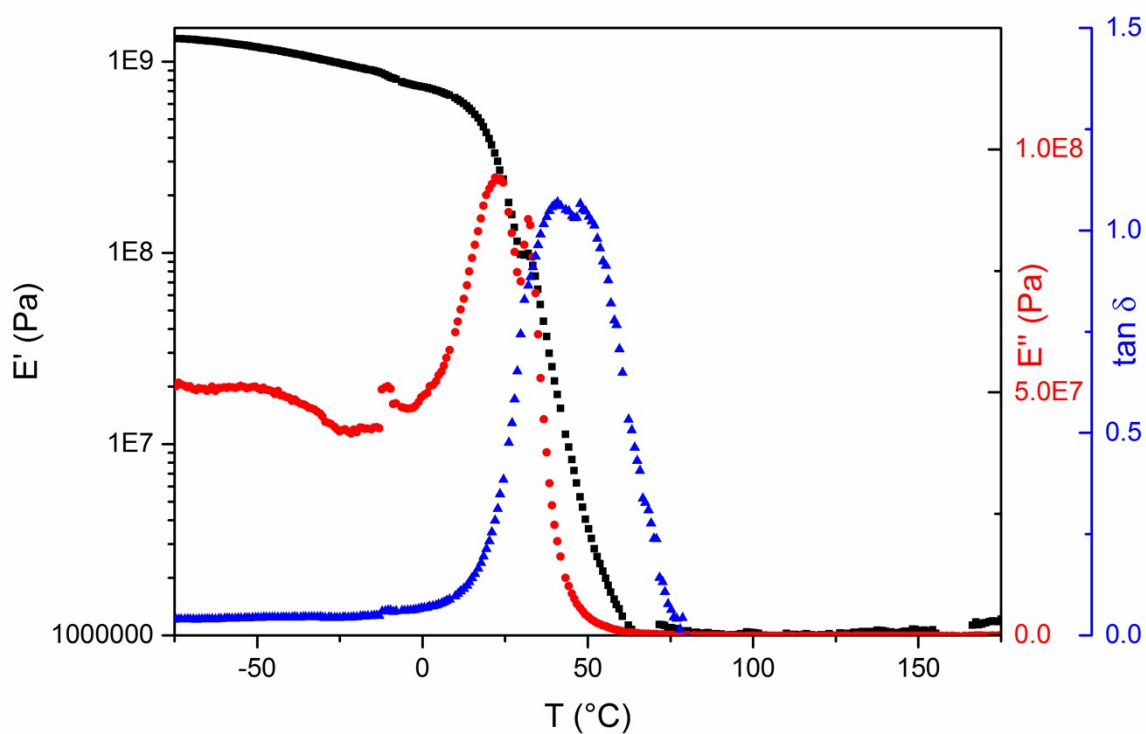

Figure S8. DMA thermograms of ELOPE (1 Hz, 3 °C/min)

Figure S9. DMA thermograms of CEPE (1 Hz, 3 °C/min)

Table S2. Relaxation times τ_{KWW} obtained by fitting the experimental data with the KWW equation and R^2 of the linear fits obtained in an Arrhenius diagram

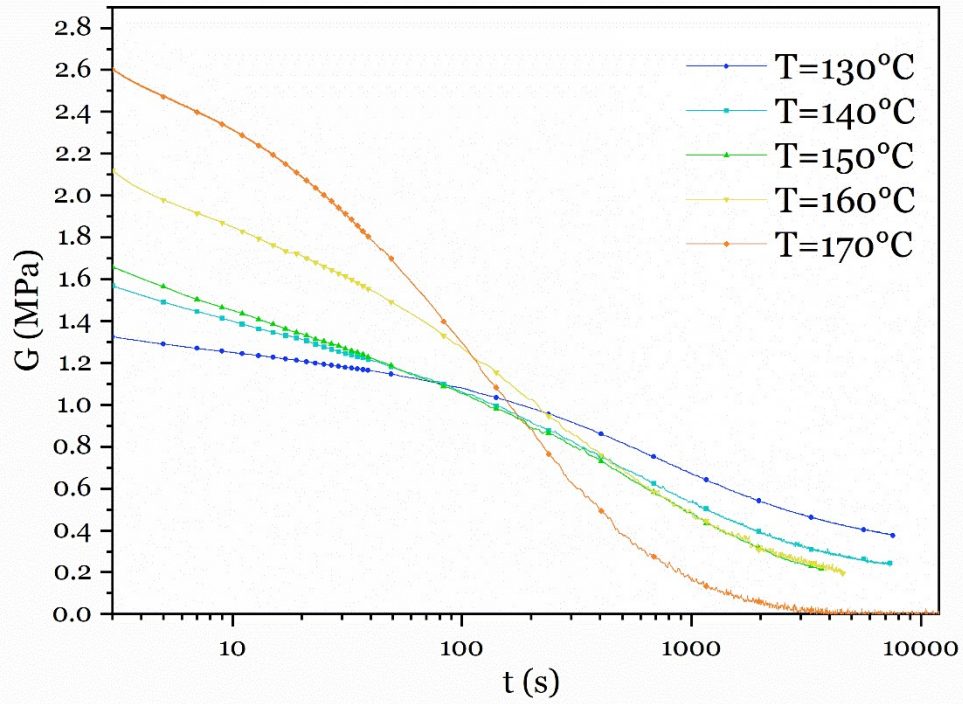| DGEVAPE	R^2 = 0.963						
T (°C)	130	140	150	160	170		
τ (s)	894	616	242	149	66		
ELOPE	R^2 = 0.985						
T (°C)	100	110	120	130	140	150	160
τ (s)	1150	826	476	242	157	84	72
CEPE	R^2 = 0.994						
T (°C)	90	100	110	120	130		
τ (s)	7337	2460	1036	455	238		

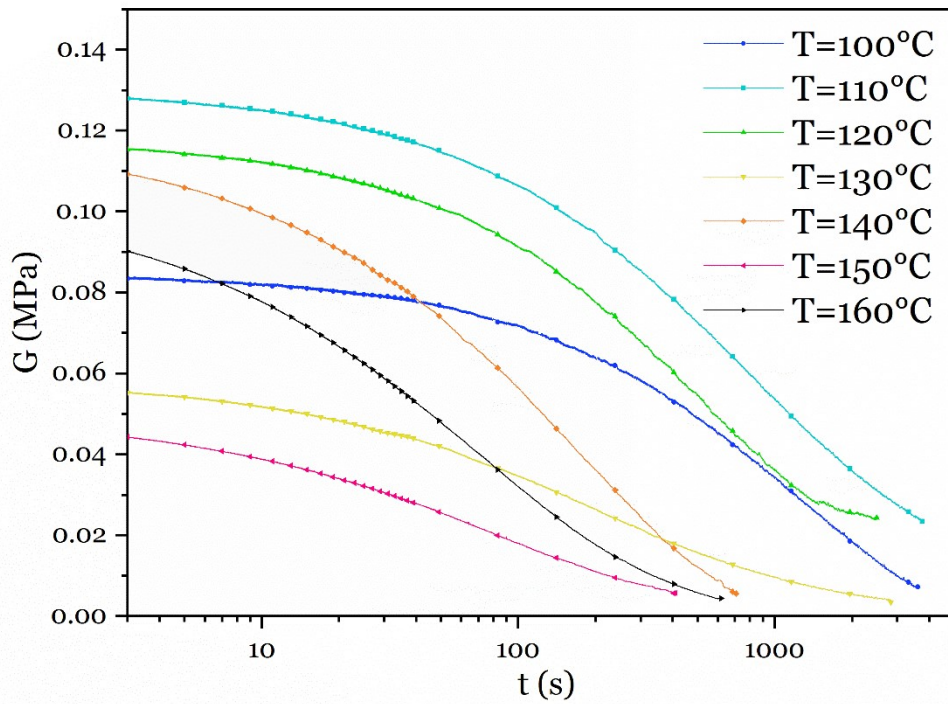*Figure S10. Non-normalized relaxation curves of DGEVAPE*

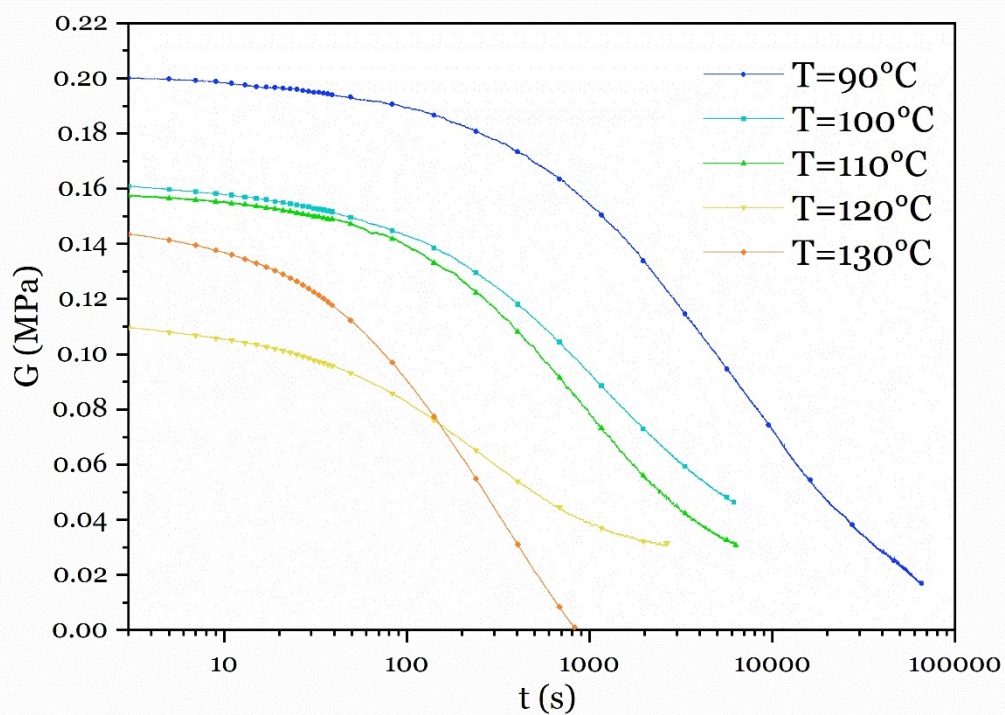*Figure S11. Non-normalized relaxation curves of ELOPE*

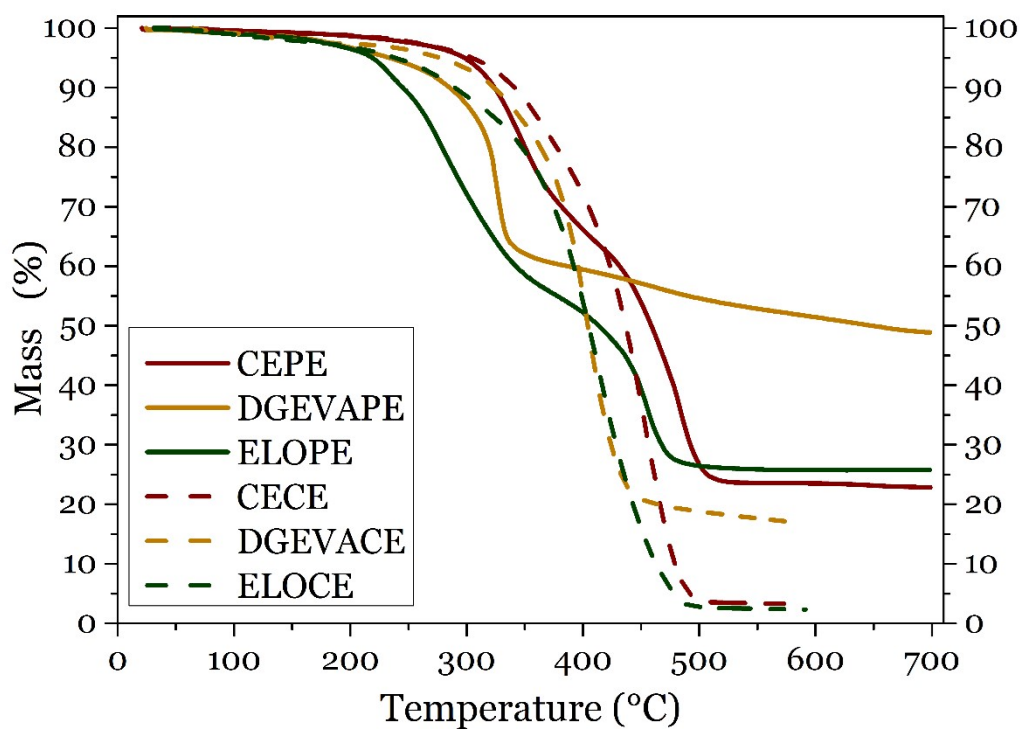*Figure S12. Non-normalized relaxation curves of CEPE*

Figure S13. TGA thermograms under nitrogen of the phosphate ester vitrimers DGEVAPE, ELOPE and CEPE and the carboxylic ester counterparts DGEVACE, ELOCE and CECE.
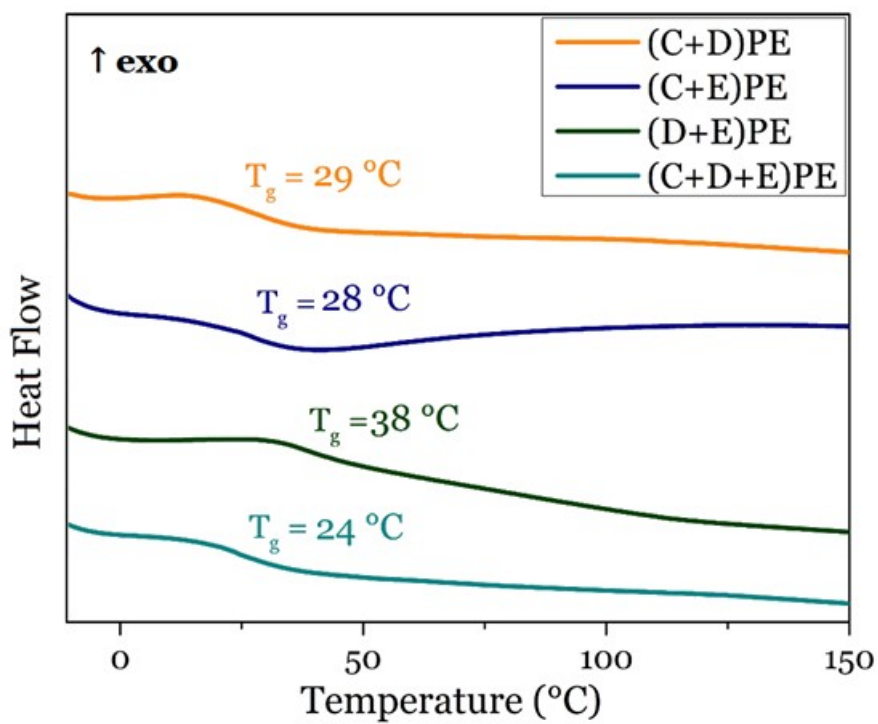
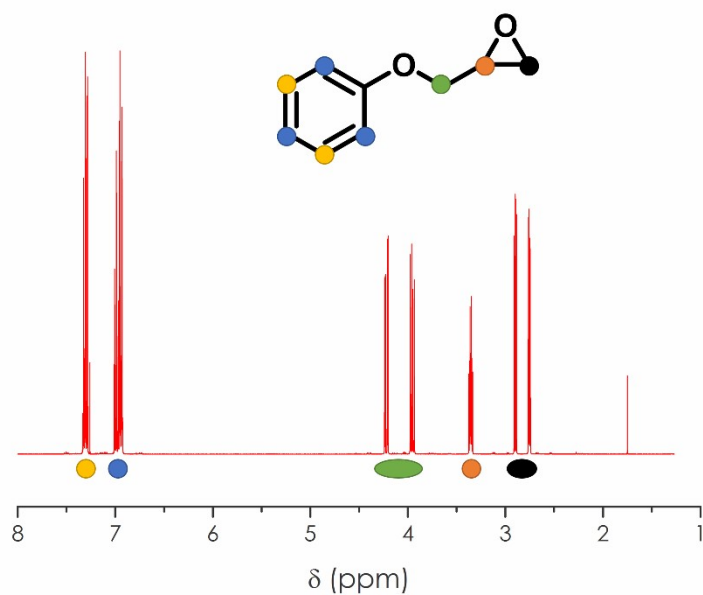*Figure S14. DSC thermograms of vitrimers from epoxy mixtures*

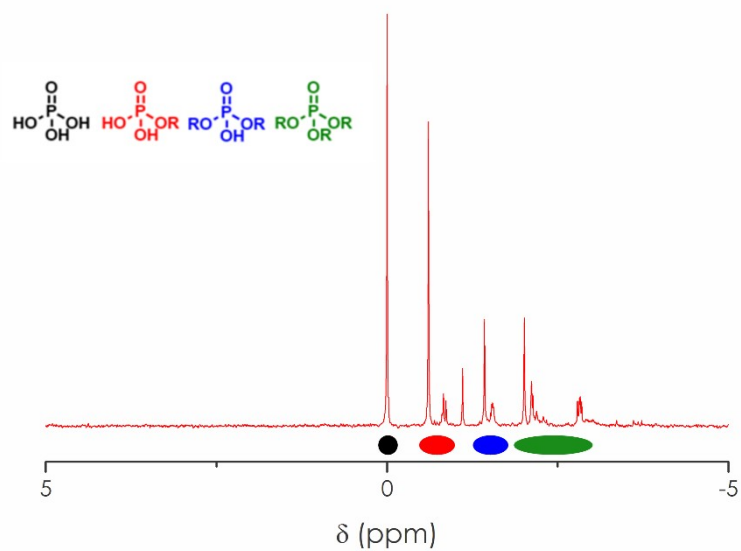*Figure S15. ^1H NMR spectrum of phenylglycidyl ether*

Figure S16. ^{31}P NMR spectrum of the reaction between phosphoric acid H_3PO_4 and phenylglycidyl ether after 2 hours. Phosphoric acid and mono-, di- and tri-substituted esters peaks are visible.
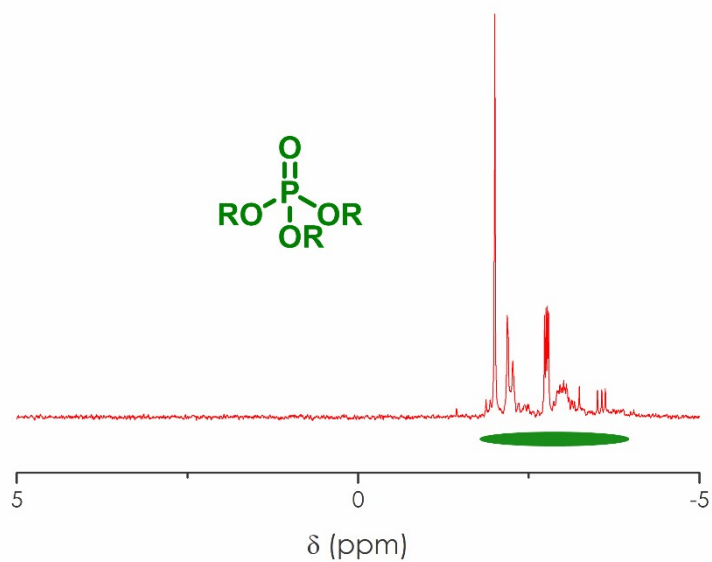

Figure S17. ^{31}P NMR spectrum of trisubstituted esters of phosphoric acid R_3PO_4. The different peaks are likely due to the mixture of different regioisomers, due to the epoxy opening on the -CH- or -CH$_2$- for each successive substitution.