

Supplementary information to “From vineyards to reshapable materials: α -CF₂ activation in 100 % resveratrol-based catalyst-free vitrimers”

Florian Cuminet,^{*a,b} Sébastien Lemouzy,^a Éric Dantras,^b Éric Leclerc,^a Vincent Ladmiral and Sylvain Caillol^{*a}

a. ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

b. CIRIMAT, Université Toulouse 3 Paul Sabatier, Physique des Polymères, 118 Route de Narbonne, 31062 Toulouse, France

Table of contents

Resveratrol α,α -difluorotriester “RvOEt” characterizations.....	2
Figure S1. ¹ H NMR spectrum of RvOEt in CDCl ₃	2
Figure S2. ¹⁹ F NMR spectrum of RvOEt in CDCl ₃	2
Resveratrol α,α -difluorotriacid “RvOH-TAF” characterizations.....	3
Figure S3. ¹³ C NMR spectrum of RvOEt in CDCl ₃	3
Figure S4. ¹ H NMR spectrum of RvOH-TAF in DMSO-d ₆	3
Figure S5. ¹⁹ F NMR spectrum of RvOH-TAF in DMSO-d ₆	4
Figure S6. ¹³ C NMR spectrum of RvOH-TAF in DMSO-d ₆	4
Figure S7. ¹ H NMR spectrum of RvOGly in acetone-d ₆	5
Figure S8. ¹³ C NMR spectrum of RvOGly in acetone-d ₆	5
A. Experimental procedure for the determination of RvOGly epoxy equivalent weight (EEW) by ¹ H NMR.....	6
Vitrimer characterizations (Vm-RvOH).....	7
Figure S9. DSC thermogram of Vm-RvOH after curing 3 h at room temperature.....	7
Figure S10. DSC thermogram of Vm-RvOH after curing 3 h at room temperature and 1 h at 150 °C.....	8
Figure S11. Curing step at 150 °C monitored by the evolution of the material storage modulus G'.....	9
Figure S12. DSC thermogram of Vm-RvOH after complete curing 10 h at 150 °C.....	9
Figure S13. DMA thermogram of Vm-RvOH after complete curing 10 h at 150 °C (0.1 % strain, 1 Hz, 3 °C/min).....	10
Figure S14. TGA thermogram under nitrogen of Vm-RvOH after complete curing 10 h at 150 °C.....	10
Figure S15. Isothermal TGA thermogram at 170 °C under air of Vm-RvOH after complete curing 10 h at 150 °C.....	11
Figure S16. Stress–relaxation curves of Vm-RvOH from 170 to 210 °C with 10 °C steps (0.3 % strain).....	11
Table S1. Equation and fitting parameters of the Kohlrausch-Williams-Watts stretched exponential model for the stress relaxation experiments.....	12
Figure S17. TGA thermogram under nitrogen of Vm-RvOH after complete curing 10 h at 150 °C recorded at 5 °C/min.....	12

Resveratrol α,α -difluorotriester "RvOEt" characterizations

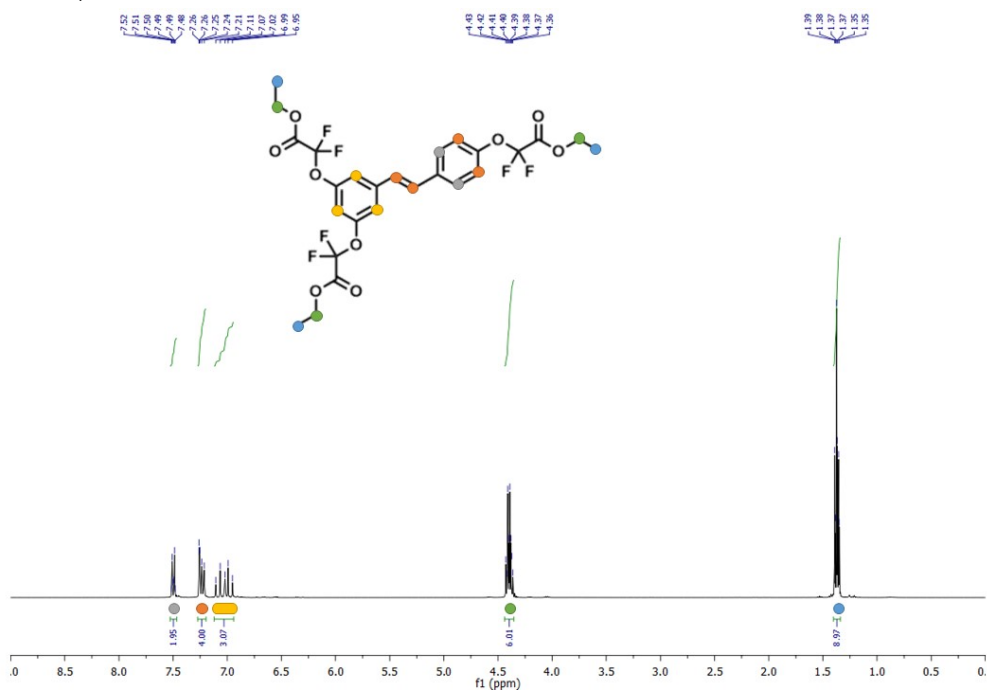


Figure S1. $^1\text{H NMR}$ spectrum of RvOEt in CDCl_3

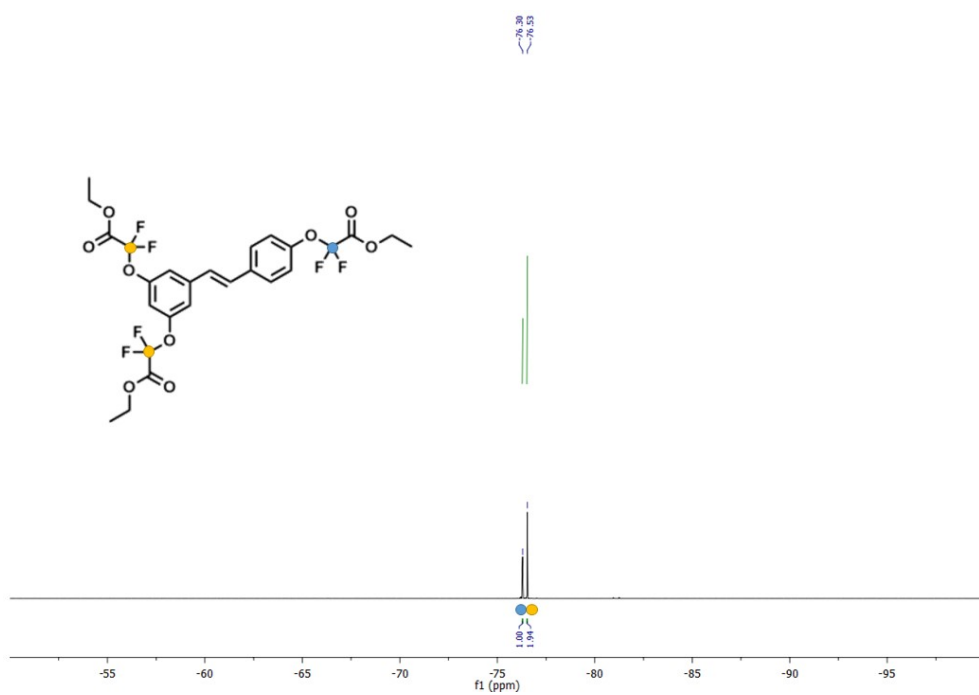


Figure S2. $^{19}\text{F NMR}$ spectrum of RvOEt in CDCl_3

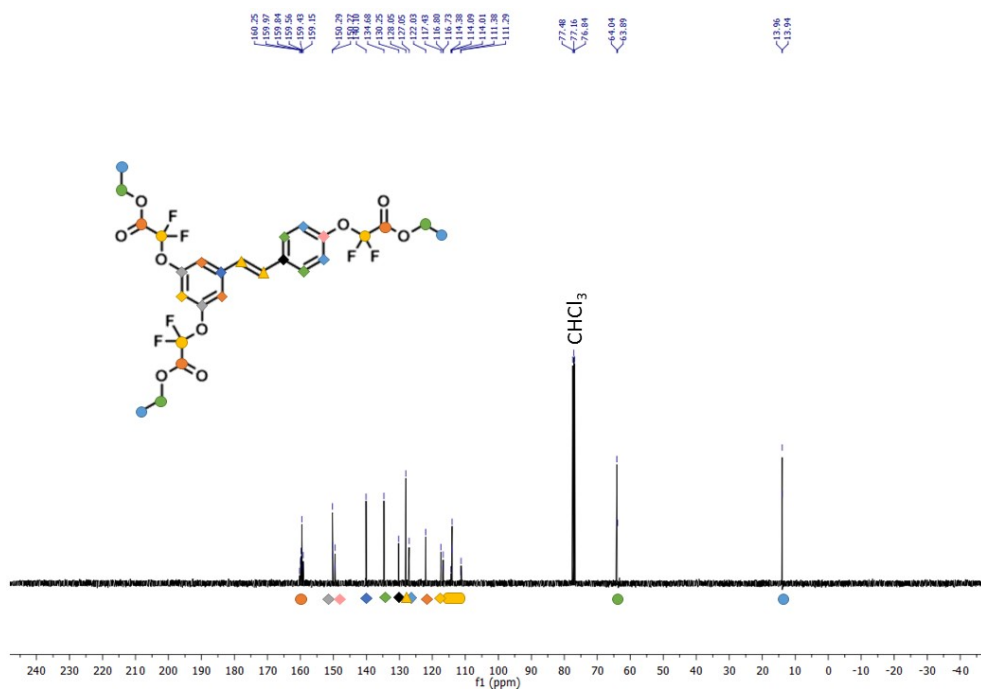


Figure S3. ^{13}C NMR spectrum of RvOEt in CDCl_3

Resveratrol α,α -difluorotriacid "RvOH-TAF" characterizations

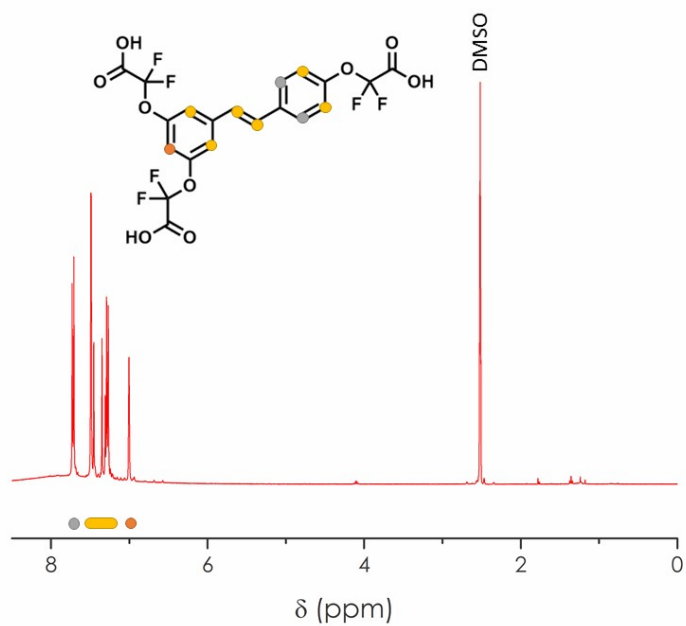


Figure S4. ^1H NMR spectrum of RvOH-TAF in $\text{DMSO}-d_6$

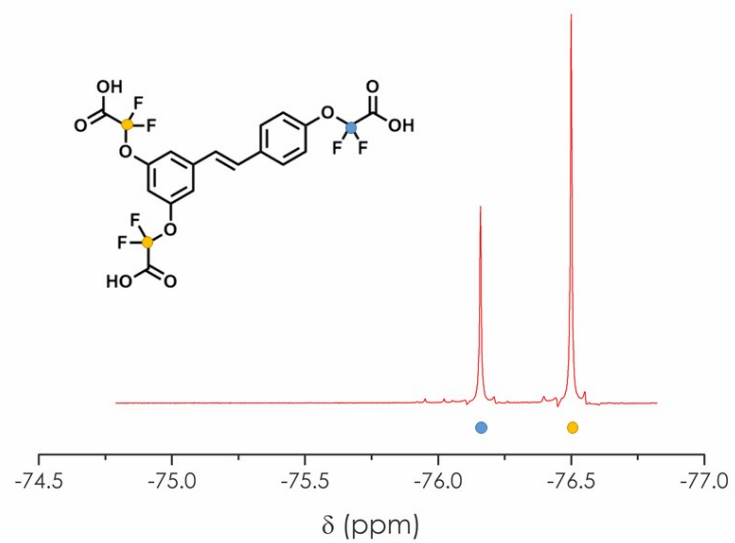


Figure S5. ^{19}F NMR spectrum of RvOH-TAF in DMSO-d_6

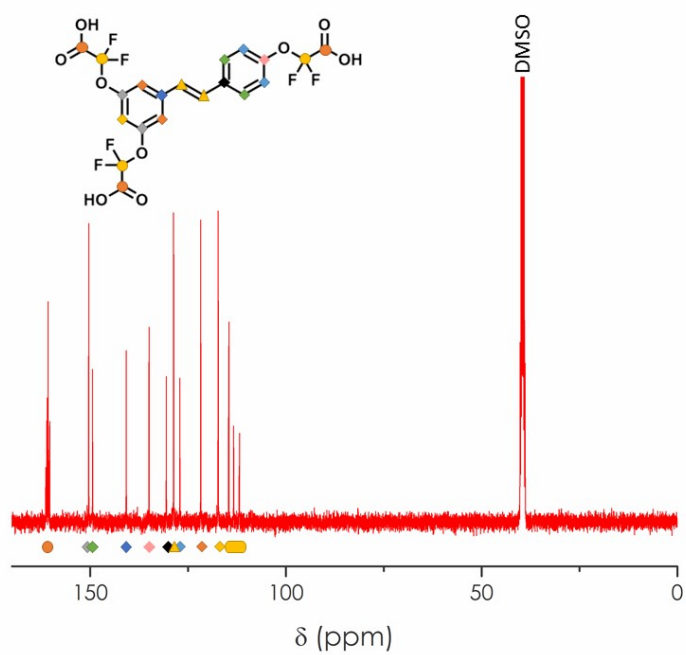


Figure S6. ^{13}C NMR spectrum of RvOH-TAF in DMSO-d_6

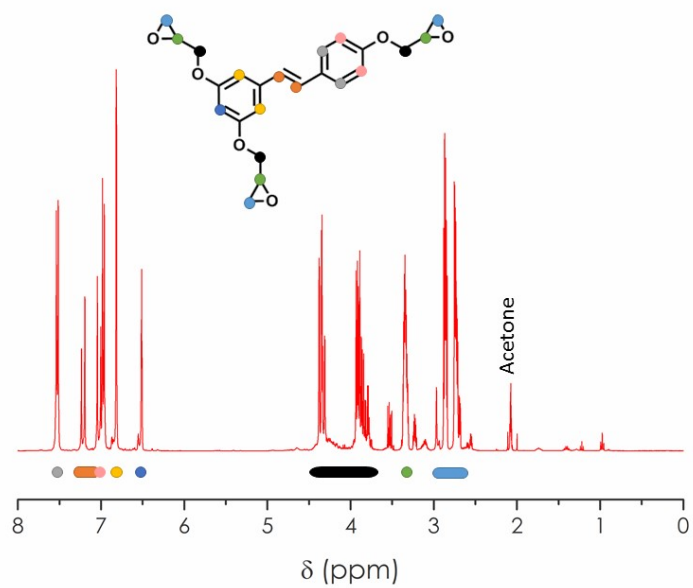


Figure S7. ^1H NMR spectrum of RvOGly in $\text{acetone-}d_6$

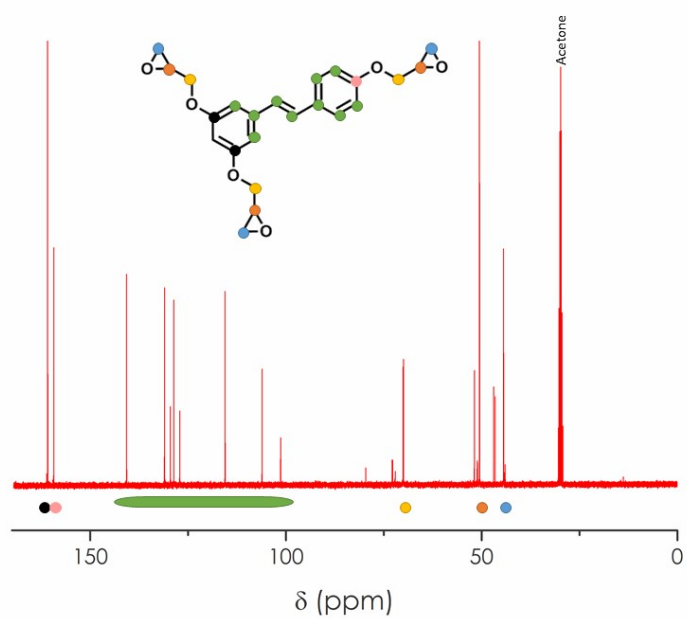
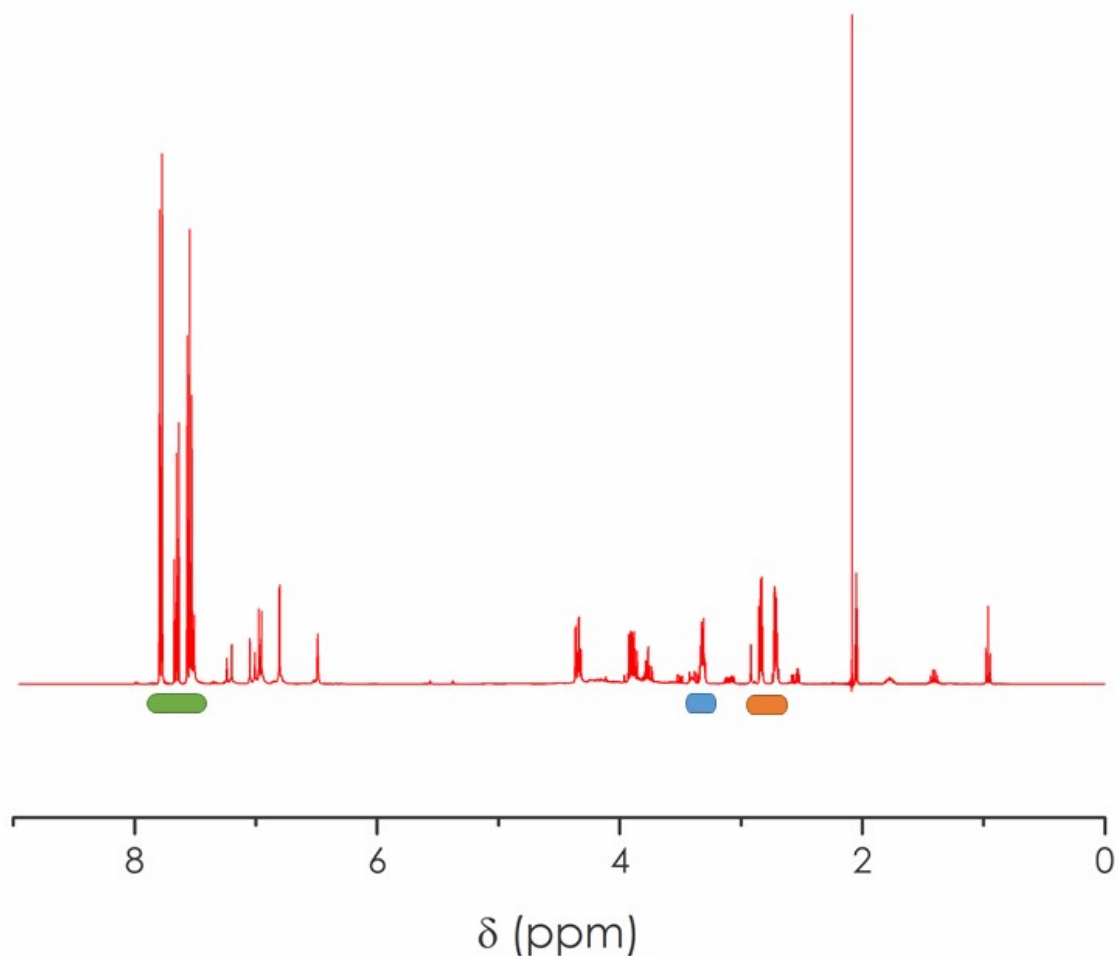


Figure S8. ^{13}C NMR spectrum of RvOGly in $\text{acetone-}d_6$

A. Experimental procedure for the determination of RvOGly epoxy equivalent weight (EEW) by ^1H NMR



50 to 70 mg of BDGE and 50 to 130 mg of RvOGly were dissolved in deuterated acetone. ^1H NMR spectra were integrated in the 7.87-7.28 ppm range for benzophenone protons (10 H), in the 3.46-3.26 ppm range for CH oxirane and in the 3.0-2.65 range for CH_2 oxirane. EEW was calculated as follows :

$$EEW_{CH} = \frac{m_{BDGE} \times \int_{7.28}^{7.87} \text{benzophenone} \times M_{\text{benzophenone}}}{10 \times m_{\text{benzophenone}} \times \int_{3.26}^{3.46} \text{CH oxirane}}$$

$$EEW_{CH_2} = \frac{2 \times m_{BDGE} \times \int_{7.28}^{7.87} \text{benzophenone} \times M_{\text{benzophenone}}}{10 \times m_{\text{benzophenone}} \times \int_{2.65}^{3.0} \text{CH}_2 \text{ oxirane}}$$

m_{epoxy} (mg)	$m_{\text{benzophenone}}$ (mg)	$\frac{\int_{2.97}^{3.19} CH \text{ oxirane}}{\int_{7.28}^{7.87} \text{benzophenone}}$	$\frac{\int_{2.45}^{2.82} CH_2 \text{ oxirane}}{\int_{7.28}^{7.87} \text{benzophenone}}$	EEW_{CH}	EEW_{CH_2}
55.9	39.9	0.157	0.283	163	180
94.8	44.8	0.227	0.390	170	198
125.9	54.8	0.245	0.402	171	208
Average EEW				182 ± 8 g/eq	

Vitrimer characterizations (Vm-RvOH)

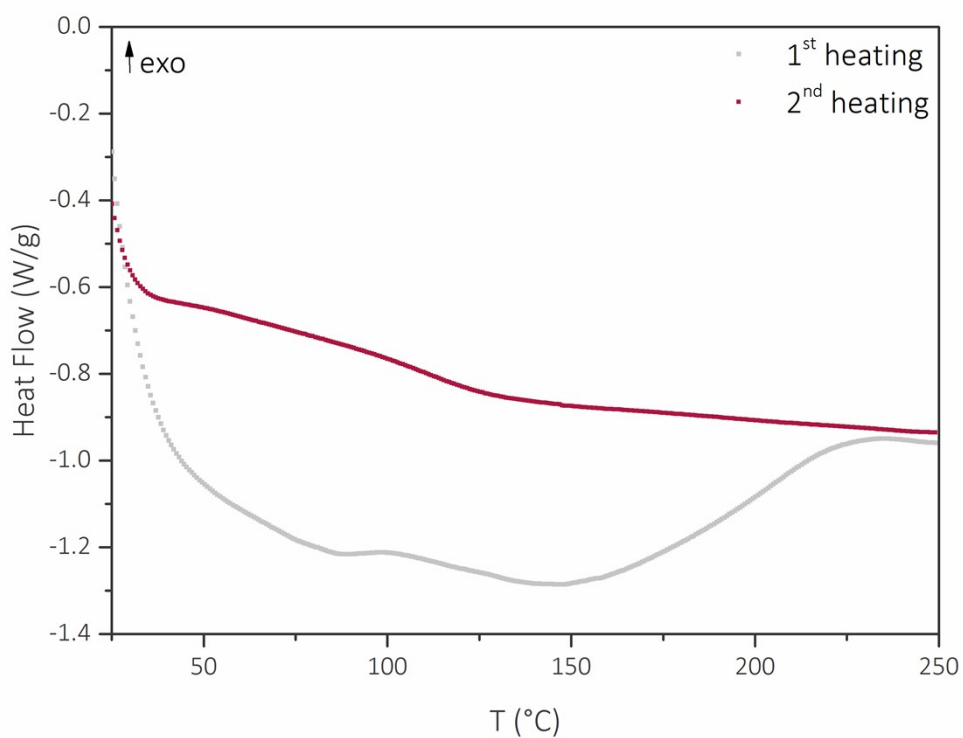


Figure S9. DSC thermogram of Vm-RvOH after curing 3 h at room temperature

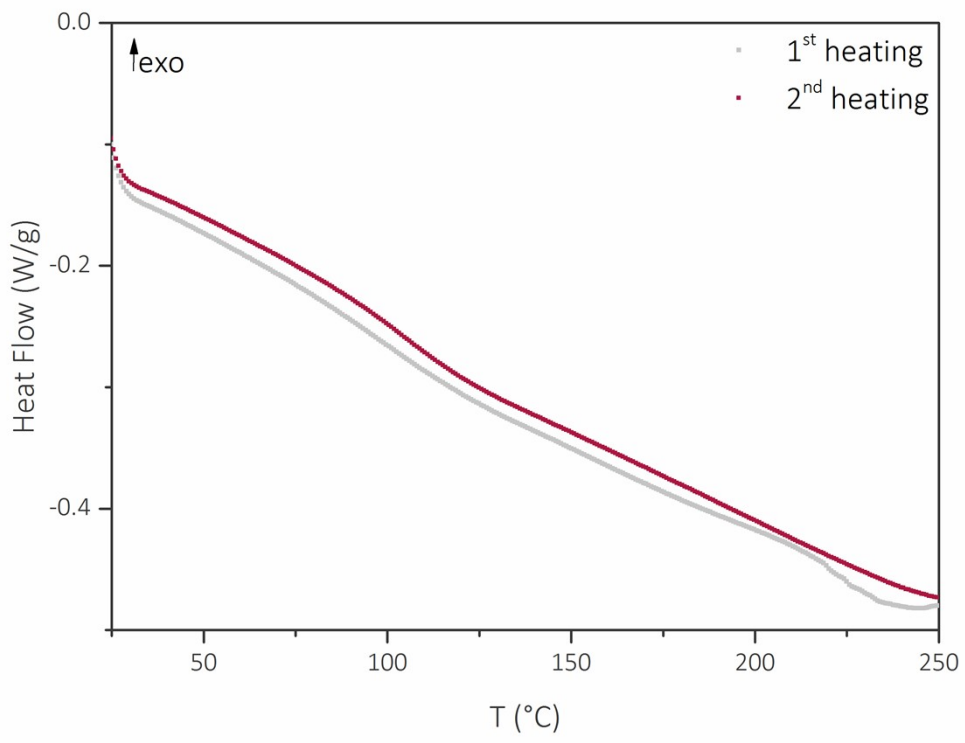


Figure S10. DSC thermogram of Vm-RvOH after curing 3 h at room temperature and 1 h at 150 °C

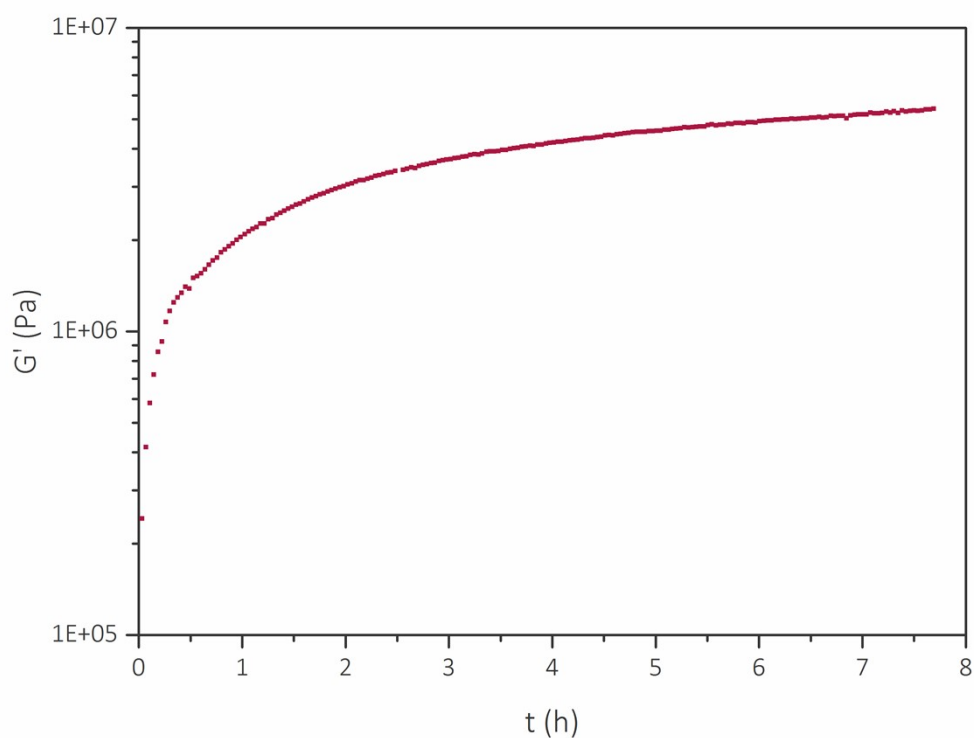


Figure S11. Curing step at 150 °C monitored by the evolution of the material storage modulus G'

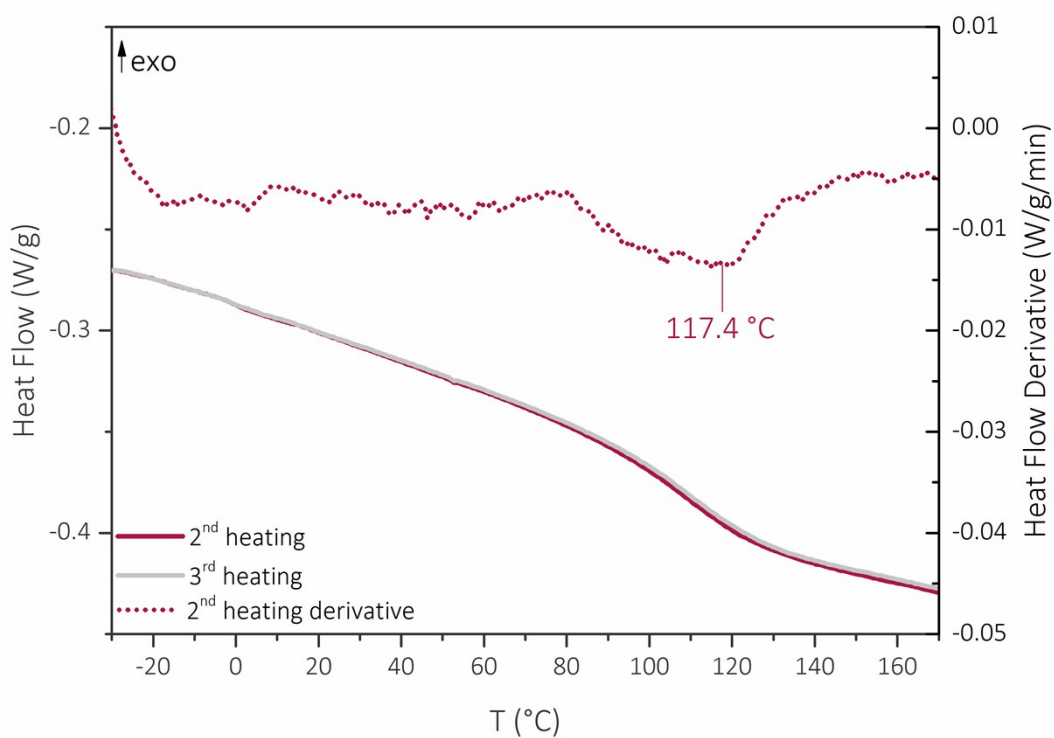


Figure S12. DSC thermogram of Vm-RvOH after complete curing 10 h at 150 °C.

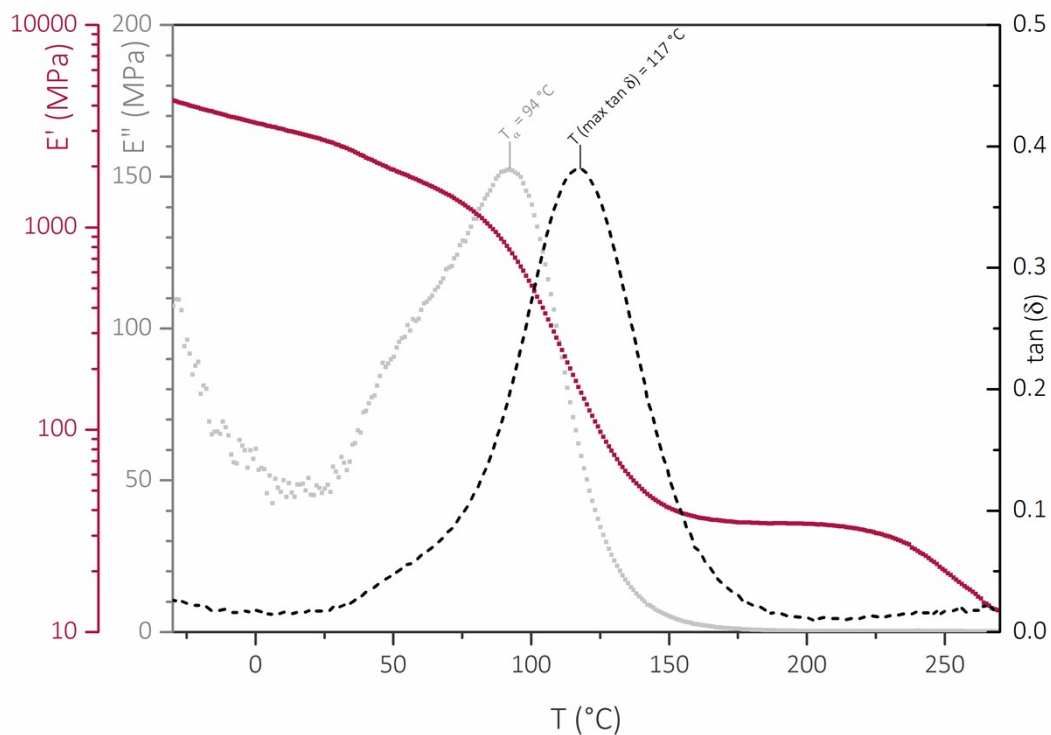


Figure S13. DMA thermogram of Vm-RvOH after complete curing 10 h at 150 $^{\circ}\text{C}$ (0.1 % strain, 1 Hz, 3 $^{\circ}\text{C}/\text{min}$)

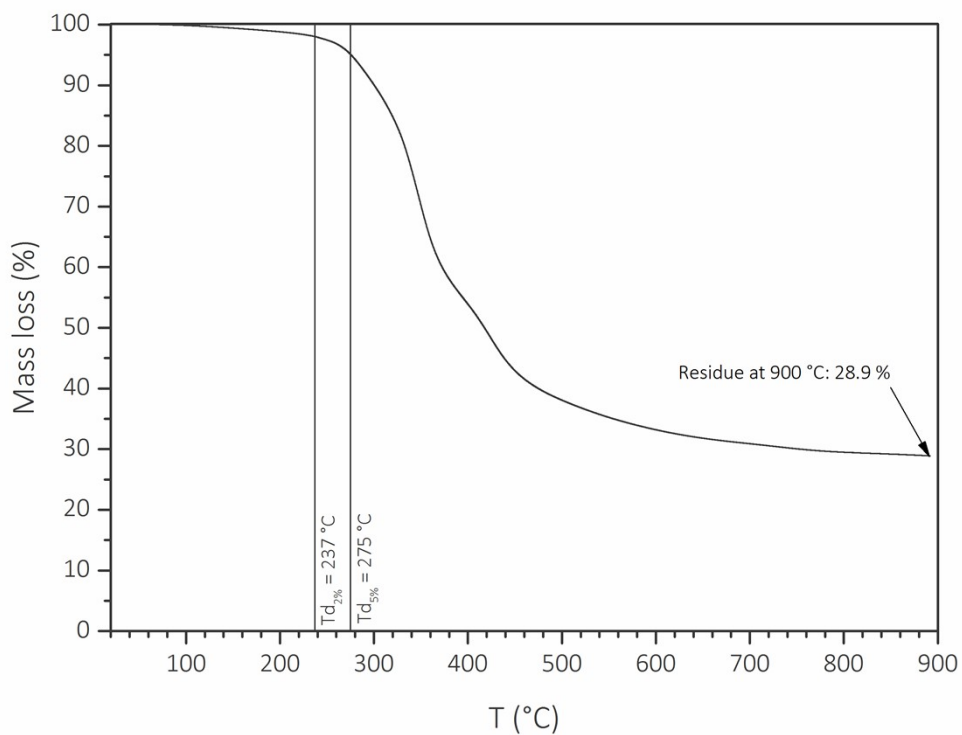


Figure S14. TGA thermogram under nitrogen of Vm-RvOH after complete curing 10 h at 150 $^{\circ}\text{C}$

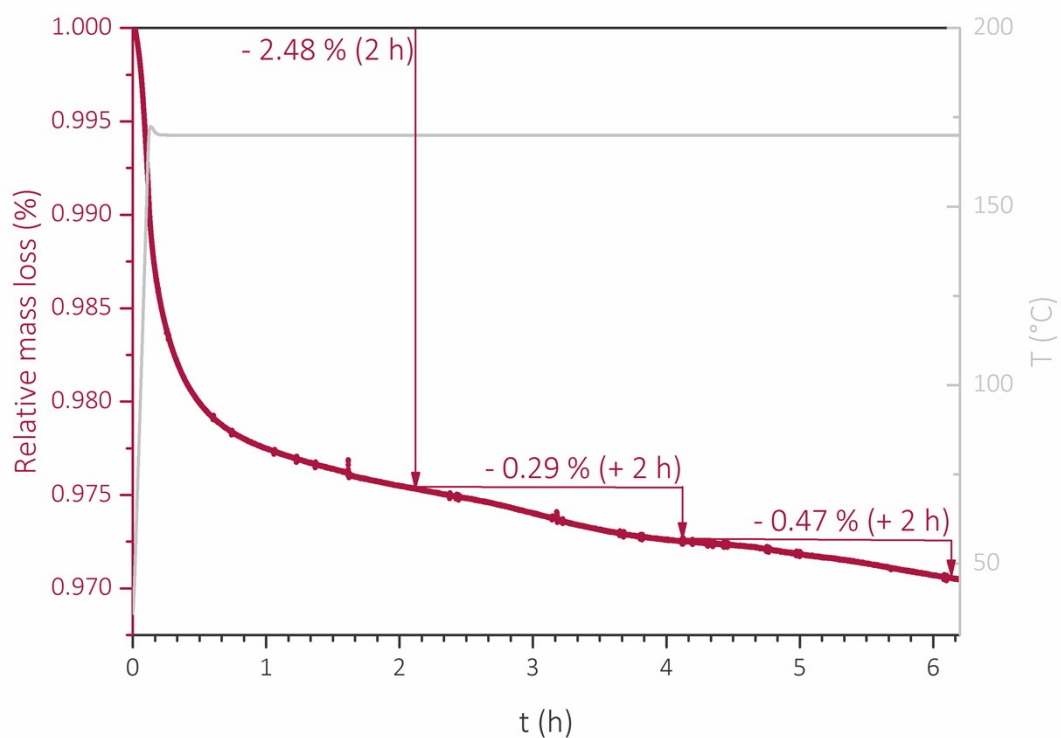


Figure S15. Isothermal TGA thermogram at 170 °C under air of Vm-RvOH after complete curing 10 h at 150 °C

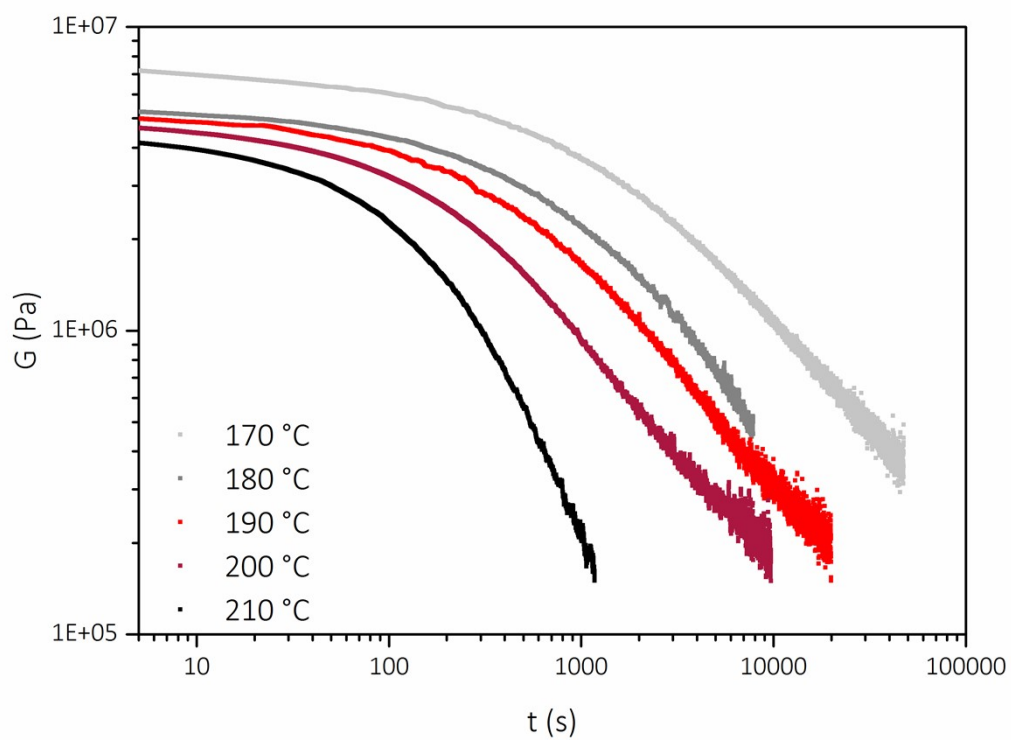


Figure S16. Stress-relaxation curves of Vm-RvOH from 170 to 210 °C with 10 °C steps (0.3 % strain)

Table S1. Equation and fitting parameters of the Kohlrausch-Williams-Watts stretched exponential for the stress relaxation experiments

$\frac{G}{G_0} = e\left(\frac{-t}{\tau}\right)^\beta + y_0$	T (°C)	170	180	190	200	210
	τ (s)	1827	1042	648	333	156
	β	0.486	0.569	0.593	0.642	0.797
	y_0	0.043	0.049	0.060	0.064	0.053
	R^2	0.99962	0.99975	0.99937	0.99974	0.99979

Note: for $\beta = 1$ and $y_0 = 0$, the KWW expression becomes a Maxwell

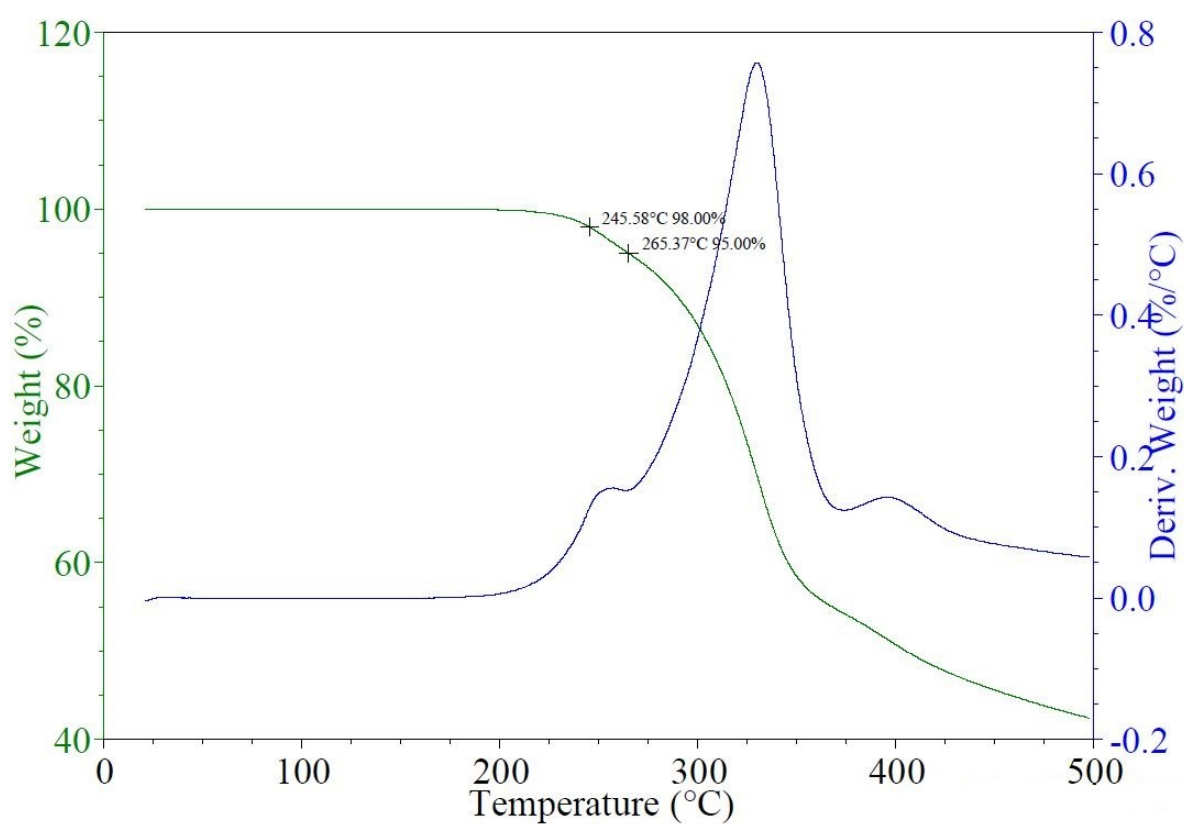


Figure S17. TGA thermogram under nitrogen of Vm-RvOH after complete curing 10 h at 150 °C recorded at 5 °C/min