

## Supporting Information

### **Streamlined concept towards spatially resolved photoactivation of dynamic transesterification in vitrimeric polymers by applying thermally stable photolabile bases**

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## Supplementary Tables

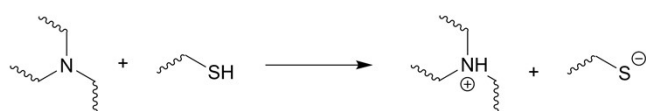
**Table S1** Spectral intensity distribution of the irradiation source used. All listed values for the UVC, UVB, UVA and UVV wavelength region are average values calculated from ten individual measurements.

UVC <sup>[a]</sup> [mW/cm <sup>2</sup> ]	UVB <sup>[b]</sup> [mW/cm <sup>2</sup> ]	UVA <sup>[c]</sup> [mW/cm <sup>2</sup> ]	UVV <sup>[d]</sup> [mW/cm <sup>2</sup> ]	Total intensity <sup>[e]</sup> [mW/cm <sup>2</sup> ]
7	13	305	382	707

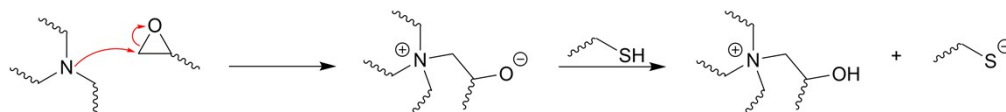
[a] 250-260 nm, [b] 280-320 nm, [c] 320-390 nm, [d] 395-445 nm, [e] 250-445 nm.

## Supplementary Schemes

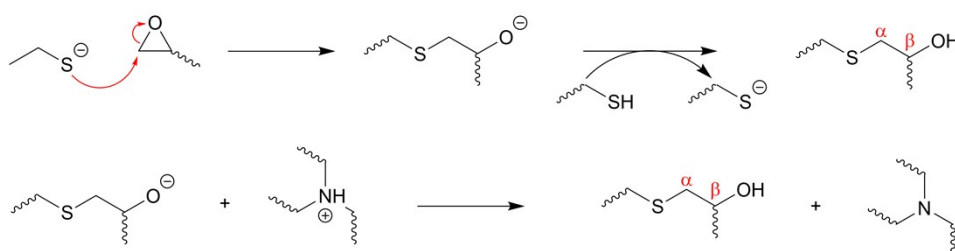
### Initiation reaction I <sup>[a]</sup>



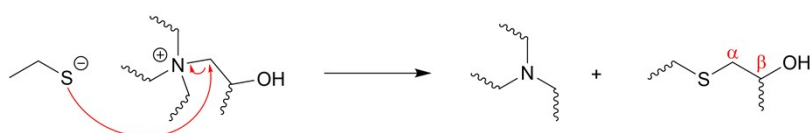
### Initiation reaction II <sup>[b]</sup>



### Propagation reaction <sup>[c]</sup>

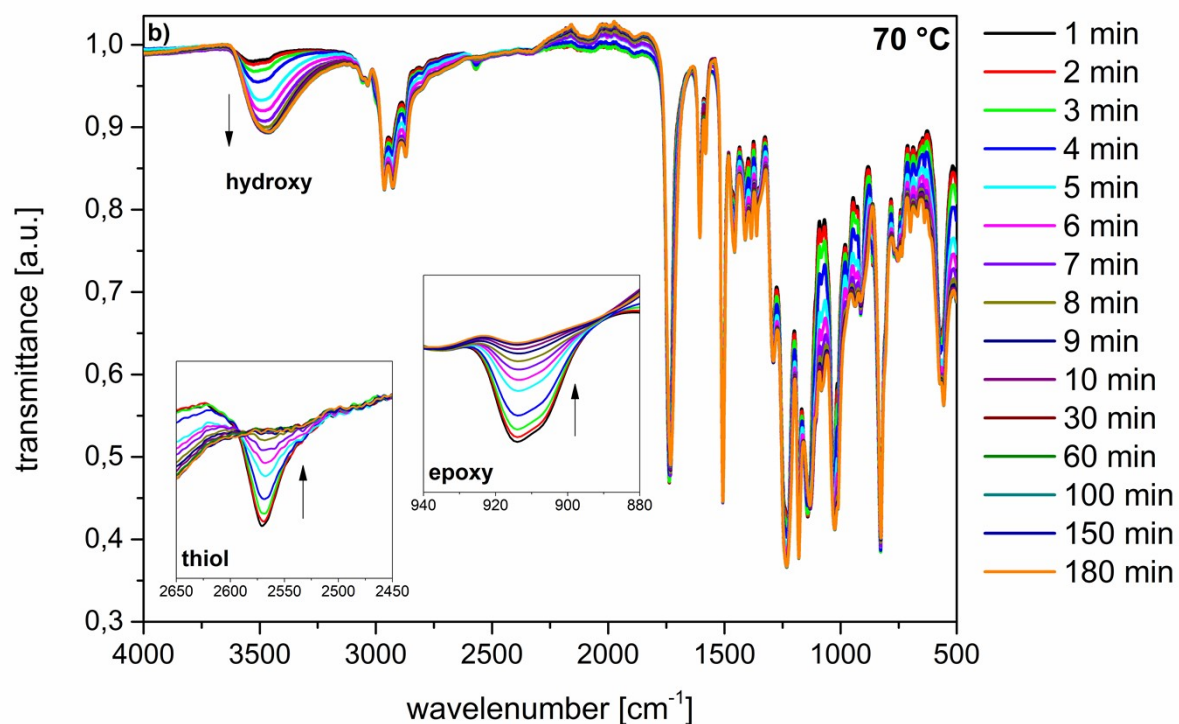
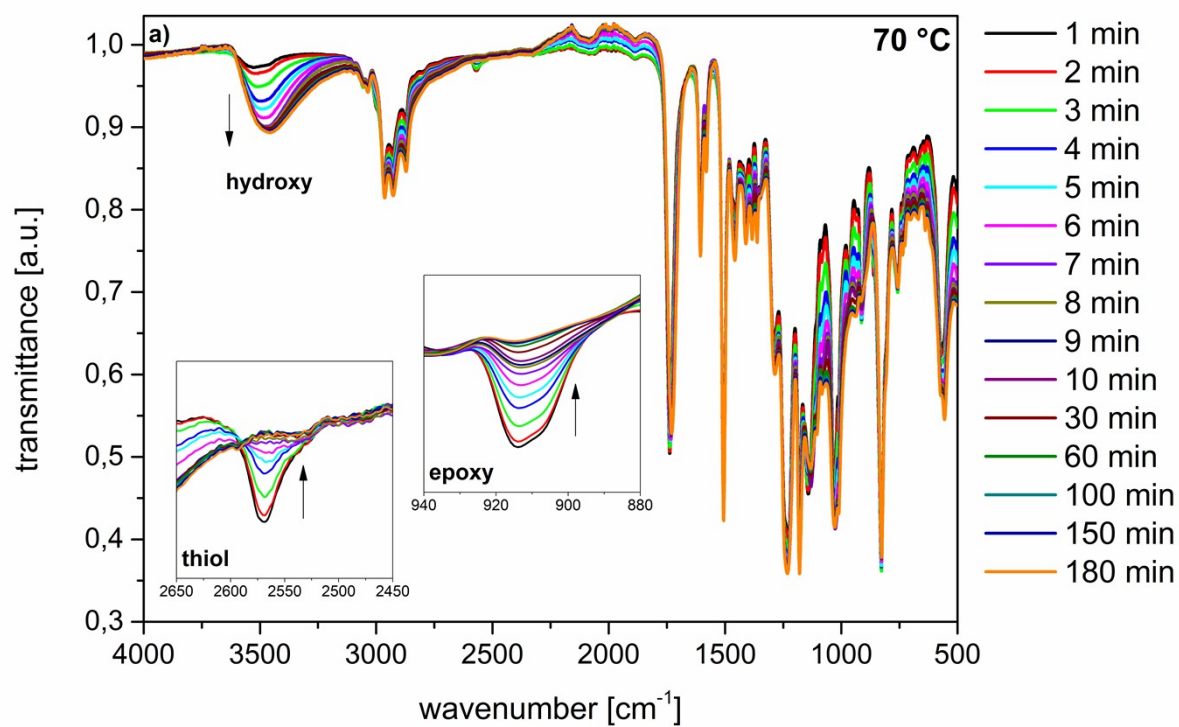


### Termination/Regeneration reaction <sup>[d]</sup>

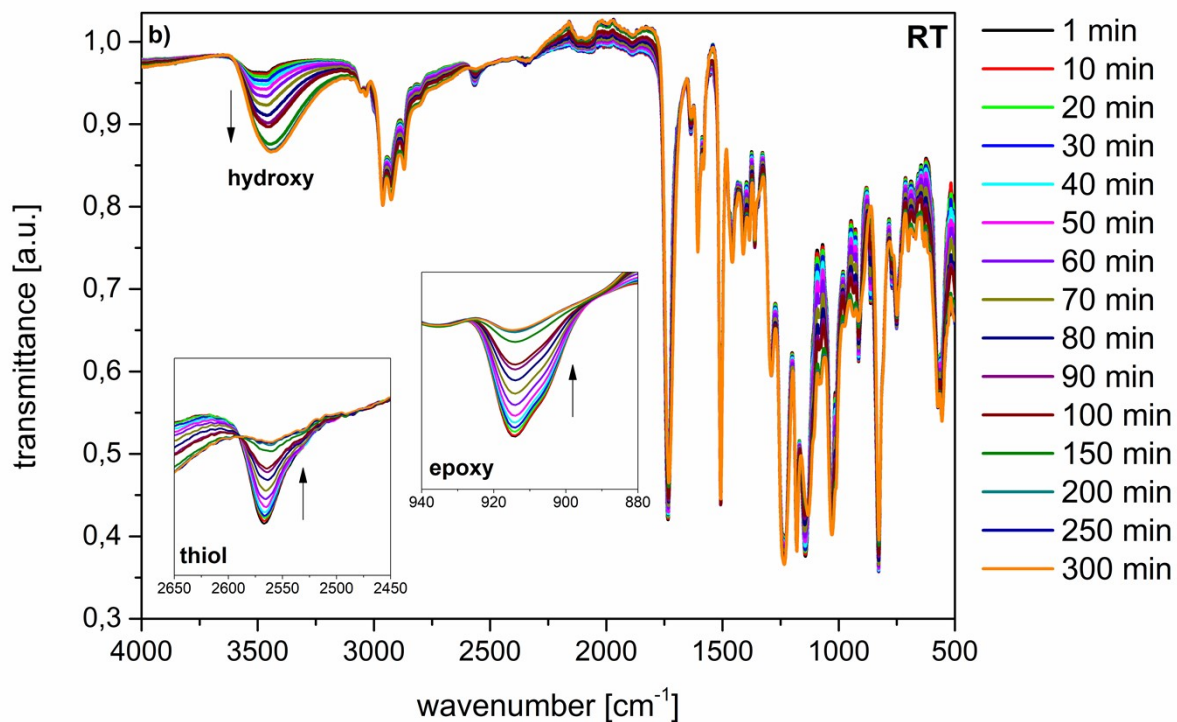
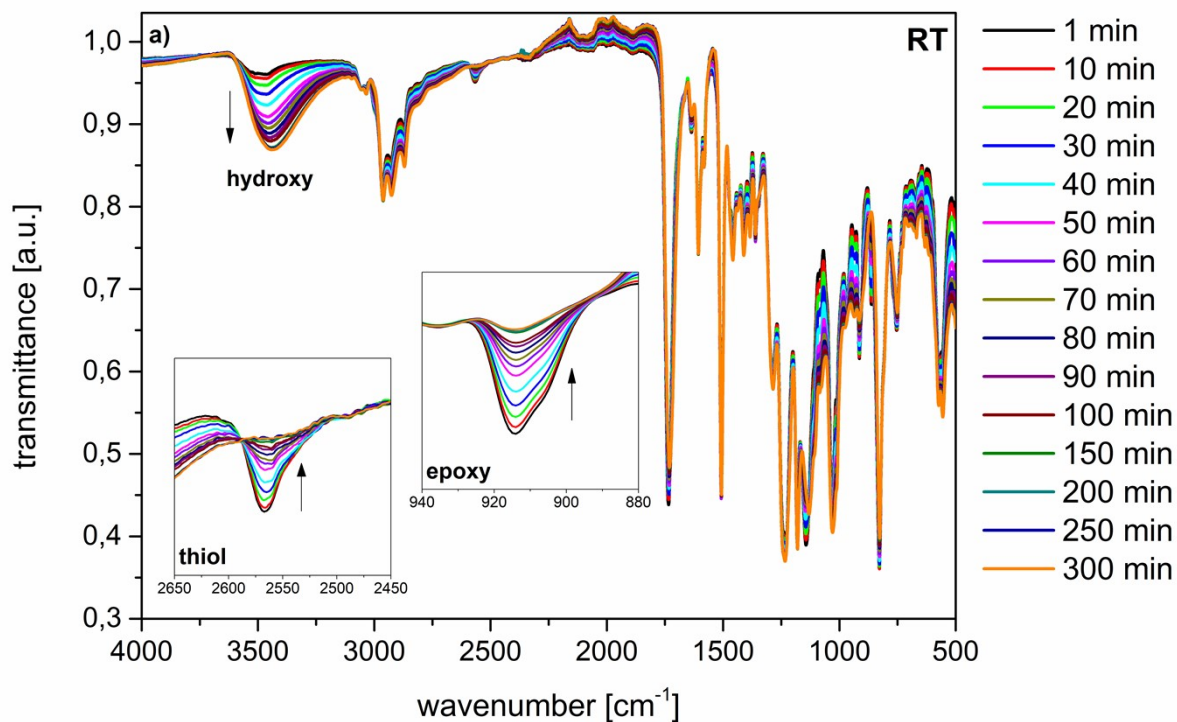


**Scheme S1** Mechanism proposed in the literature for curing of thiol-epoxy resins by nucleophilic tertiary amines<sup>1</sup>: [a] direct deprotonation of the thiol group, [b] nucleophilic ring opening of an epoxy group by a nucleophilic tertiary amine catalysed by hydroxy groups, [c] nucleophilic ring opening of an epoxy group by a thiolate group, followed by a protonation of the generated alkoxide by a thiol group or the protonated tertiary amine, resulting in the formation of a β-hydroxythioether link, [d] nucleophilic displacement of the initiator i.e. regeneration of the tertiary amine.

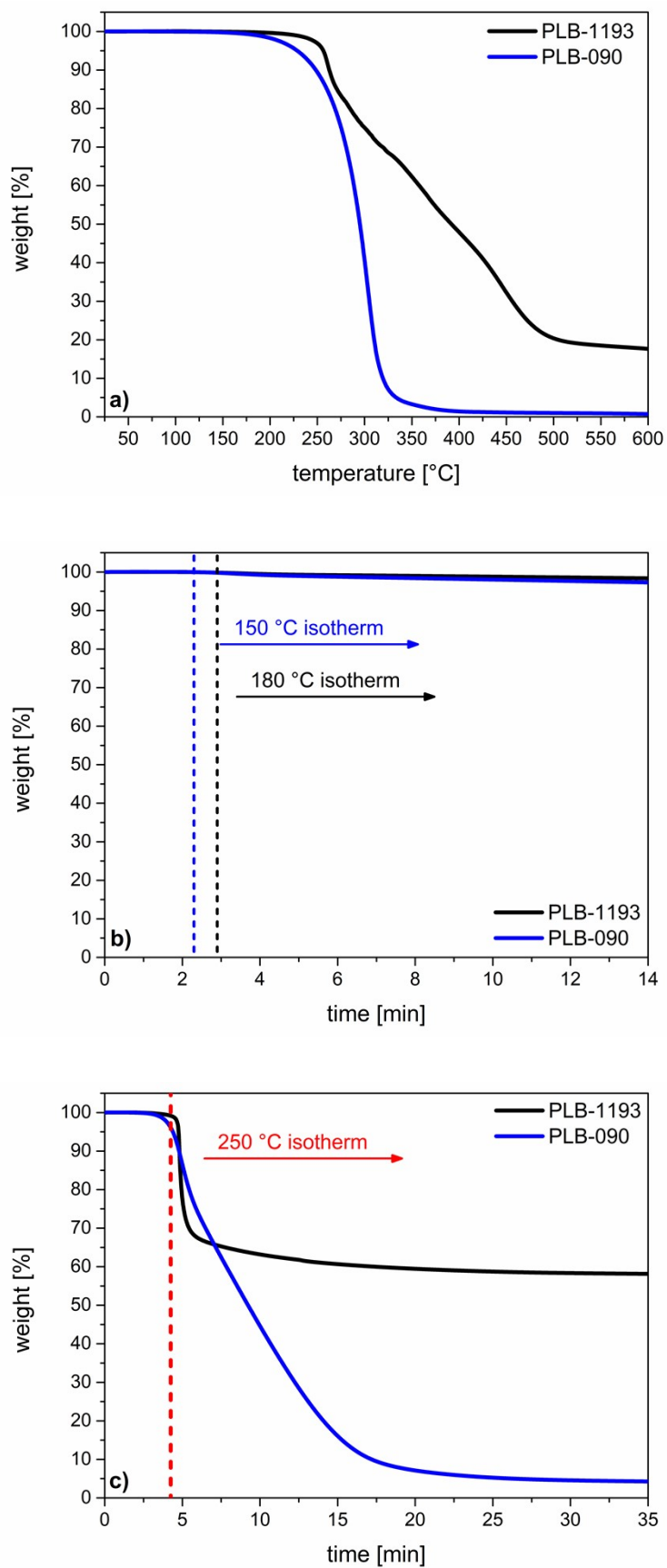
## Supplementary Figures



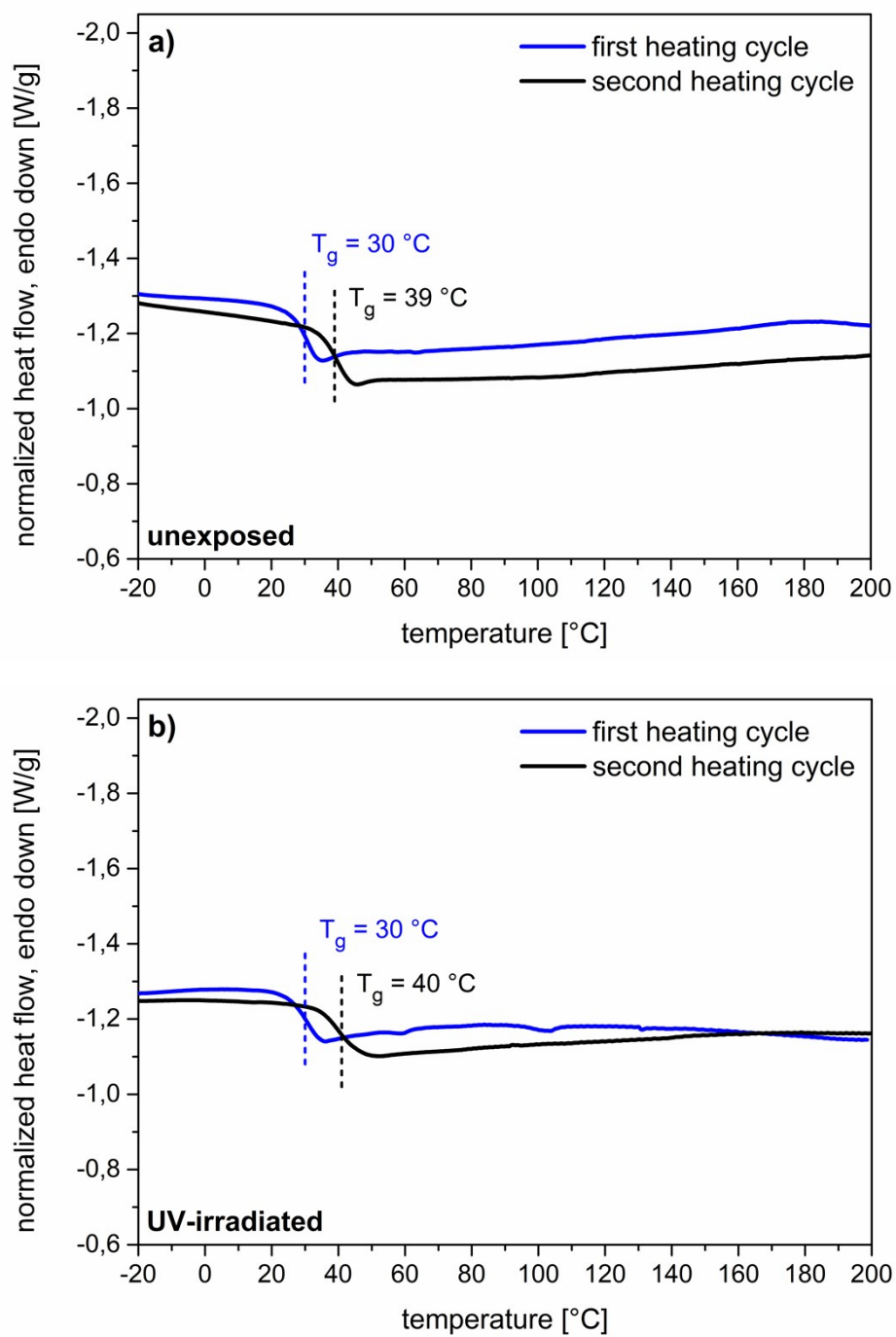
**Fig. S1** Curing behaviour of unirradiated a) TE-PLB-1193-ITX and b) TE-PLB-090 formulations examined by FTIR-ATR measurements conducted at a constant temperature of 70 °C.



**Fig. S2** Curing behaviour of unirradiated a) TE-PLB-1193-ITX and b) TE-PLB-090 formulations examined by FTIR-ATR measurements conducted at room temperature.



**Fig. S3a** TGA curves of PLB-1193 and PLB-090 recorded under nitrogen atmosphere. a) Dynamic measurement using a heating rate of 20 °C/min. Isothermal measurements carried out b) below the decomposition temperatures of PLB-1193 and PLB-090 at 180 °C and 150 °C, respectively and c) above the decomposition temperature of PLB-1193 and PLB-090 at 250 °C.



**Fig. S4** DSC data obtained under nitrogen atmosphere in two heating cycles for a) unexposed and b) UV-irradiated (424 J/cm<sup>2</sup> applied at 60 °C) TE-PLB-1193-ITX.

## References

- 1 a) A. O. Konuray, X. Fernández-Francos and X. Ramis, *Polym. Chem.*, 2017, **8**, 5934–5947; b) C. F. Carlborg, A. Vastesson, Y. Liu, W. van der Wijngaart, M. Johansson, T. Haraldsson, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 2604-2615.