

## Supporting information

# Cardanol-based polybenzoxazine vitrimer: recycling, reshaping and reversible adhesion

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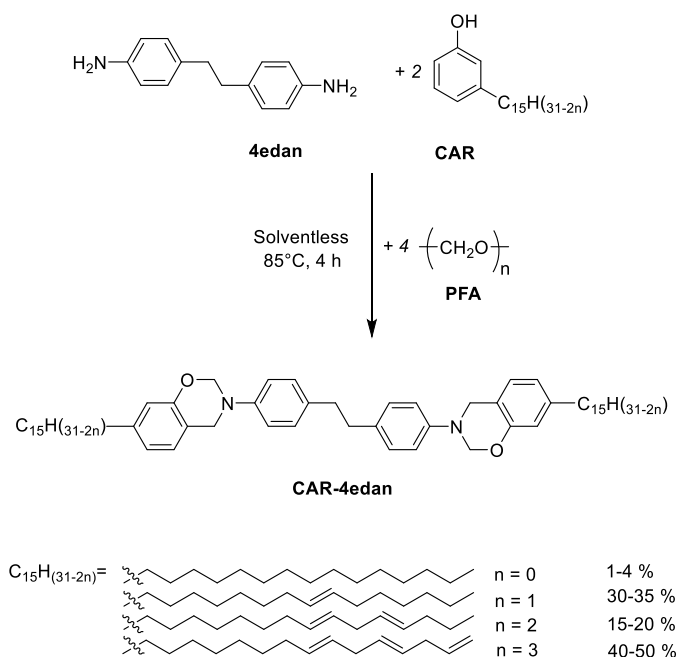
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## EXPERIMENTAL

### Synthesis of CAR-4edan

Cardanol (2.98 g, 10 mmoles, 1 eq.), 4,4'-ethylenedianiline (1.06 g, 5 mmoles, 0.5 eq.), paraformaldehyde (601 mg, 20 mmoles, 2 eq.) were reacted together in a round bottom flask under mechanical stirring at 85 ° C during 4 h (Scheme S1).



Scheme S1. Synthesis of CAR-4edan.

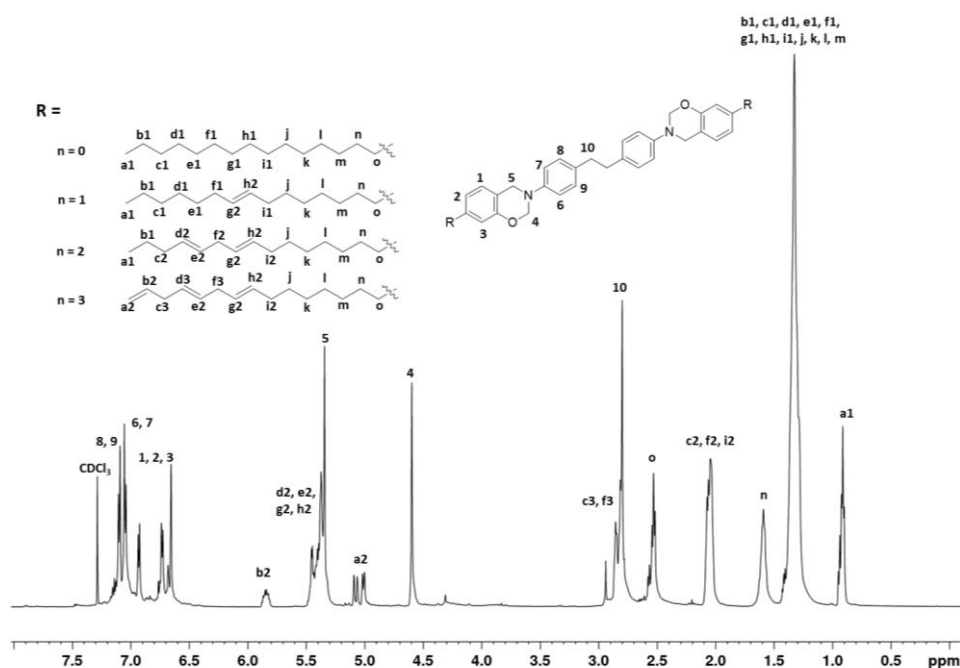


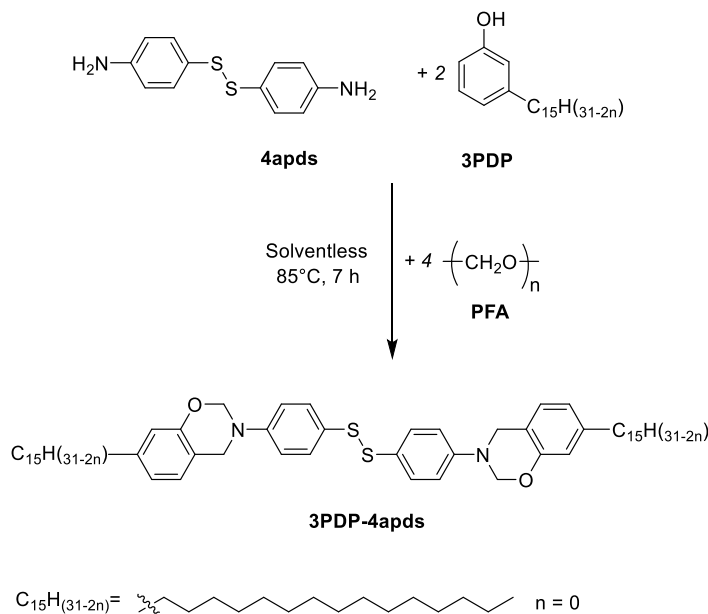
Figure S1.  $^1H$  NMR spectrum (in  $CDCl_3$ ) of CAR-4edan.

$^1H$  NMR ( $CDCl_3$ , 400 MHz, 298 K),  $\delta$  (ppm) = (assignment, multiplicity (coupling constant), attribution, experimental integration, theoretical integration);  $\delta = 0.87-0.97$  (-CH<sub>3</sub>, m, [a1] from cardanol alkyl chain, exp 3.99H, th 3.54H), 1.18-1.46 (-CH<sub>2</sub>, s, [b1, c1, d1, e1, f1, g1, h1, i1, j, k, l, m] from cardanol alkyl chain, exp 26.33H, th 27.12H), 1.52-1.66 (-CH<sub>2</sub>  $\beta$  from Ar [n], s, **aliphatic proton reference 4.00H**) 1.96-2.12 (CH<sub>2</sub>\*=CH, m, [c2, f2, i2], exp 6.54H, th 6.20H), 2.46-2.61 (CH<sub>2</sub>-Ar, m, [o], exp 4.00H, th 4.00H), 2.70-2.90 (CH<sub>2</sub>\* (=CH)<sub>2</sub>) from

cardanol, d, [c3, f3]; Ar-CH<sub>2</sub>-CH<sub>2</sub>- from 4,4'-methylenediamine, s, [10], exp 7.44H, th 8.20H), 4.60 (Ar-CH<sub>2</sub>-N, s, [4], exp 3.66H, th 4.00H), 5.34 (O-CH<sub>2</sub>-N, s, [5], exp 4.01H, th 4.00H), 4.96-5.88 (CH=, m, m, m, [a2, (d2, e2, g2, h2), b2], exp 1.42, 5.43, 0.65H, th 1.64, 6.48, 0.82H), 6.60-6.90 (H-Ar from cardanol, s, d, d, [1, 2, 3], exp 2.01, 2.12, 2.08H, th 2.00, 2.00, 2.00H), 7.05 (H-Ar from 4,4'-methyleneamine, d, [6,7], **benzoxazine structure reference th 4.00H**), 7.10 (H-Ar from 4,4'-methyleneamine, d, [8,9], exp 4.08H, th 4.00H).

### Synthesis of 3PDP-4apds

3-Pentadecylphenol (3 g, 9.85 mmol, 1 eq.), 4-Aminophenyl disulfide (1.22 g, 4.93 mmol, 0.5 eq.), paraformaldehyde (0.59 g, 19.7 mmol, 2 eq.) were reacted together in a round bottom flask under mechanical stirring at 70 ° C during 1 h (Scheme S2).



Scheme S2. Synthesis of 3PDP-4apds.

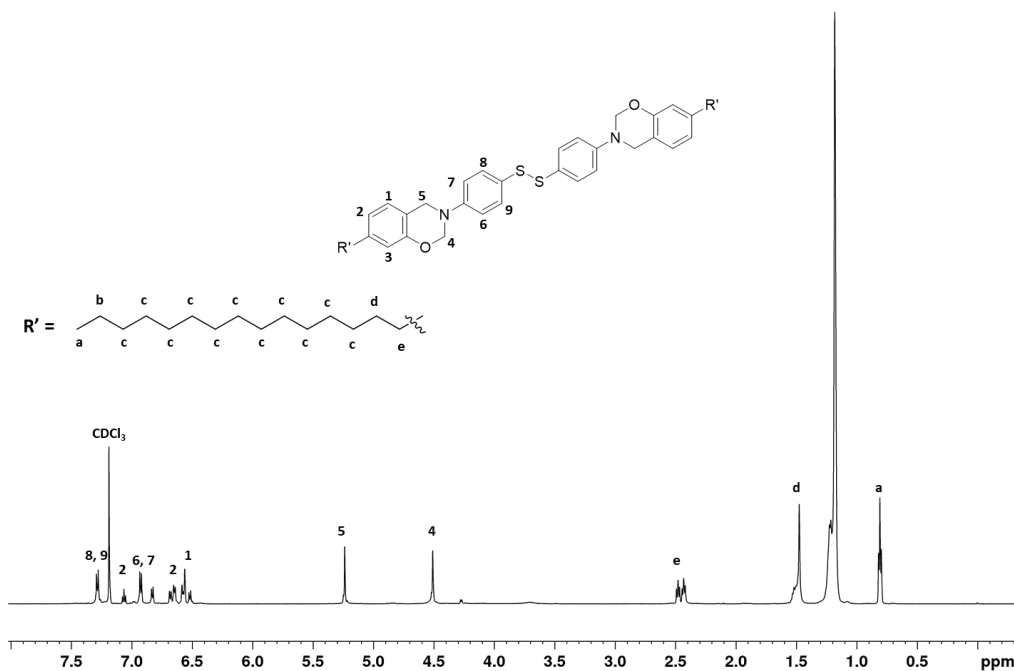
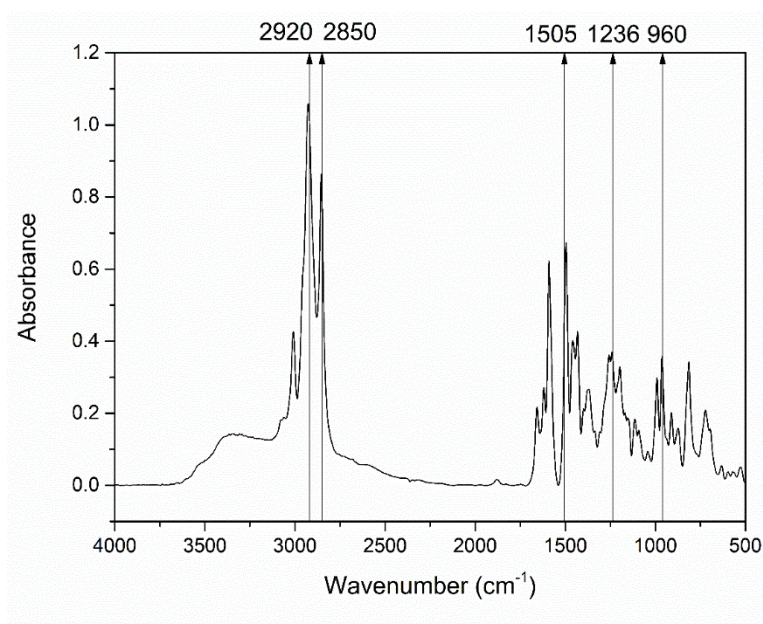


Figure S2. <sup>1</sup>H NMR spectrum (in CDCl<sub>3</sub>) of 3PDP-4apds

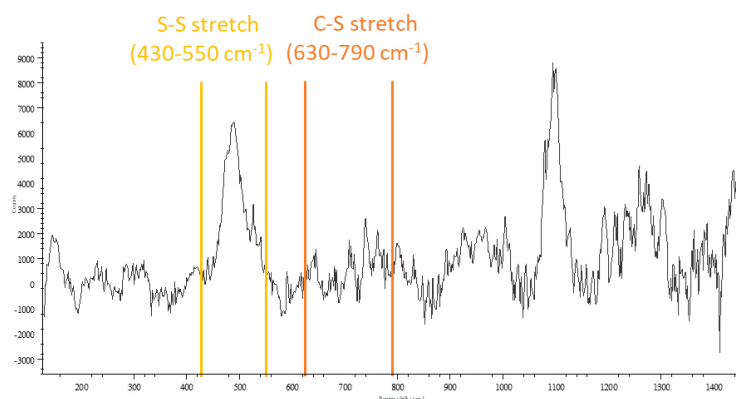
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K),  $\delta$  (ppm) = (assignment, multiplicity (coupling constant), attribution, experimental integration, theoretical integration);  $\delta = 0.77\text{-}0.83$  ( $-\text{CH}_3$ , m, [a], **Reference 6.00H**), 1.14 - 1.26 ( $-\text{CH}_2$ , d, [b, c,], exp 49.95H, th 48.00H), 1.42-1.53 ( $-\text{CH}_2$   $\beta$  from Ar [d], s, exp 4.66H, th 4.00H), 2.40 - 2.49 ( $\text{CH}_2\text{---Ar}$ , m, [e], exp 3.86H, th 4.00H), 4.51 ( $\text{Ar-CH}_2\text{-N}$ , s, [4], exp 2.96H, th 4.00H), 5.24 ( $\text{O-CH}_2\text{-N}$ , s, [5], exp 2.37H, th 4.00H), 6.50-6.86 ( $\text{H-Ar}$  from cardanol, s, d, d, [1, 2, 3], exp 6.60H, th 6.00H), 6.93 ( $\text{H-Ar}$  from 3-pentadecylphenol, d, [6, 7], exp 1.97H, th 2.00H), 7.29 ( $\text{H-Ar}$  from 3-pentadecylphenol, d, [8, 9], exp 2.30H, th 2.00H).

## RESULTS AND DISCUSSION

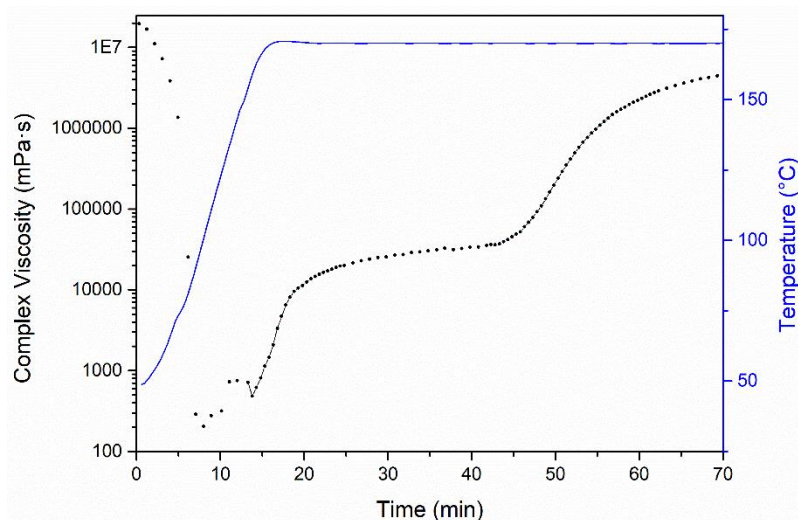
### Synthesis, characterization and polymerization of CAR-4apds



**Figure S3.** FTIR spectrum of CAR-4apds.



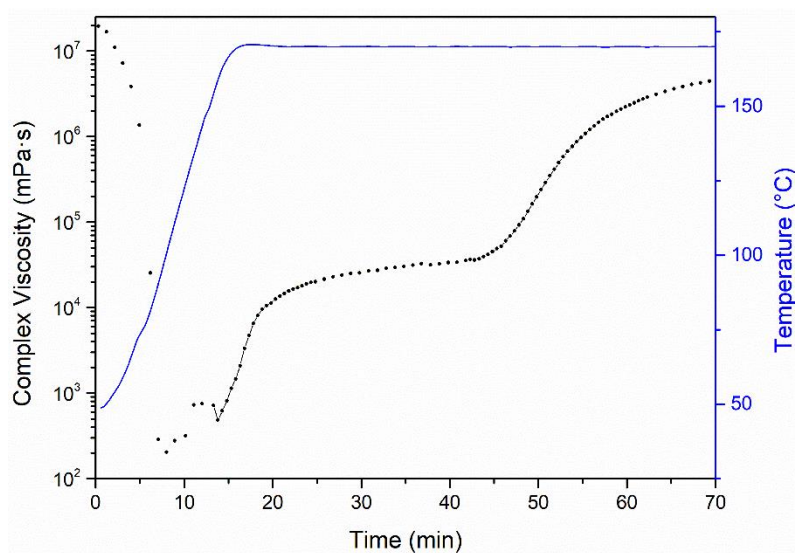
**Figure S4.** RAMAN spectrum of CAR-4apds.



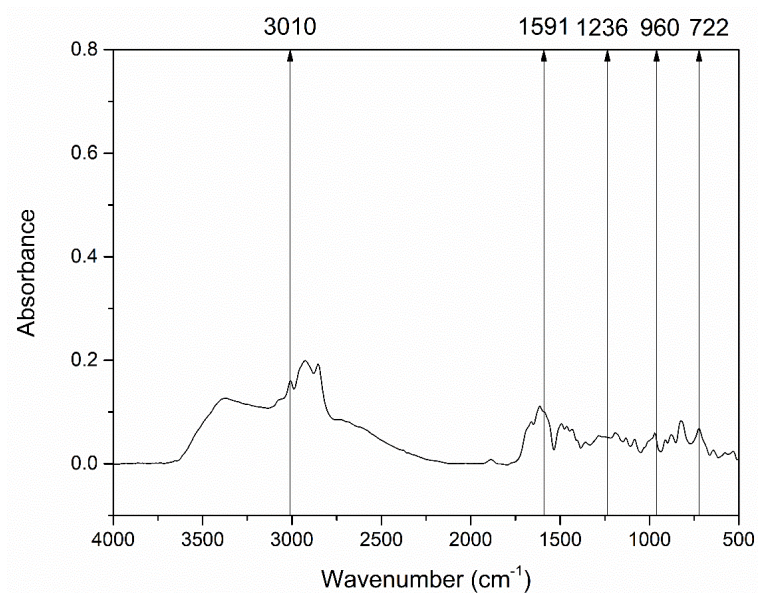
**Figure S5.** Rheology monitoring of the curing of CAR-4apds with a heating ramp of 20 °C/min from 50 °C to 170 °C, followed by isothermal measurement at 170 °C - Complex viscosity as a function of time.

#### **Additional tests: Investigation of CAR-4apds curing mechanism**

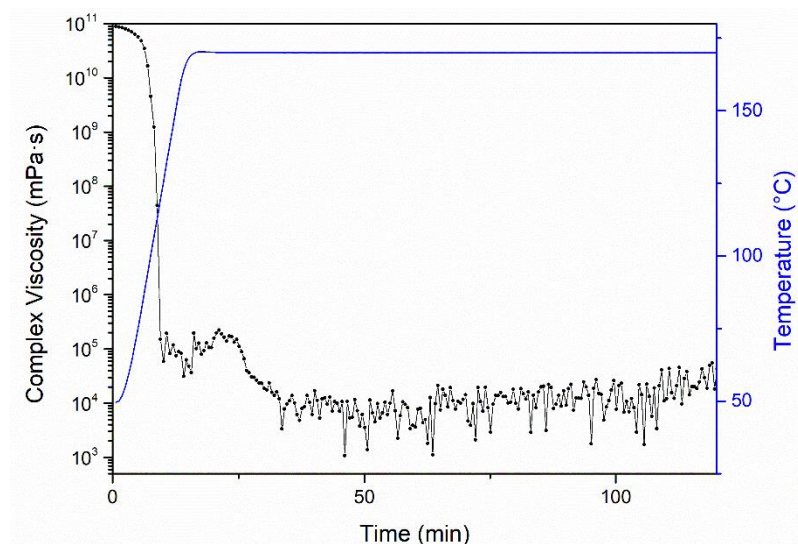
It was the first time such a double gelation process was observed for cardanol-based benzoxazine. A first explanation may be given by the cleavage of the disulfide bonds forming free radicals able to react with the unsaturations of the cardanol alkyl side chain. In such a case, the disulfide bonds would be irreversibly consumed, annihilating any possible use of the material as a vitrimer. Traditional molecular characterizations did not help to understand the mechanism. Following a *Reductio ad Absurdum* approach, we decided to investigate how a similar molecule than CAR-4apds which would not contain a disulfide bond in its structure would behave upon heating. This molecule, so-called CAR-4edan (see details of the synthesis and molecular characterizations at the beginning of SI, Scheme S1), was subjected to the same rheological measurement than CARD-4apds and showed interestingly a similar behavior, i.e. a two-step curing process (Figure S6). The involvement of the -S-S- in the benzoxazine curing process may then not be considered anymore. The only remaining possibility was the reaction of the cardanol double bonds on themselves during heating, as it has been already reported. Actually, FTIR spectrum of the poly(CAR-4apds) shows a decrease in the intensity of the characteristic absorption band of the unsaturations of cardanol after the curing (Figure S7). To confirm this matter, a second molecule similar to CAR-4apds, excepting the C15 alkyl side chains are saturated, was prepared and characterized (see details of the synthesis and characterization at the beginning of the SI Scheme S2). Interestingly, this new molecule (CAR-3pdp) was not crosslinking, the complex viscosity starting slightly to increase after 150 minutes (Figure S8). The crosslinking of CAR-apds is thus the combination of both the benzoxazine ring cross-linking and the cardanol side chains' unsaturations homo-reaction, chemically independent from each other.



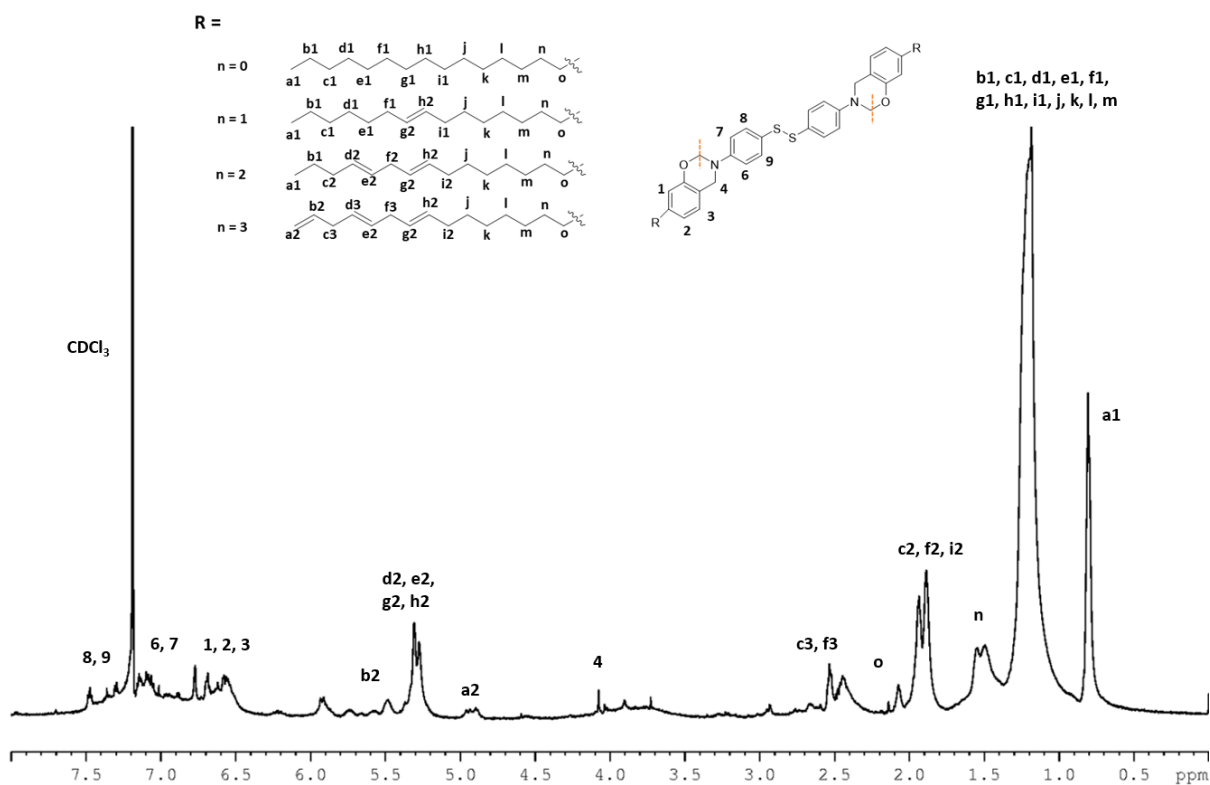
**Figure S6.** Rheology monitoring of the curing of CAR-4edan with a heating ramp of 20 °C/min from 50 °C to 170 °C, followed by isothermal measurement at 170 °C - Complex viscosity as a function of time.



**Figure S7.** FTIR spectrum of poly(CAR-4apds).

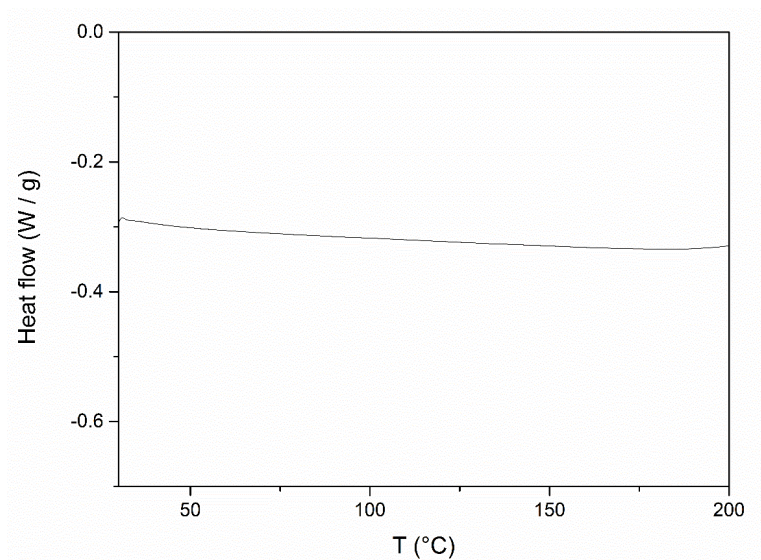


**Figure S8.** Rheology monitoring of the curing of 3PDP-4apds with a heating ramp of 20 °C/min from 50 °C to 170 °C, followed by isothermal measurement at 170 °C - Complex viscosity as a function of time.



**Figure S9.**  $^1\text{H}$  NMR of the soluble fraction of poly(CAR-4apds) after 48h swelling in DMF.

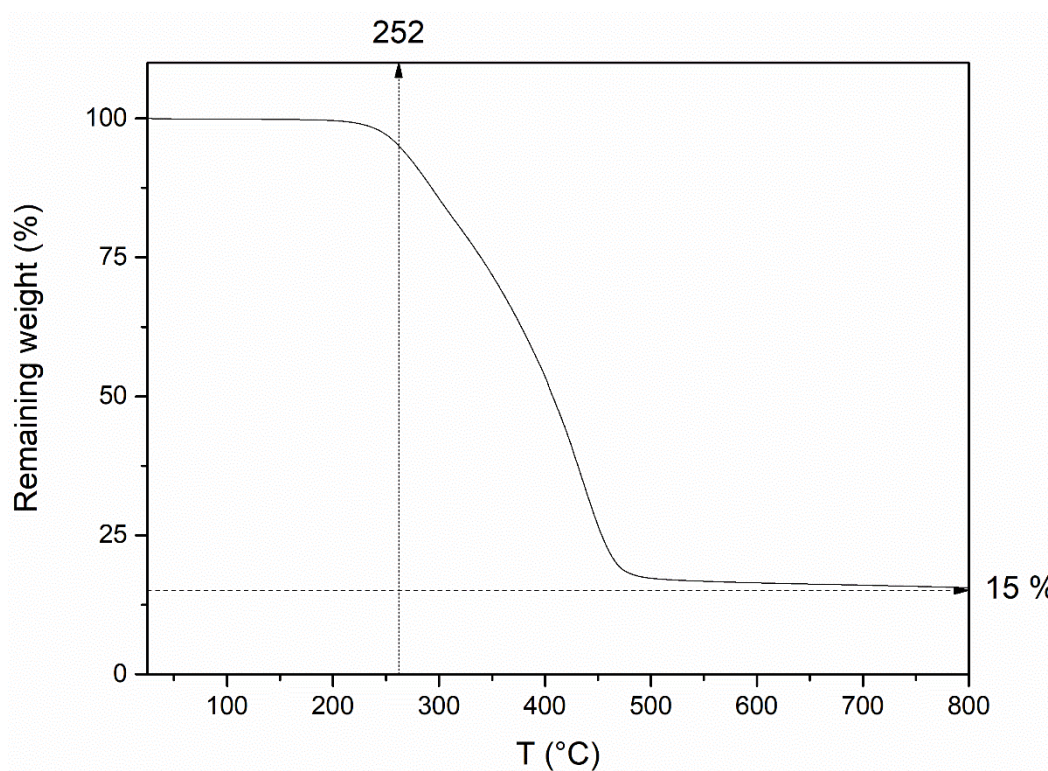




**Figure S10.** DSC thermograms (N<sub>2</sub>, 10 K min<sup>-1</sup>) of poly(CAR-4apds).

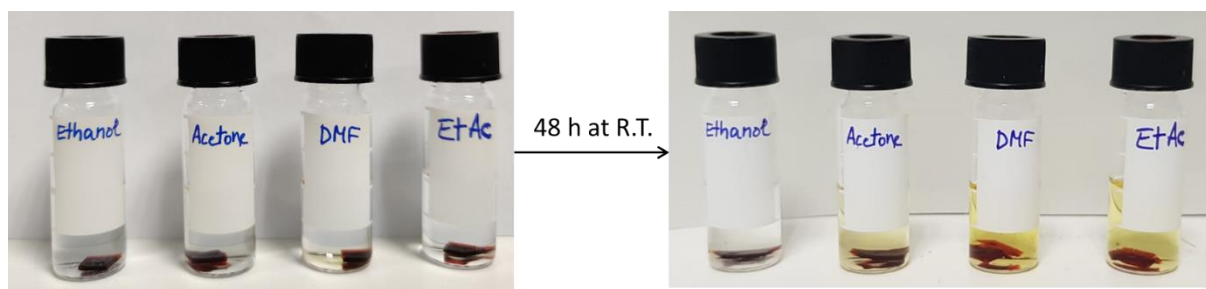
Crosslinking density ( $\nu$ ) was calculated using the modulus obtained from the rubbery plateau of the DMTA measurement at 373.15 K and the following equation:

$$\nu = \frac{E'}{3 \cdot R \cdot T} = \frac{1.94 \cdot 10^6}{3 \cdot 8.314 \cdot 373.15} = 208.4 \text{ mol/m}^3$$

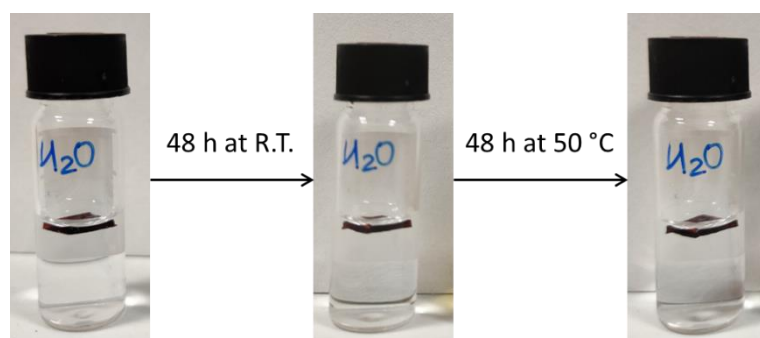


**Figure S11.** TGA (N<sub>2</sub>, 10 K min<sup>-1</sup>) of poly(CAR-4apds).

## Swelling properties



**Figure S12.** Swelling of poly(CAR-4apds) in ethanol, acetone, DMF, and EtAc after immediate immersion (left) and after 48h at 25 °C (right).



**Figure S13.** Swelling of poly(CAR-4apds) in neutral H<sub>2</sub>O, after immediate immersion (left), after 48h at 25 °C (middle) and after 48h at 50 °C (right).

## Stress relaxation

### Calculation of activation energy

Equation obtained from Arrhenius law:  $y = 7.75 x - 16.68$  ( $R^2 = 0.993$ )

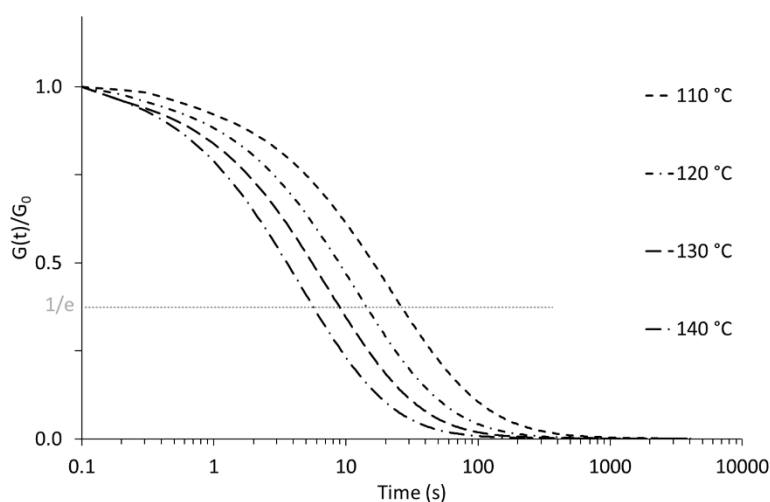
Which corresponds to:  $\ln(\tau^*) = 7.75 \cdot 1000/T - 16.68$

The Arrhenius law related to the activation energy is:  $\tau^* = \tau_0 \exp(E_a/RT)$  ( $R = 8.314$ )

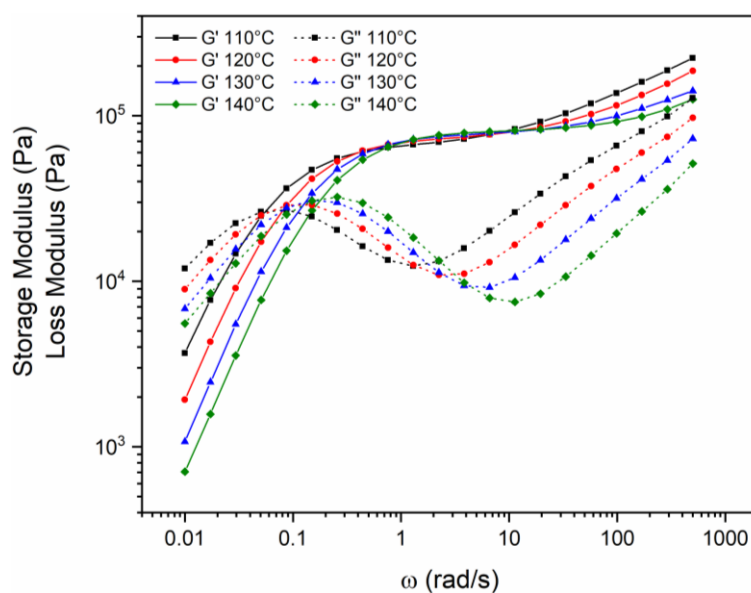
Therefore:  $\ln(\tau^*) = \ln(\tau_0) + E_a/RT$

Identifying this to the experimental equation:  $E_a/R = 7.75 \cdot 1000$

$E_a = 7.75 \cdot 1000 \cdot 8.314 = 64.5 \text{ kJ/mol}$



**Figure S14.** Stress relaxation curves for poly(CAR-4apds) between 110 °C and 140 °C



**Figure S15.** Frequency sweep curves (from 0.01 to 500 rad/s) for poly(CAR-4apds) between 110 and 140 °C.

#### Calculation of a topology freezing transition of vitrimers $T_v$

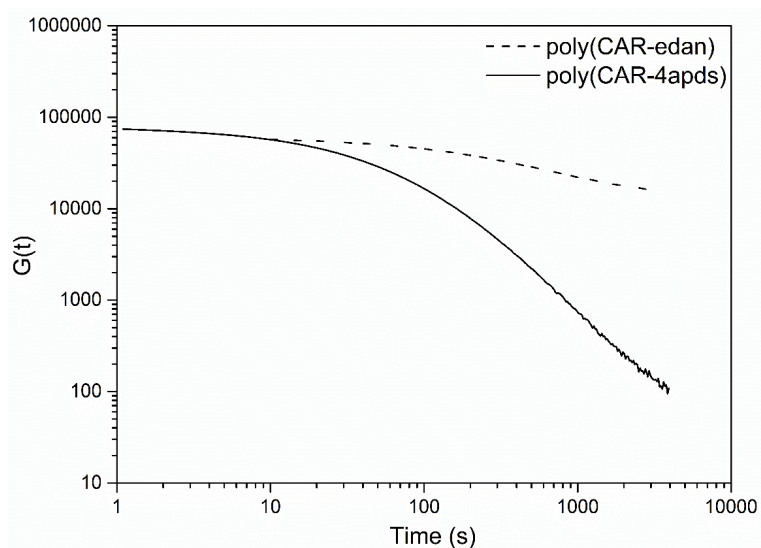
Equation obtained from Arrhenius law:  $y = 7.75 x - 16.68$  ( $R^2 = 0.993$ )

$T_v$  is calculated by extrapolation for a viscosity of  $\eta = 10^{12}$  Pa s

$$\tau^* = 3 \cdot 10^5 \text{ s} \rightarrow \ln(\tau^*) = 12.6$$

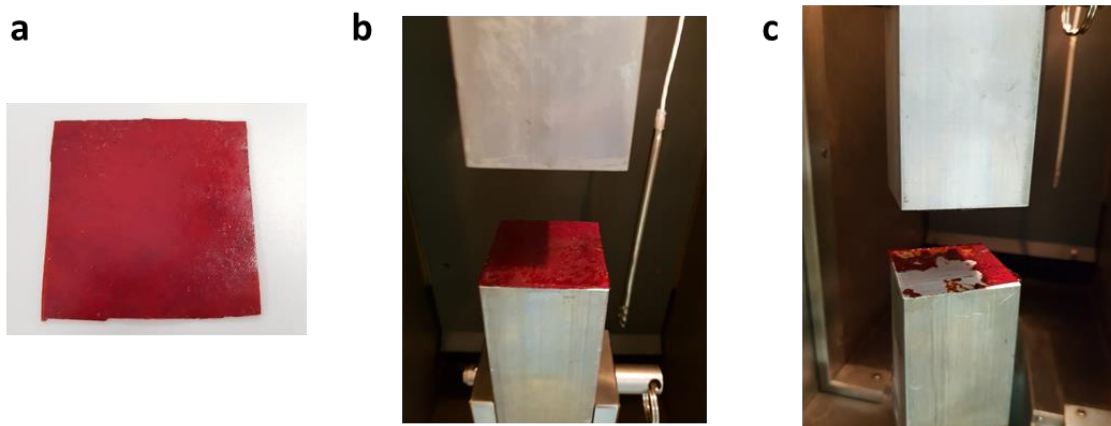
$$x = 1000/T = (\ln(\tau^*) + 16.68) / 7.75 = 3.78$$

$$T_v = 1000 / x = 264.55 \text{ K} \rightarrow T_v = -8.5 \text{ °C}$$

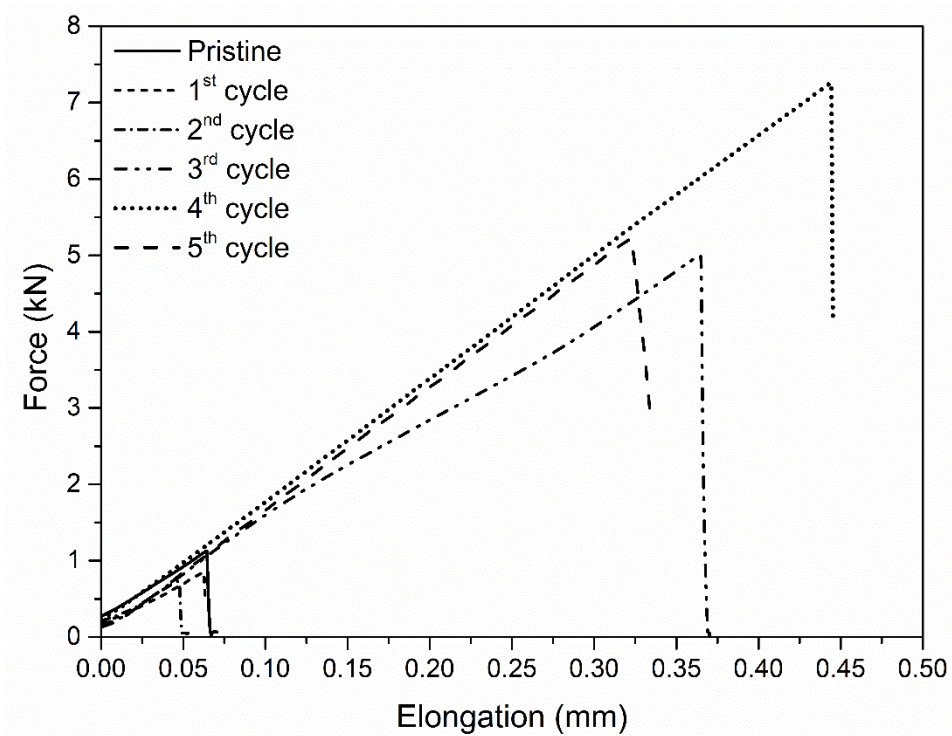


**Figure S16.** Stress relaxation curves for poly(CAR-4apds) and poly(CAR-edan) at 100 °C.

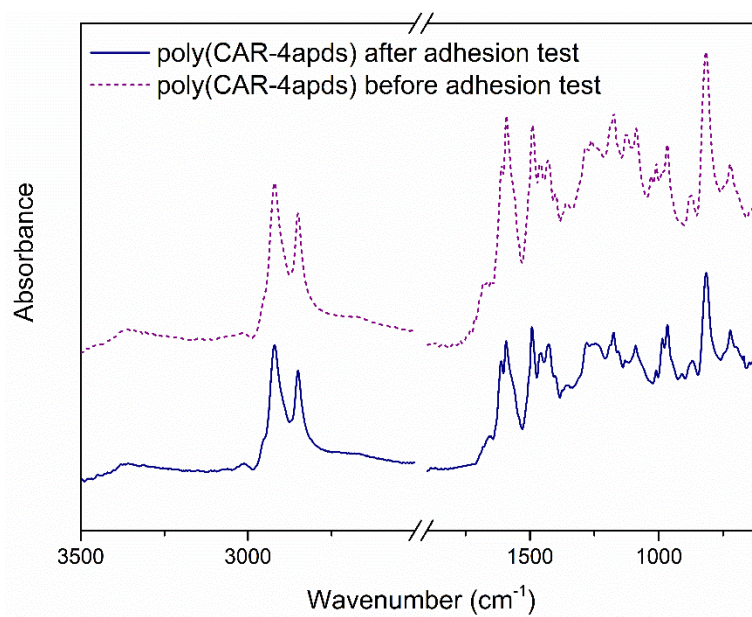
### Application as a self-healing adhesive



**Figure S17.** Pictures from tensile adhesion test a) Film of poly(CAR-4apds), b) Film sandwiched between two aluminum cubed, c) Adhesive fracture after tensile test.



**Figure S18.** Tensile adhesion force after five repair cycles (3 first curves pressure applied for repairing was 1 bar and the last 3 cycles  $P = 8$  bars).



**Figure S19.** FTIR spectra before and after adhesion test.