SUPPORTING INFORMATION

A direct comparison of the thermal reprocessing potential of associative and dissociative reversible bonds in thermosets

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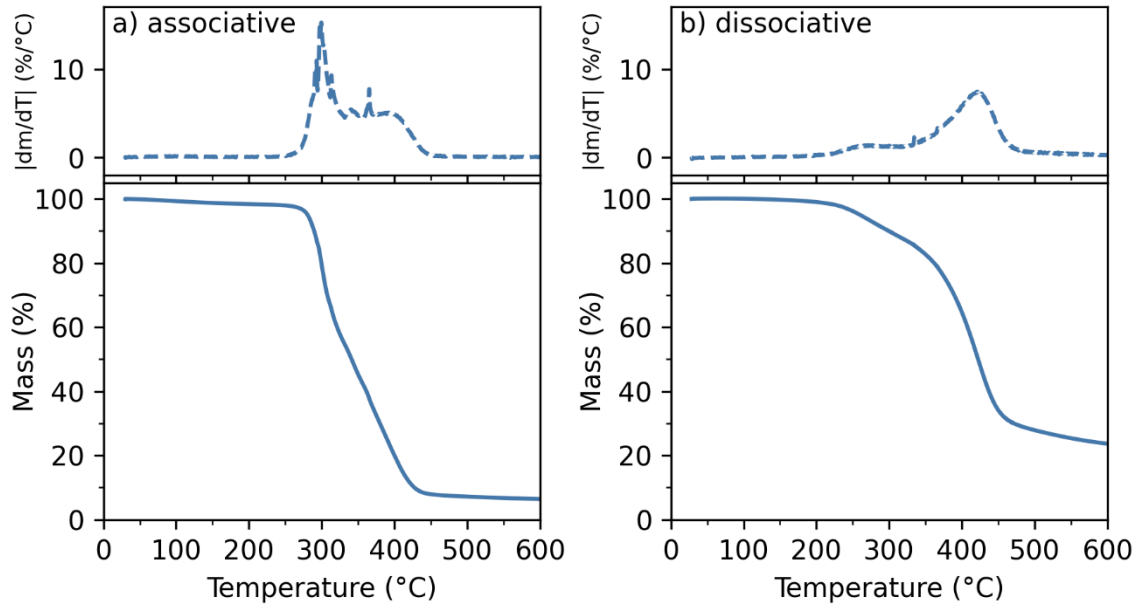

Figure S1: Mass loss and derivative mass loss as a function of temperature for a) the associative (vinylogous urethane) and b) the associative (Diels-Alder) thermoset. All TGA measurements were performed under a nitrogen atmosphere.

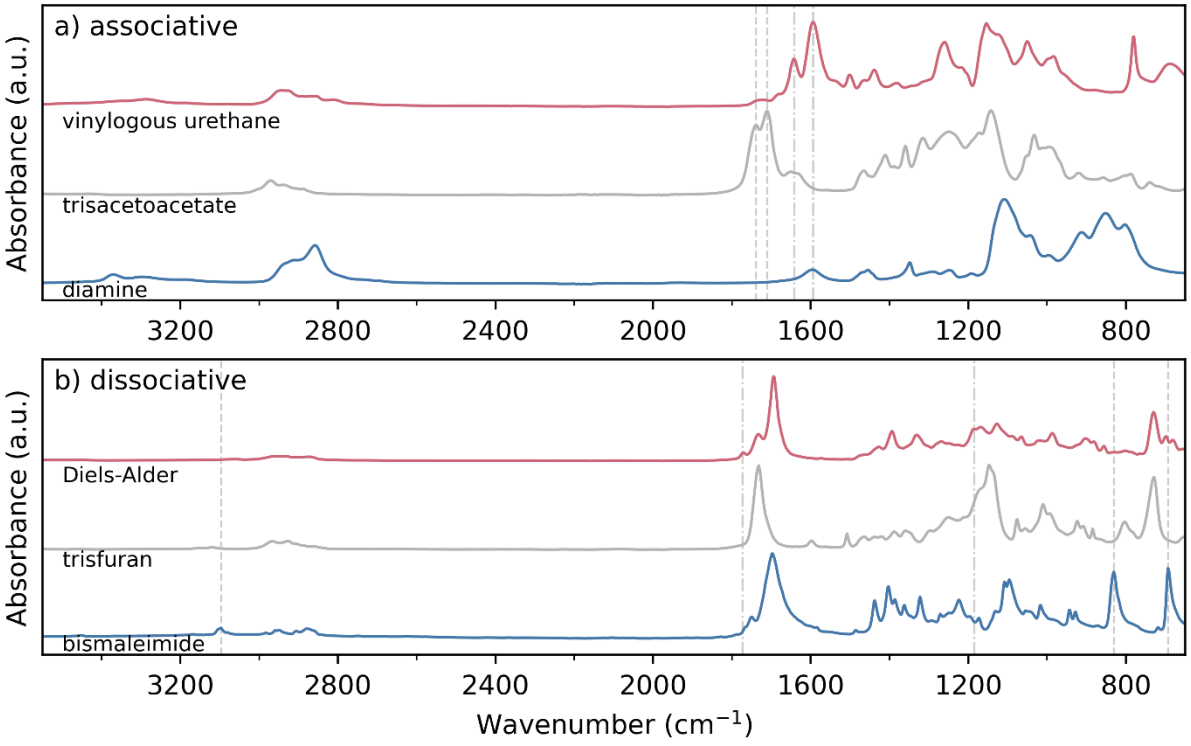

Figure S2: Full scale ATR-FTIR spectra of the monomers and the cured thermosets recorded at room temperature. a) Trisacetoacetate and the cured vinylogous urethane thermoset. b) Bismaleimide, trisfuran, and the cured DA thermoset

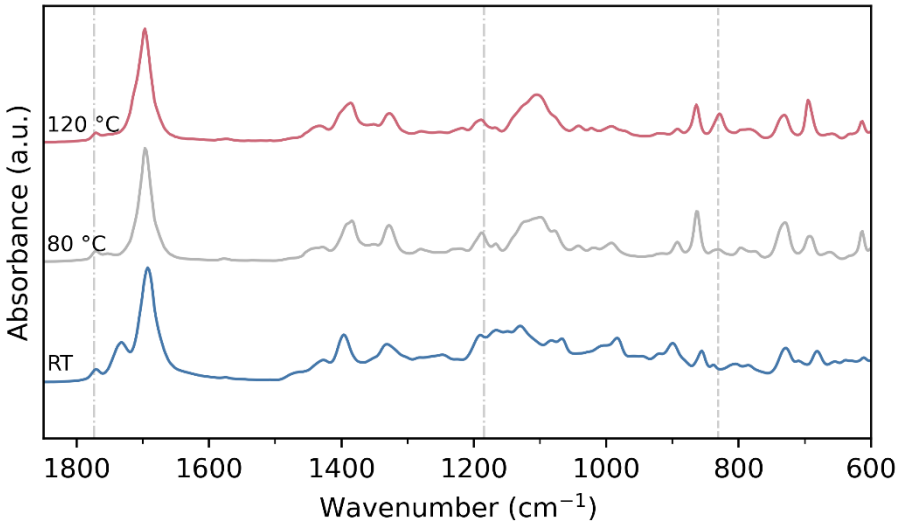

Figure S3: Hot stage FTIR measurements on the dissociative (Diels-Alder) thermoset at room temperature (RT), 80 °C and 120 °C. Note that the upper temperature limit of the hot stage FTIR is 120 °C, at this temperature there are still Diels-Alder adducts present (signals at 1174 and 1185 cm^{-1}).

Table S1: Enthalpy of the retro Diels-Alder reaction in the DA specimen for the endo and exo adduct determined from the DSC thermograms.

	ΔH_{endo} (J/g)	ΔH_{exo} (J/g)
1st heat treatment	3.41	3.16
2nd heat treatment	1.88	3.14
3rd heat treatment	1.64	3.24
4th heat treatment	1.64	3.15
5th heat treatment	1.62	3.17

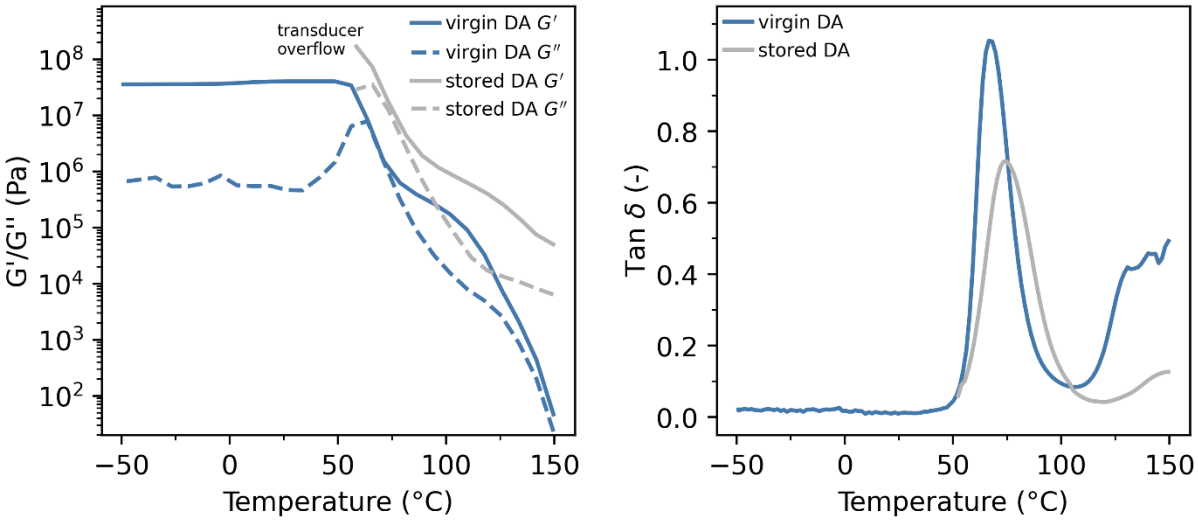

Figure S4: Temperature dependent dynamic behaviour of the dissociative DA polymer, in its' virgin – as synthesized – state (blue lines) and the same polymer after being stored for approximately 2 years at room temperature (grey lines). a) Storage (G') and loss (G") modulus, b) tan(δ).

Figure S4 shows the comparison of the temperature dependent dynamic behavior of the dissociative DA thermoset, as a function of storage time. The sample was re-tested under the same

conditions after approximately 2 years of being stored in a dark cupboard at room temperature. While the virgin sample exhibited a clear terminal flow with a steep G' slope in the high temperature region (above 120 °C), its' aged counterpart does no longer exhibit the terminal flow in the tested temperature region. The reduced mobility after sample storage is also visible in the Tg region, as the tanδ maximum value is reduced by approximately 30%. A minor shift to higer Tg is observed as well. It is likely that the sample has undergone irreversible crosslinking (the formation of poly(maleimide) resulting from self-polymerization) to such an extent that prevents it to exhibit the terminal flow again up to 150 °C.

To further quantify this effect, repeated FTIR scans were obtained (Figure S5). These results do not show any significant differences as function of the storage time, which could indicate that only a small percentage of the reversible bonds has irreversibly crosslinked. It therefore seems that, based on the observed reduced mobility in Figure S4, only a small amount of crosslinks is necessary to hamper the dynamic covalent response of these specfic thermoset materials.

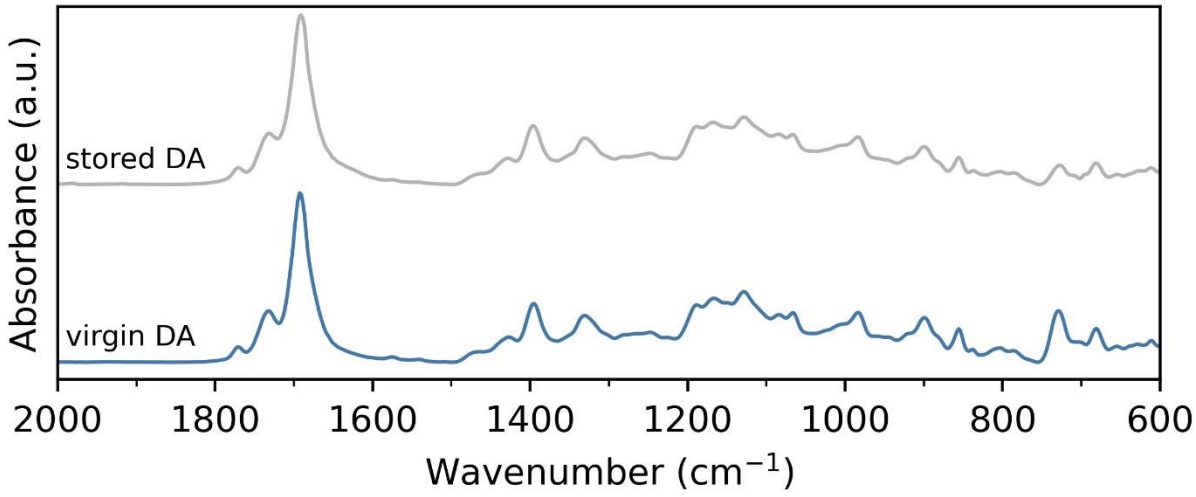

Figure S5: Full scale ATR-FTIR spectra of the cured dissociative (DA) thermosets recorded at room temperature, in its' virgin – as synthesized – state (blue line) and the same polymer after being stored for 2 approximately 2 years at room temperature (grey line).