Electronic Supplementary Material (ESI) for Green Chemistry.

# Re-Usable Thermally Reversible Crosslinked Adhesives from Robust Polyester and Poly(ester urethane) Diels-Alder Networks

Laxmisha M. Sridhar,[b] Murielle O. Oster,[b#] Donald E. Herr,[b≠] Jonathan B.D. Gregg,[a] James A. Wilson [a] and Andrew T. Slark [a*]

[a] *Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK*
[b] *Henkel Corporation, 1 Henkel Way, Rocky Hill, CT06067, USA*
[#] Present address: *Corbion Biomaterials, Arkelsedijk 46, 4206 AC Gorinchem, NL*
[≠]Present address: *Sartomer Americas, 502 Thomas Jones Way, Exton, PA19341, USA*

[*] To whom correspondence should be addressed, a.slark@sheffield.ac.uk

## Experimental

The following materials were all used as supplied. 1,3,5-benzenetricarbonyl chloride, triethylamine, furfuryl alcohol, dibutyltin dilaurate (DBTL) and anhydrous $MgSO_4$ were obtained from Sigma-Aldrich. 2-Hydroxyethylmaleimide was sourced from Shanghai Jinshan Pharmaceutical Co. Ltd. China. 4,4'-methylene-diphenyl diisocyanate (MDI, Desmodur 44M), isophorone diisocyanate (IPDI) trimer (Desmodur Z4470) and hexane diisocyanate (HDI) trimer (Desmodur N3300) were obtained from Covestro, Germany. Semi-crystalline polyester polyol Dynacoll 7360 (copolymer of 1,6-hexane diol and adipic acid) with $M_n$ = 3500 g.mol$^{-1}$ and amorphous copolyester polyol Dynacoll 7231 (copolymer of ethylene glycol, 1,6-hexane diol, neopentyl glycol, adipic acid, terephthalic acid and isophthalic acid) with $M_n$ = 3500 g.mol$^{-1}$ were provided by Evonik Industries, Germany. **M-1** is an aliphatic bismaleimide prepolymer provided by Henkel Corporation. **PUR** was also provided by Henkel UK as PF-9021, a moisture curing reactive hot melt adhesive used for a variety of industrial applications and utilized here as a reference for material property evaluations.

### Synthesis of multifunctional furan F-1

In a 3-necked flask equipped with a mechanical stirrer and nitrogen inlet 1,3,5-benzenetricarbonyl chloride (20.0 g, 75.3 mmol) was weighed in $CH_2Cl_2$ (200 mL). The mixture was cooled using an ice-water mixture to approximately 0 °C. Triethylamine (26.7 g, 263 mmol) was added and the mixture stirred for 15 minutes at the same temperature. Furfuryl alcohol (22.2 g, 226 mmol) was added dropwise using an addition funnel. The rate of addition was carefully controlled so that the reaction temperature did not rise above 20 °C. After the addition was complete, the reaction mixture was stirred further for two hours. TLC monitoring gave an indication about completion of the reaction. $CH_2Cl_2$ was evaporated under reduced pressure and 500 mL of ethyl acetate added to the mixture. The triethylamine salt was filtered and washed with ethyl acetate. The filtrate was washed three times with water (100 mL) to remove any amine salt and dried over anhydrous $MgSO_4$. Solvent evaporation gave **F-1** as a light brown colored solid.

### Synthesis of multifunctional furan F-2

In a 4-necked flask equipped with a mechanical stirrer, reflux condenser and nitrogen inlet, HDI trimer Desmodur N3300 (500 g, 2590 mmol isocyanate) was mixed with toluene (300 ml) and 4 drops of dibutyltin dilaurate and the mixture was stirred with a mechanical stirrer and heated to 85 °C in an oil bath. Furfuryl alcohol (254 g, 2592 mmol) was added dropwise with mechanical stirring and heated for 3 hours until infra-red spectroscopy indicated disappearance of the isocyanate band at 2200 $cm^{-1}$. Toluene was removed under vacuum using a rotary evaporator and residual solvent was evaporated using Kugelrohr distillation set up at 70 °C. The product was further dried in a vacuum oven overnight at 60 °C. This gave multifunctional furan **F-2** as an off-white liquid which solidified upon cooling to room temperature. For comparison, **F-2** was also synthesized in bulk using a similar procedure but without the need for solvent removal.

### Synthesis of multifunctional furan F-3

In a 4-necked flask equipped with a mechanical stirrer, reflux condenser and nitrogen inlet 4 drops of dibutyltin dilaurate was added to 142.87 g of IPDI trimer (Desmodur Z 4470) supplied as a 70% solution in butyl acetate (397 mmol isocyanate) and the mixture was stirred with a mechanical stirrer and heated at 85 °C using an oil bath. Furfuryl alcohol (40.2g, 410 mmol) was added dropwise with mechanical stirring and heated for 4 hours until infra-red spectroscopy indicated disappearance of the isocyanate band at 2200 $cm^{-1}$. After cooling to room temperature, the butyl acetate was removed under vacuum in a rotary evaporator and residual solvent was evaporated using Kugelrohr distillation set up at 70 °C. The product was further dried in a vacuum oven overnight at 60 °C. This gave multifunctional furan **F-3** as an off-white powder.

### Synthesis of bismaleimide prepolymers M-2 and M-3

In a 4-necked flask equipped with a mechanical stirrer Dynacoll 7360 (350 g, 100 mmol) was weighed and heated to 120 °C with vacuum applied for one hour. MDI was added (50 g, 200 mmol) and allowed to react with the hydroxyl groups for one hour under vacuum. The NCO terminated prepolymer produced was heated to 120 °C with a mechanical stirrer and 2-hydroxyethylmaleimide (28.2 g, 200 mmol) was added in batches. The IR showed disappearance of the isocyanate band in about 1.5 hours.

The prepolymeric **M-2** was obtained in quantitative yield as a white solid. Using a similar method, **M-3** was obtained using Dynacoll 7231 as the polyester polyol for reaction with MDI to prepare an isocyanate terminated prepolymer which was further reacted with 2-hydroxyethyl maleimide. The prepolymeric **M-3** was obtained in quantitative yield as an off-white amorphous material.

### Networks *via* copolymerization of multifunctional furans and bifunctional maleimides

Crosslinked network compositions **DA-1**, **DA-2**, **DA-3** and **DA-4** were made by combining different types of multifunctional furan and bifunctional maleimide using a stoichiometry of 1:1 maleimide:furan functional groups. Specific bifunctional maleimides and multifunctional furans were weighed in a glass container (typically 20 g) and heated in an oven at 120-150 °C for 30 minutes with occasional manual stirring until a homogeneous mixture was obtained. Materials were coated directly onto silicone release paper to produce films with a thickness of 250 μm using a metal applicator and allowed to copolymerize at room temperature.

### Characterization

$^1$H NMR spectroscopy measurements of monomers and prepolymers were recorded on a Bruker AV or AVIIIHD 400 MHz spectrometer at room temperature with the sample fully dissolved in deuterated chloroform ($CDCl_3$). Chemical shifts were recorded in parts per million (ppm) relative to a reference peak of chloroform solvent at $\delta$ = 7.26 ppm. IR measurements were recorded using a PerkinElmer FT-Infra-red spectrometer equipped with a UATR Two accessory. Eight scans were taken in the range of 4000 – 500 cm$^{-1}$. Liquid samples were simply spread over the crystal, whereas for solid prepolymers (ground to a powder) and cured films the pressure arm was applied to ensure intimate contact between the sample and the prism. Gel permeation chromatography (GPC) was performed using an Agilent Technologies 1260 Infinity II system equipped with a refractive index detector. Two Agilent PL gel 5 µm Mixed-C columns and a guard column were connected in series and maintained at 35 °C. HPLC grade chloroform containing 0.25 %w/w triethylamine ($NEt_3$) was used as the eluent and the flow rate was set at 1.0 mL.min$^{-1}$. The refractive index detector was used for calculation of molecular weights and dispersity by calibration using a series of near-monodisperse poly(methyl methacrylate) standards. Differential scanning calorimetry (DSC) was performed using a TA instruments Discovery DSC 25. 5-8 mg of sample was accurately weighed and loaded into a $T_{zero}$ aluminum pan, with heating and cooling ramps conducted under a nitrogen atmosphere at a standard rate of 10 °C.min$^{-1}$. The effect of heating rate on transitions was also investigated by varying the heating rate at 1, 2, 5 and 10 °C.min$^{-1}$. Dynamic mechanical thermal analysis (DMTA) was generated on 250 μm films of the crosslinked networks using a TA Instruments Q800 DMA with tensile clamps. Sample dimensions were typically length 15.0 mm, width 5.0 mm and thickness 0.25 mm. Samples were evaluated between -100 °C and 110 °C at a rate of 5 °C.min$^{-1}$. A frequency of 1 Hz and strain of 0.1% were used. Melt viscosity was measured using a Brookfield Viscometer model RVDV-1 with a Model 74R temperature controller and Thermosel unit using spindle no. 27. 12 g of preheated polymer was weighed into an aluminum viscometer tube. The tube was inserted into the Thermosel unit and allowed to equilibrate at the required temperature for 30 minutes. The melt viscosity was then measured regularly over a period of 6 hours while holding the material at constant temperature. Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA by PerkinElmer. Samples of approximately 5 mg were heated to 400 °C at a rate of 10 °C/ min under a nitrogen atmosphere.

**Mechanical Properties, Adhesion and Creep**

A film of polymer 250 μm thick was cast onto silicone paper at 120-150 °C using a metal coating block and left for 7 days to cure at ambient temperature. After that time, 70 mm length of cured polymer film were cut from the sample. Pieces of beechwood (25 × 25 mm) were applied to the ends of the film using a moisture curing polyurethane adhesive. This provided better grip with the clamps of the tensiometer preventing film slippage. The samples were tested after being conditioned for 7 days at 23 °C, 50 %RH. The tensile properties of the materials were measured using an Instron tensiometer with a 100 N load cell and a crosshead speed of 100 mm.min$^{-1}$. The modulus, strength at break and elongation to break were determined by evaluating 5 samples for each material.

Different substrates were evaluated with thickness 1.5-2.0 mm and surface area 25 × 100 mm. (*Wood)* 250 μm films of molten polymer were applied to an area 25 × 25 mm at the end of three beechwood coupons using a preheated coating block. A second beechwood coupon was immediately placed on top of each coated substrate so that the overlap area of the joint was 25 × 25 mm. Pressure was applied using metal clips. The bonded joints were then evaluated in the following ways:

1. Strength as a function of time after forming the joint.
2. Evaluation of the joints after 7 days at 23 °C /50 %RH to allow cure of the adhesive:
    a. Strength at ambient temperature.
    b. Strength at 80 °C using an air circulated oven.

The shear strengths were measured using a JJ Lloyd tensiometer, with a load cell of 10 kN and a crosshead speed of 100 $mm.min^{-1}$. The shear strength was determined from an average of three bonded samples.

(Polycarbonate) Polycarbonate coupons (Rocholl GmbH) were wiped with isopropanol before use to remove contaminants. Lap shear joints were prepared in the same way as the wood and evaluated at ambient temperature after conditioning for 7 days at 23 °C /50 %RH to allow cure of the adhesive. The shear strengths were measured in the same way as 2a) above.

(Aluminum) Aluminum test pieces were grit blasted and cleaned with acetone. For the Diels-Alder networks cured films 250 $\mu$m thick were cut to 12.5 × 25 mm. Lap shear joints were assembled carefully applying the film between Aluminum test pieces using glass bead spacers and an overlap of 12.5 mm, applying light pressure with a Hoffman clamp. The materials were placed in an oven for 1 hour at 125 °C for **DA-1** and 150 °C for **DA-4** to thermally reverse the networks into a melt. Bonded samples were then allowed to cure for 8-10 days at 23 °C / 50 %RH before measurement. The lap shear strength was determined from an average of four bonded samples using an Instron tensiometer with a load cell of 30 kN and a displacement speed of 1.27 $mm.min^{-1}$. The **PUR** reference was evaluated in the same way, except it was applied as a liquid at 120 °C since film samples could not be re-melted due to the irreversible cure.

Creep resistance was evaluated using lap shear joints on beechwood, made in the same way as above. After allowing to cure for 7 days at ambient temperature, the bonded samples were arranged vertically with a 1 Kg load suspended from each bonded joint in an oven at a fixed temperature for 24 hours. Materials were evaluated between 70-110 °C at 10 °C intervals with two joints measured for each sample in order to determine the temperature at which the bonded joints failed.

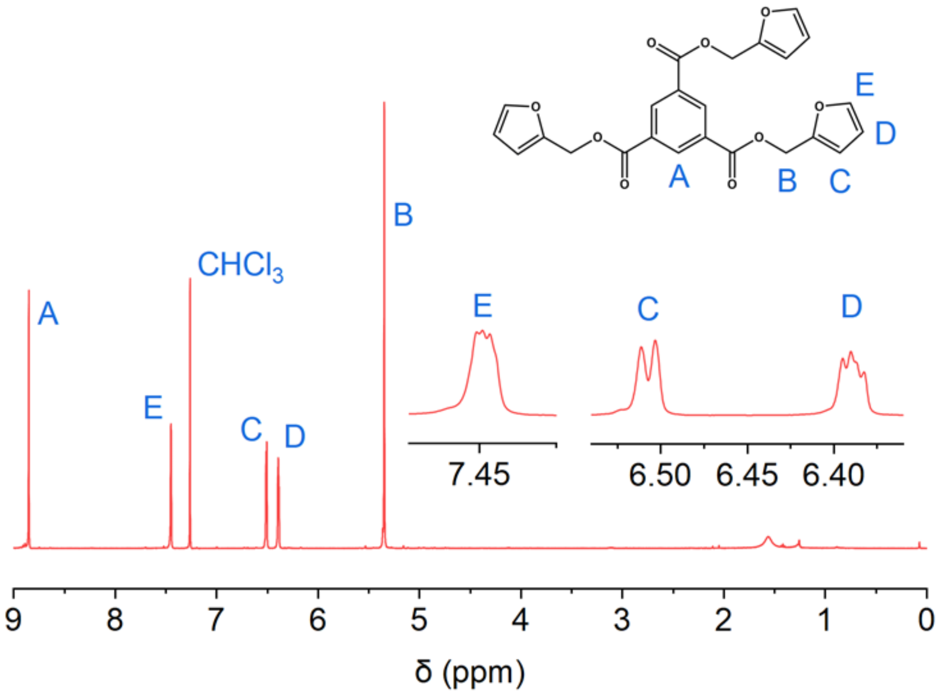


**Figure S1** $^1$H NMR spectrum of trifunctional furan **F-1** (400 MHz, $CDCl_3$, 298 K).

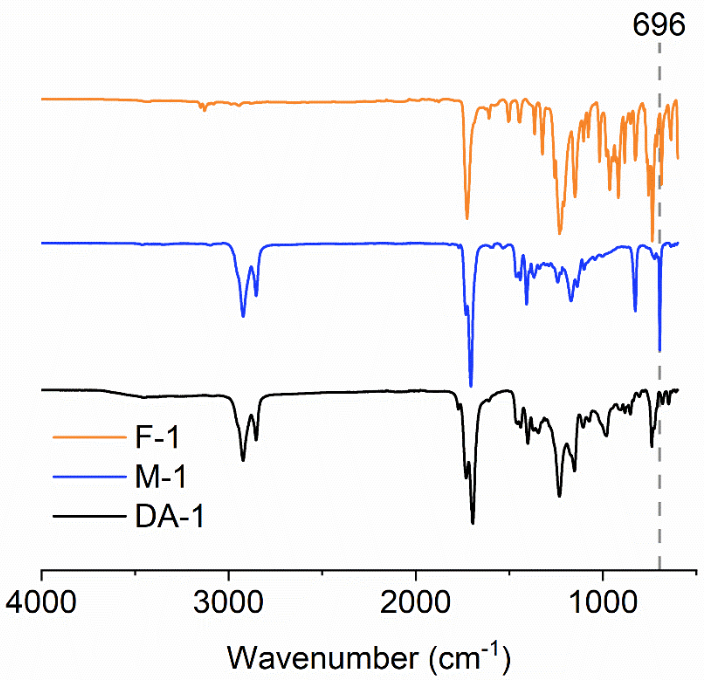


**Figure S2** IR spectra of **F-1**, **M-1** and **DA-1,** highlighting the absorbance at 696 cm$^{-1}$ due to maleimide C-H stretching.

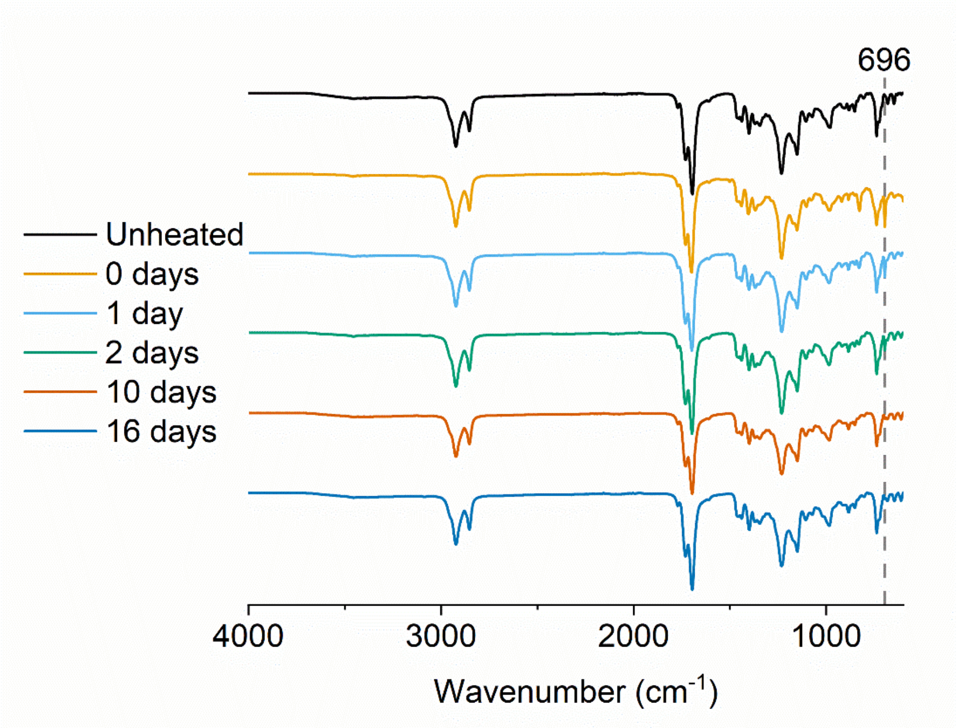


**Figure S3** IR spectrum from 400-4000 cm$^{-1}$ of **DA-1** before heating and over time at ambient temperature post-deposition.

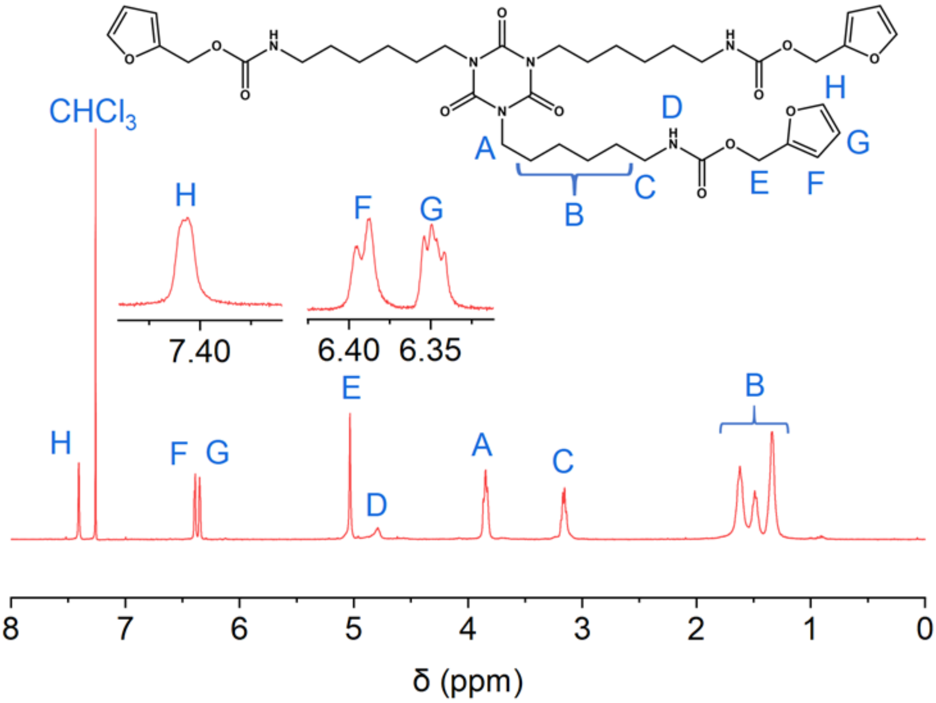


**Figure S4** $^1$H NMR spectrum of polyfunctional furan **F-2** (400 MHz, CDCl$_3$, 298 K).

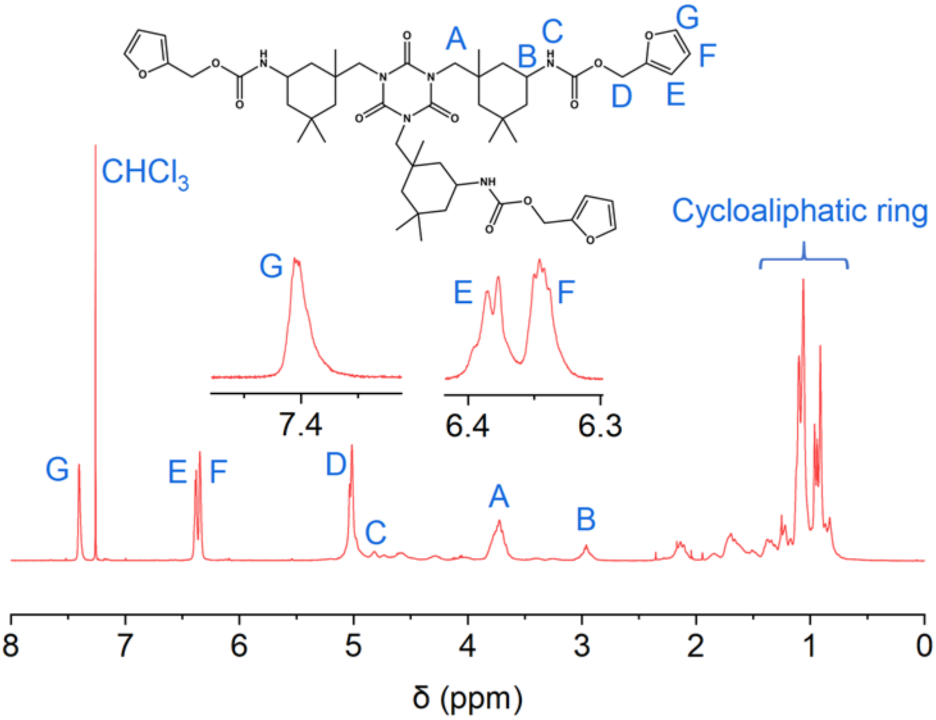


**Figure S5** $^1$H NMR spectrum of polyfunctional furan **F-3** (400 MHz, CDCl$_3$, 298 K).

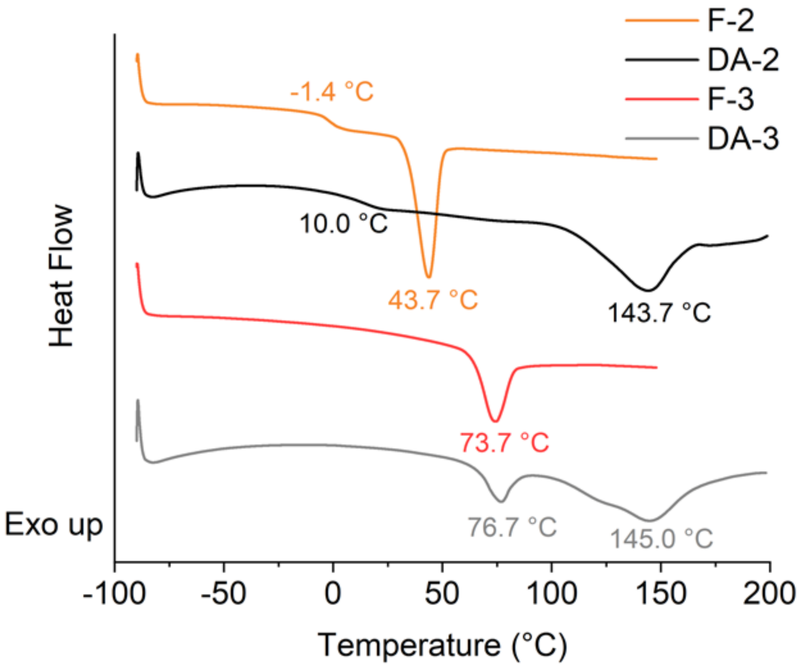


**Figure S6** DSC thermograms of **F-2**, **F-3**, **DA-2** and **DA-3** (first heating cycle).

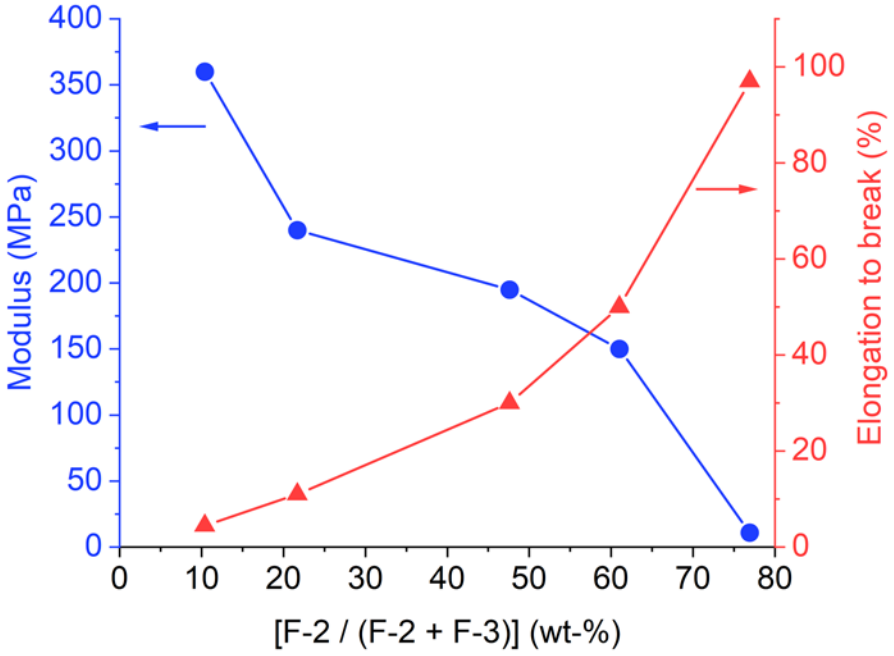


**Figure S7** The variation of film mechanical properties of networks combining **M-1** with mixtures of polyfunctional furans **F-2** and **F-3**.

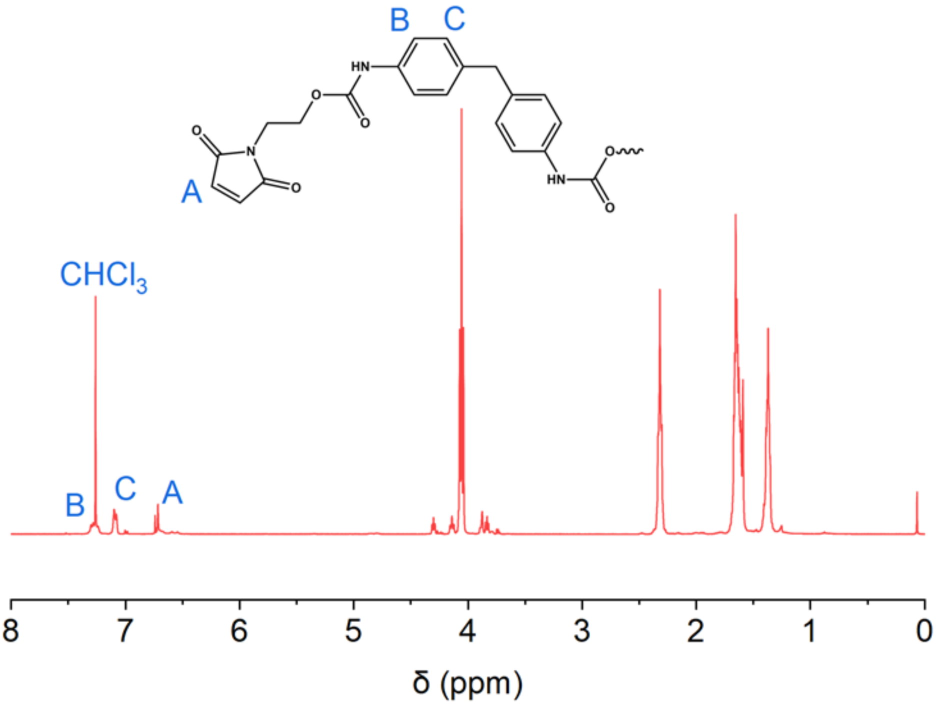


**Figure S8** $^1$H NMR spectrum of maleimide-functionalised polyester **M-2** (400 MHz, CDCl$_3$, 298 K).

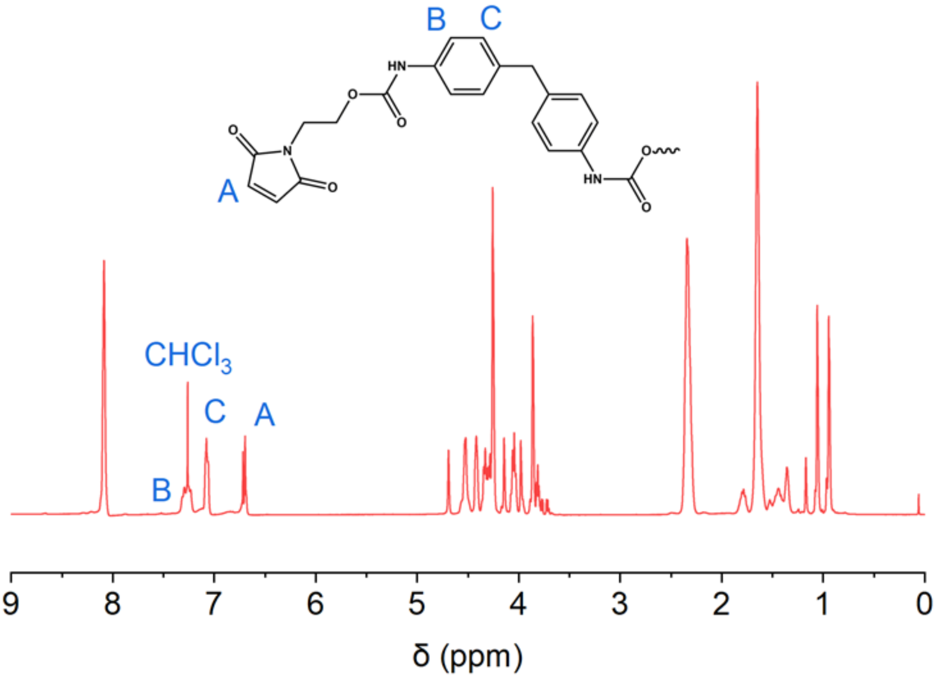
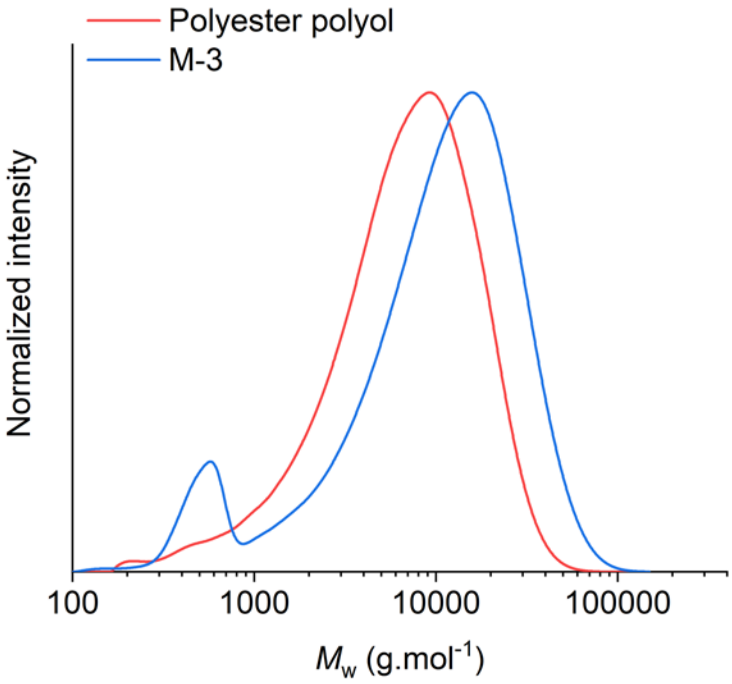


**Figure S9** $^1$H NMR spectrum of maleimide-functionalised polyester **M-3** (400 MHz, $CDCl_3$, 298 K).



| Material | $M_n$ (g.mol$^{-1}$) | $M_w$ (g.mol$^{-1}$) | $M_w/M_n$ |
|---|---|---|---|
| Dynacoll 7231 | 3625 | 8760 | 2.4 |
| **M-3** | 7120 | 15015 | 2.1 |
| Dynacoll 7360 | 8430 | 16325 | 1.9 |
| **M-2** | 10475 | 25455 | 2.4 |

**Figure S10** GPC of maleimide terminated prepolymers compared to corresponding polyester polyols, showing typical chromatograms and apparent molecular weights.

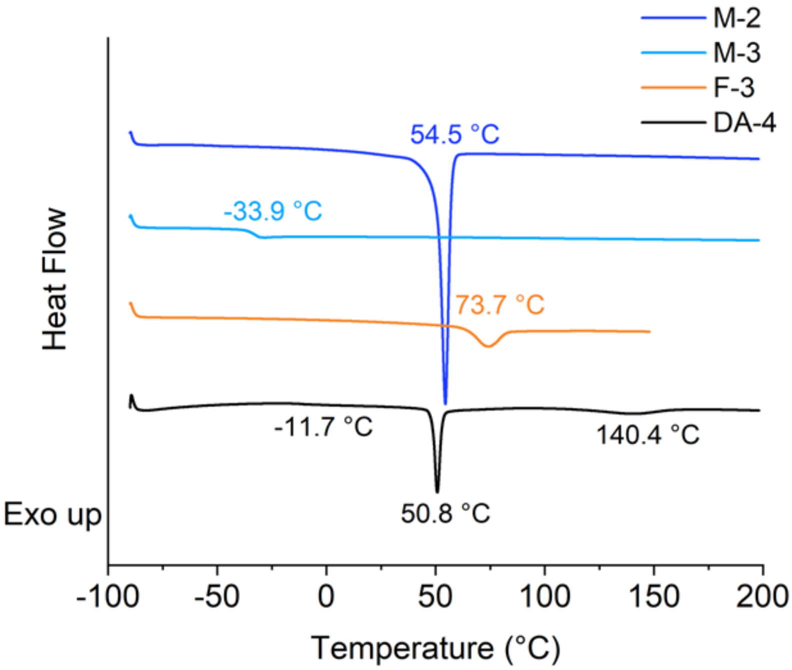


**Figure S11** DSC thermograms of **M-2**, **M-3**, **F-3** and network **DA-4** (first heating cycle).

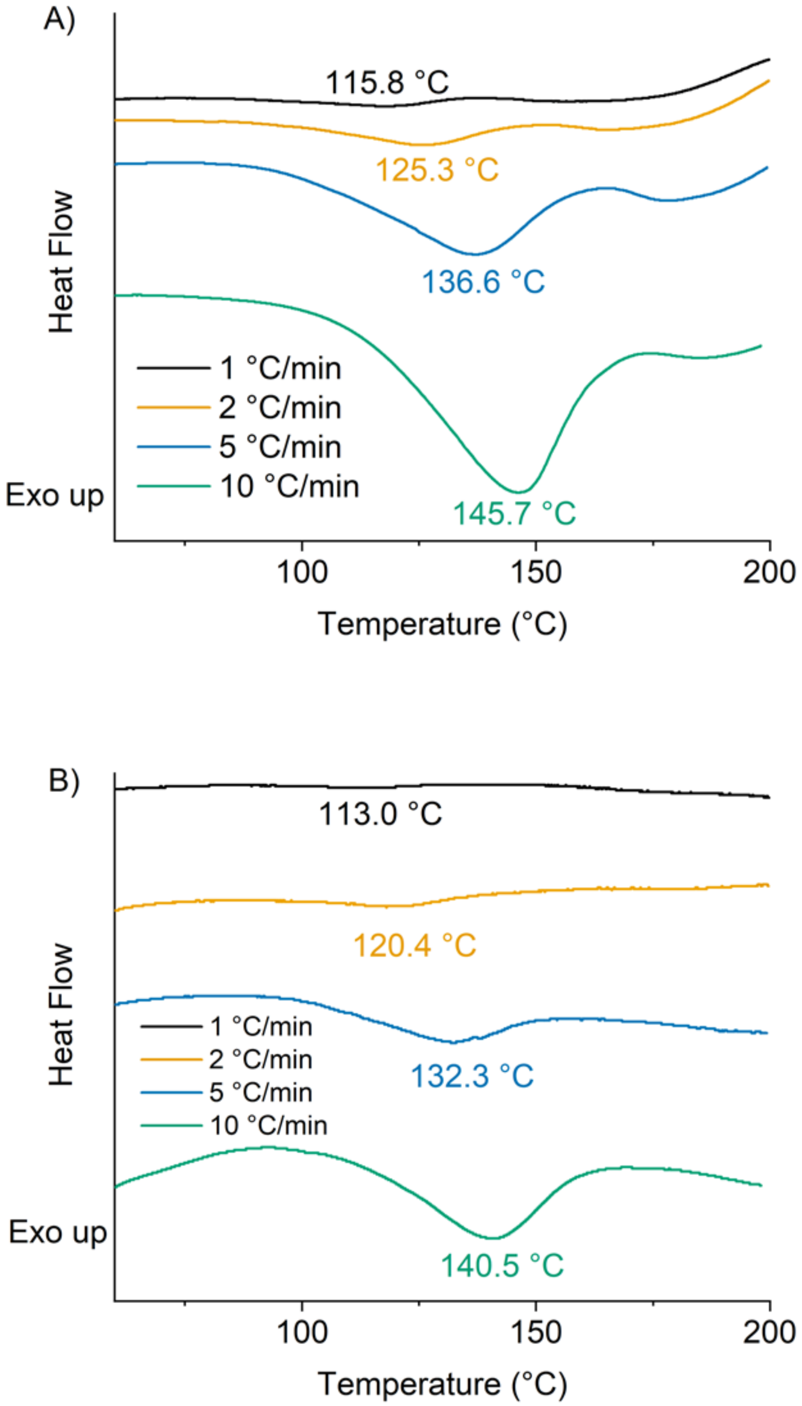


**Figure S12** Comparison of DSC thermograms using various heating rates (first heating curves) for (A) **DA-1** and (B) **DA-4.**

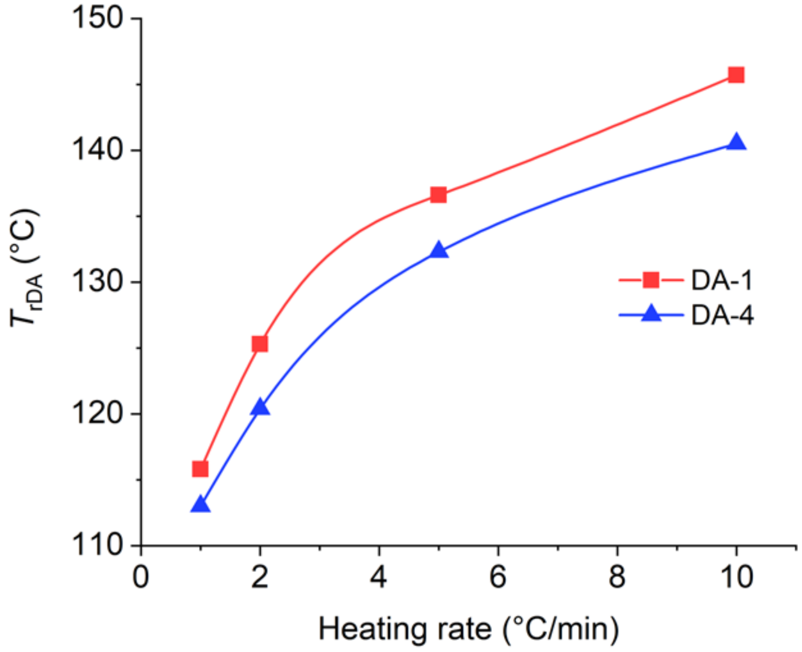


**Figure S13** The effect of DSC heating rate on the peak endotherm attributed to retro Diels-Alder for **DA-1** and **DA-4**.

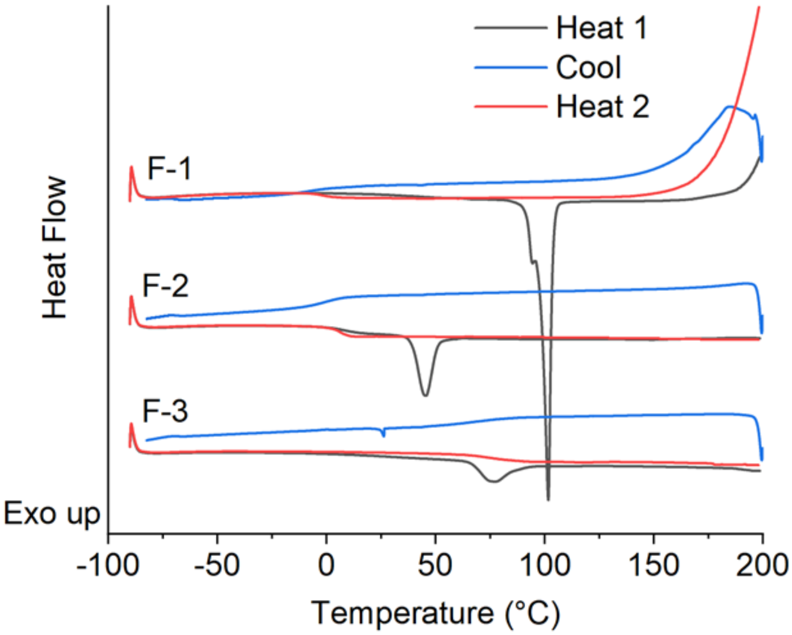


**Figure S14** DSC thermograms of **F-1**, **F-2** and **F-3** showing first heating, cooling and second heating. The materials are crystalline in the first heating but amorphous during the second heating since there is insufficient time for crystallisation to occur during the DSC experiment.

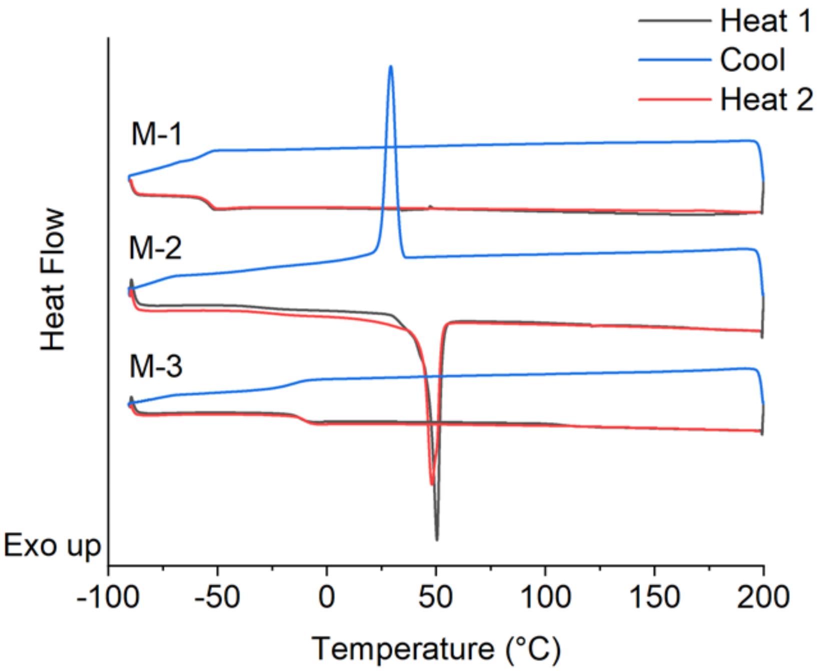


**Figure S15** DSC thermograms of **M-1**, **M-2** and **M-3** showing first heating, cooling and second heating. The thermograms of amorphous **M-1** and **M-3** are identical in the first and second heating. **M-2** is semi-crystalline and crystallizes during cooling.

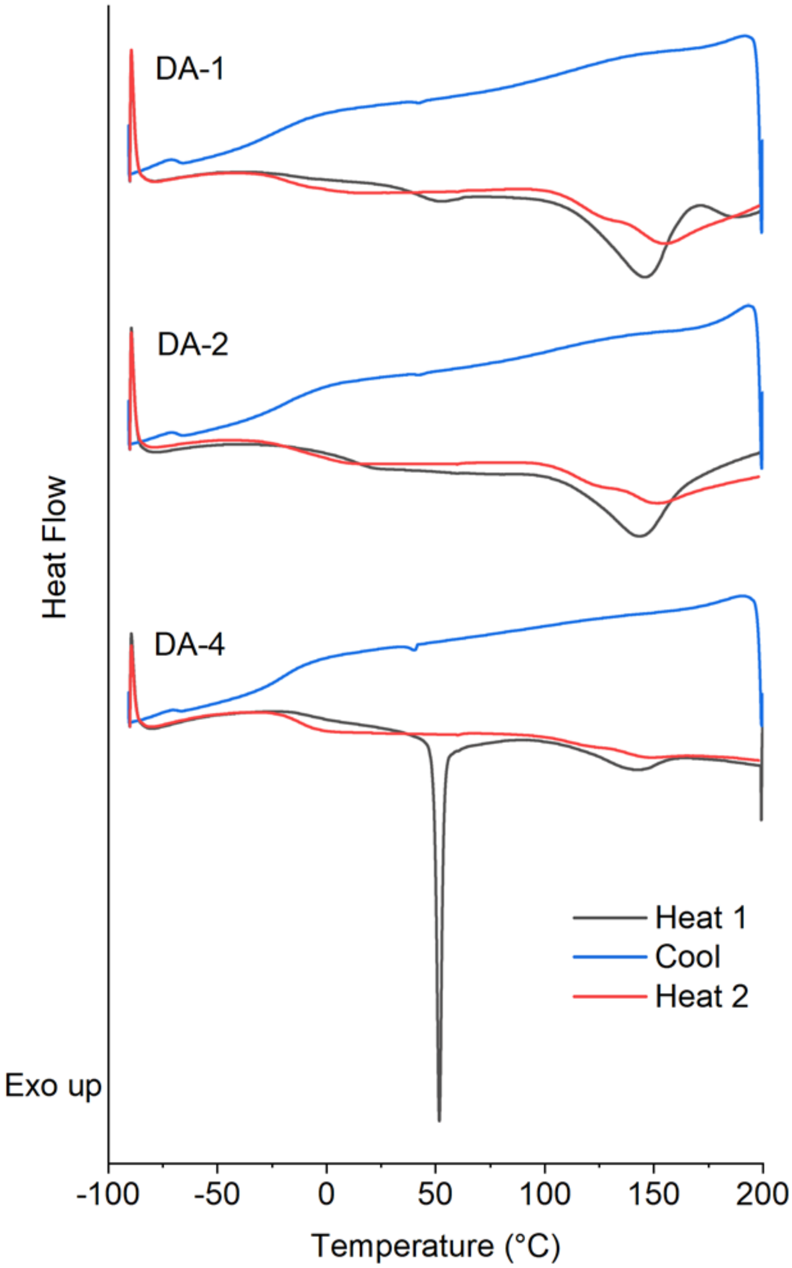


**Figure S16** DSC thermograms of **DA-1**, **DA-2** and **DA-4** showing first heating, cooling and second heating. Materials prepared and analysed for the first heating run were melt applied as coatings and cured at ambient temperature, replicating practical application. During the second heating runs (red) the overall enthalpy changes above 100 °C are lower in each case and corresponding $T_g$'s are also lower, since the networks are only able to partly reform during the timescale of the DSC experiment. Also, there is insufficient time for crystallisation to occur for **DA-4** during cooling and subsequently there is no melting point in the second heating run.

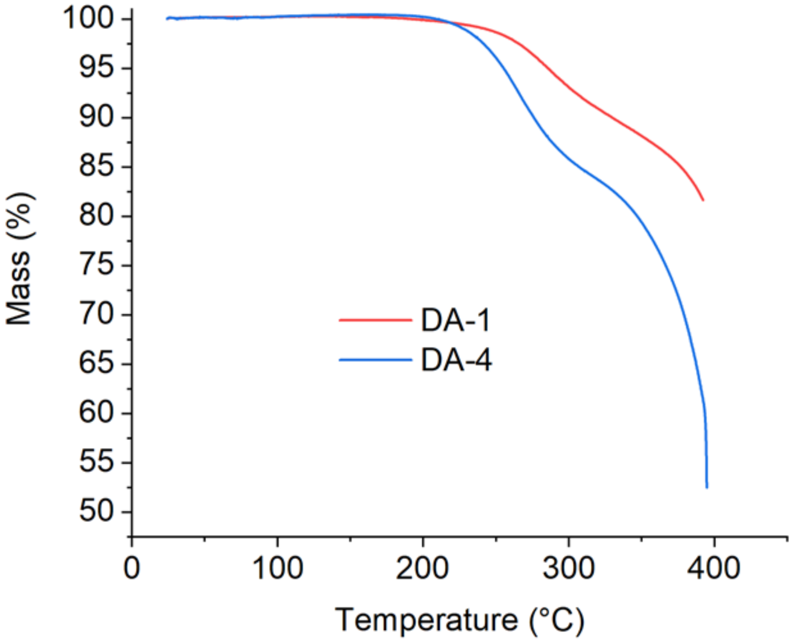


**Figure S17** TGA thermograms of **DA-1** and **DA-4**, demonstrating that the materials are thermally stable to 200 $^{o}$C without any weight loss.

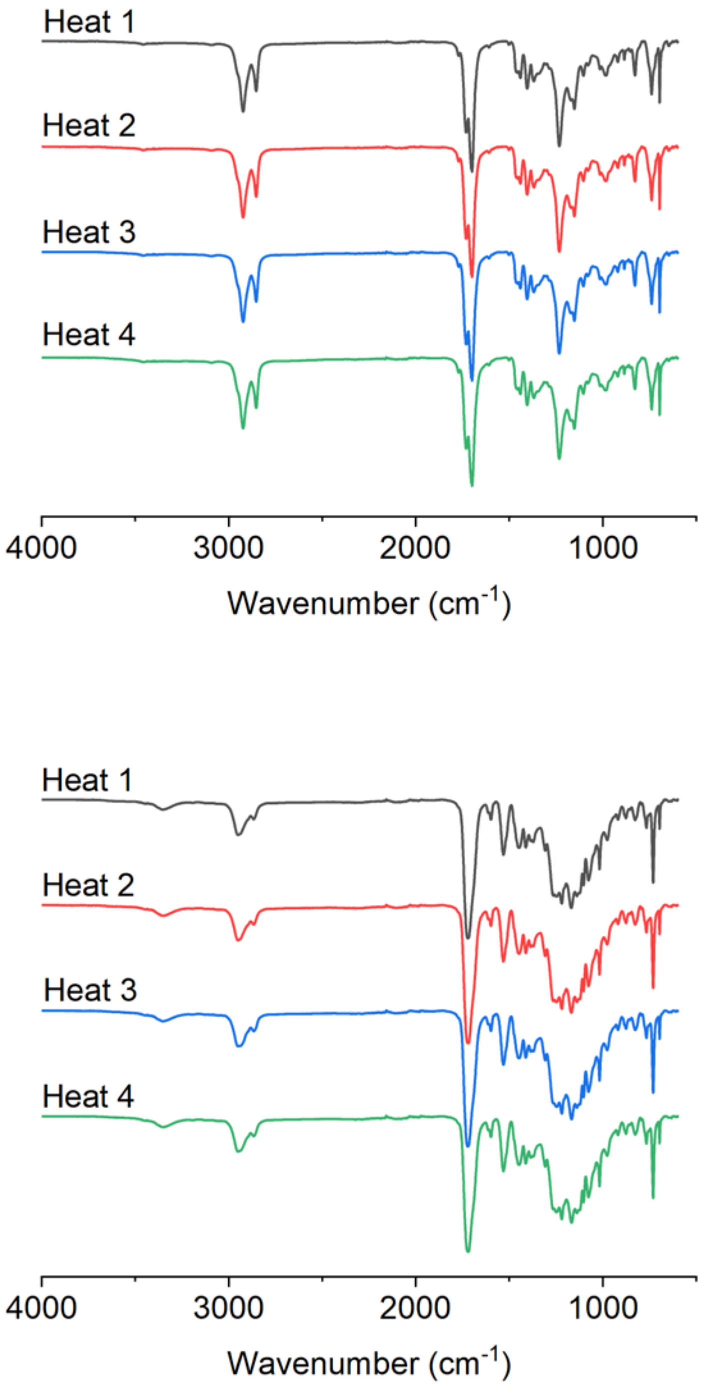


**Figure S18** IR spectra of **DA-1** (top) and **DA-4** (bottom) during recycling. Each material is heated for 1 hour at 150 °C to dissociate the network and allowed to cure for 7 days at room temperature before reheating with the overall process repeated four times. The spectra are taken immediately after heating at 150 °C for 1 hour each time.

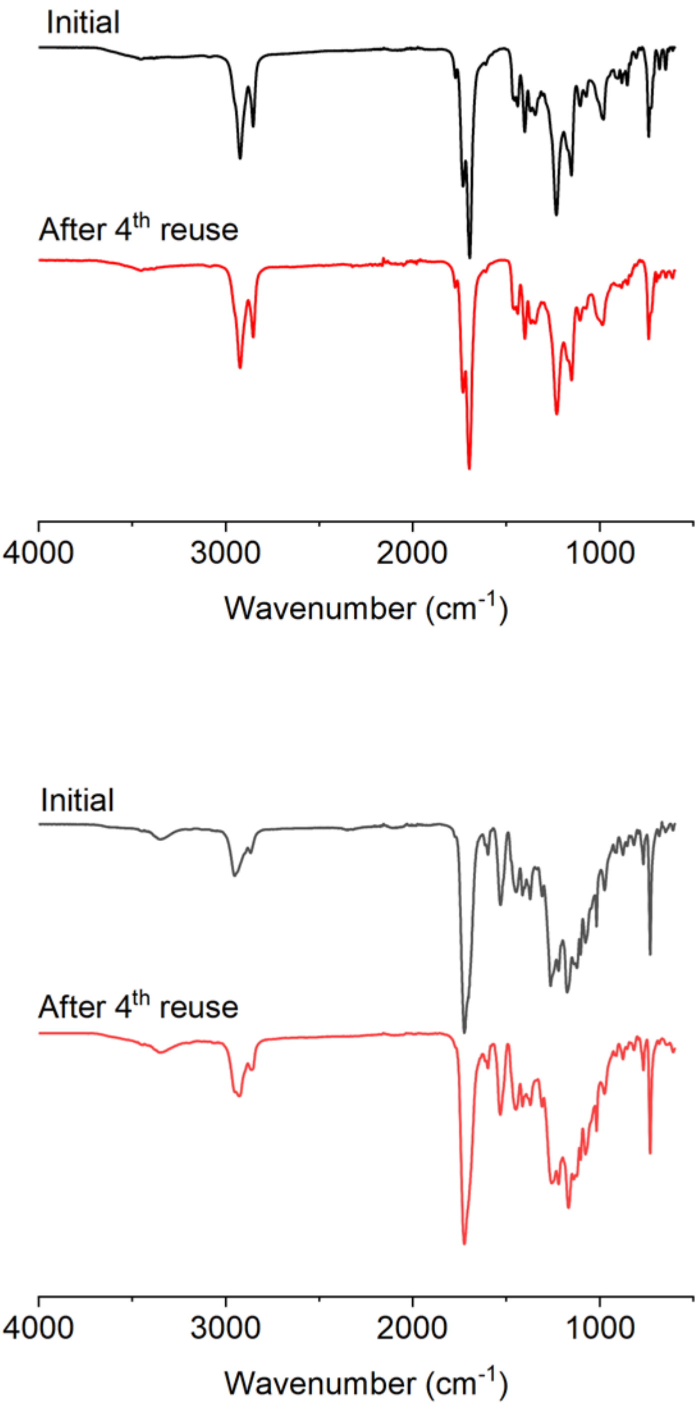


**Figure S19** The effect of recycling on the IR spectra of **DA-1** (top) and **DA-4** (bottom). “Initial” spectra (black) are for melt applied films cured at ambient temperature before being used as adhesives. “After 4th reuse” (red) are the spectra of cured adhesives remaining on the aluminium substrates (shown in Fig. 8C) after repeated bonding, curing and mechanical separation.

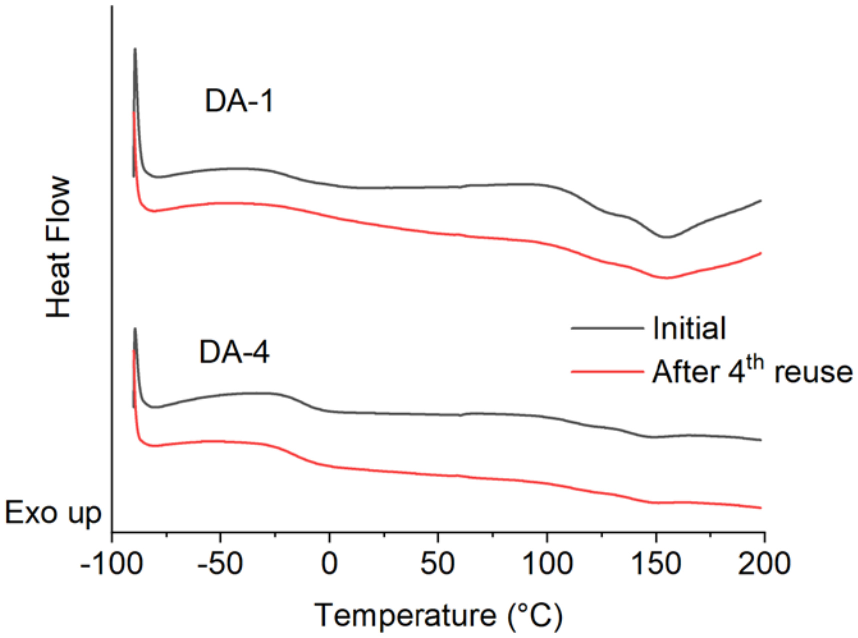


**Figure S20** The effect of recycling on the DSC thermograms (2nd heating) of **DA-1** (top) and **DA-4** (bottom). "Initial" thermograms (black) are for melt applied films cured at ambient temperature before being used as adhesives. "After 4th reuse" (red) are for cured adhesives remaining on the aluminium substrates (shown in Fig. 8C) after repeated bonding, curing and mechanical separation.