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Supporting Information for

Synergistic Reinforcement of Diels-Alder Cycloadducts with Hydrogen Bonding Interactions in Recyclable Dual-Dynamic Polyurethane Networks

Jennifer C. Hughes,[a] James A. Wilson,[b] Devanshi Singh,[a] Nick Hawkins,[c] Yi. Zhang,[d] Chris Holland[e] *and* Andrew T. Slark[a*]

[a] *Department of Chemistry, School of Mathematical and Physical Sciences, The University of Sheffield, Sheffield, S3 7HF, UK.*

[b] *Chemical Engineering and Biotechnologies, Aston University, Birmingham, B4 7ET, UK.*

[c] *Department of Engineering Science, Oxford University, Oxford, OX1 3PJ, UK.*

[d] *ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK.*

[e] *School of Chemical Materials and Biological Engineering, The University of Sheffield, Sheffield, S1 3JD, UK.*
[*] E-mail: a.slark@sheffield.ac.uk

Experimental

Materials

Capa® 2200J (OH value = 56.38 mg.KOH/g) was supplied by Ingevity. Krasol® LBH P 2000 (OH value = 53.53 mg.KOH/g) was supplied by Cray Valley. Desmodur® N 3300 was supplied by Covestro. Butyl acetate (BuOAc), dibutyltin dilaurate (DBDTL), dichloromethane (DCM), dimethylformamide (DMF), deuterated chloroform ($CDCl_3$, 99.8 atom % D), deuterated dimethyl sulfoxide (DMSO-d_6, 99.5 atom % D), furfuryl amine (FAM), furfuryl alcohol (FA), furfuryl mercaptan (FM), 4,4'-methylene bis(phenyl isocyanate) (MDI, 98 %), tris[2-(acryloyloxy)ethyl] isocyanurate (TAEICN), and triethylamine (NEt_3) were all purchased from Sigma-Aldrich. 2-Hydroxyl ethyl maleimide was provided by Henkel Corporation. All materials were used as supplied.

Synthesis of TF-ester crosslinker

Tris[2-(acryloyloxy)ethyl] isocyanurate (TAEICN, 3 g, 7.09 mmol) was dissolved in DCM (5.4 mL) in the presence of TEA (0.5 mL) in a 100 mL round bottom flask. Furfuryl mercaptan (FM, 2.55 g, 22.33 mmol) was added to the solution and the mixture was stirred in an ice bath for 1 h. The stirring was continued for 14 h at 40 °C, followed by the removal of the solvent in vacuo. The excess FM was removed under high vacuum to produce a pale-yellow viscous liquid (TF-ester, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K,): δ = 7.35 (d, $^3J^{H\text{-}H}$ = 1.2 Hz, 3H, OC*H*=CH-CH)), 6.30 (d, $^3J^{H\text{-}H}$ = 2.5 Hz, 3H, OCH=CH-C*H*), 6.19 (d, $^3J^{H\text{-}H}$ = 3.1 Hz, 3H, OCH=C*H*-CH), 4.32 (t, $^3J^{H\text{-}H}$ = 5.2 Hz, 6H, SCH$_2$C*H*$_2$COO), 4.15 (t, $^3J^{H\text{-}H}$ = 5.1 Hz, 6H, S-C*H*$_2$CH$_2$COO), 3.71 (s, 6H, CH$_2$CH$_2$SC*H*$_2$C(O)=CH), 2.73 (t, $^3J^{H\text{-}H}$ = 7.3 Hz, 6H, NCH$_2$C*H*$_2$OOC), 2.53 (t, $^3J^{H\text{-}H}$ = 7.3 Hz, 6H, NC*H*$_2$CH$_2$OOC) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ = 171.9 (*C*=O), 151.5 (N-*C*=O), 149.2 (O-*C*=C), 142.5 (O-C=*C*), 110.7 (CH$_2$-C=*C*), 107.9 (CH$_2$-*C*=C), 61.5 (N-CH$_2$-*C*H$_2$), 42.2 (N-*C*H$_2$-CH$_2$), 34.5 (*C*H$_2$-CH$_2$-S), 28.5 (S-*C*H$_2$-), 26.6 (CH$_2$-*C*H$_2$-S) ppm. ATR-FTIR*:* ν_{max} = 1730 (C(=O)-O), 1686 (N-C(=O)-N), 1504 (Ar C=C), 1237 and 1148 (C-O) and 737 (FA C-H) cm^{-1}.

Synthesis of TF-urethane crosslinker

In a 4-necked flask equipped with a mechanical stirrer, reflux condenser and nitrogen inlet, Desmodur N3300 (HDI trimer, 500 g, 2590 mmol isocyanate) was combined with toluene (300 mL) and 4 drops of DBDTL and the mixture was stirred with a mechanical stirrer and heated to 85 °C in an oil bath. Furfuryl alcohol (FA, 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 TF-urethane as an off-white liquid which solidified upon cooling to room temperature (84 % yield).

^{1}H NMR (400 MHz, CDCl3, 298 K): δ = 7.40 (d, $^3J_{\text{H-H}}$ = 2.2 Hz, 3H, OCH=CH-CH), 6.38 (d, $^3J_{\text{H-H}}$ = 3.3 Hz, 3H, OCH=CH-CH), 6.34 (s, 3H, OCH=CH-CH), 5.03 (s, 6H, COOCH2 C(O)=CH), 4.81 (s, 3H, NH), 3.84 (m, 6H, NCH2), 3.15 (m, 6H, CH2 NH), 1.75-1.25 (m, 24H, CH2) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, 298 K): δ = 156.2 (O-*C*(=O)-NH), 150.28 (N-C(=O)-N), 149.16 (furfuryl C-O), 143.29 (furfuryl CH-O), 110.70 (CH=*C*H-CH), 110.45 (CH-*C*H=C), 58.52 (C-*C*H$_2$-O), 42.96 (NH-*C*H$_2$-CH$_2$), 41.05 (N-*C*H$_2$-CH$_2$), 29.87 (NH-CH$_2$-*C*H$_2$), 27.82 (N-CH$_2$-*C*H$_2$) and (CH$_2$-CH$_2$-CH$_2$), 26.38 (CH$_2$-*C*H$_2$-CH$_2$) ppm. ATR-FTIR ν_{max} = 3328 (N-H), 2994 – 2835 (C-H), 1740-1610 (C(=O)-O) and (N-C(=O)-N), 1532 (Ar C=C), 1250 & 1153 (C-O) and 733 (FA C-H) cm^{-1}.

Synthesis of TF-urea crosslinker

In a 4-necked flask equipped with a mechanical stirrer, reflux condenser and nitrogen inlet, Desmodur N3300 (HDI trimer, 500 g, 2590 mmol isocyanate) was combined with ethyl acetate (300 mL) and 4 drops of DBDTL and the mixture was stirred with a mechanical stirrer and heated to 80 °C in an oil bath. Furfuryl amine (FAM, 251.7 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 TF-urea as a yellow powder (90% yield).

^{1}H NMR (400 MHz, DMSO-d$_6$, 298 K): δ = 7.53 (s, 3H, OC*H*=CH-CH), 6.36 (d, $^3J_{H-H}$ = 3.3 Hz, 3H, OCH=CH-C*H*), 6.16 (dd, $^3J_{H-H}$ = 1.8 Hz, 3H, OCH=C*H*-CH and s, 3H, N*H*CH$_2$C(O)=CH), 5.73 (s, 3H, CH$_2$N*H*CONH), 4.16 (s, 6H, NHC*H*$_2$C(O)=CH), 3.71 (m, 6H, NC*H*$_2$), 3.32 (s, 2H, *H*$_2$O), 2.96 (s, 8H, C*H*$_2$NHCONH), 1.7-1.0 (m, 24H, C*H*$_2$) ppm. ^{13}C NMR (125 MHz, DMSO-d$_6$, 298 K): δ = 158.63 (NH-*C*(=O)-NH), 154.71 (furfuryl *C*-O), 149.80 (N-C(=O)-N), 142.71 (furfuryl CH-O), 111.28 (CH=*C*H-CH), 106.98 (CH-*C*H=C), 43.05 (N-*C*H$_2$-CH$_2$), ~40.00 (NH-*C*H$_2$-CH$_2$), 37.26 (NH*C*H2C(O)=C), 30.80 (NH-CH$_2$-*C*H$_2$), 28.11 (N-CH$_2$-*C*H$_2$), 26.92 and 26.81 (CH$_2$-*C*H$_2$-CH$_2$) ppm. ATIR-FTIR ν_{max} = 3320 (N-H), 2976– 2810 (C-H), 1730-1620 (C(=O)-O) and (N-C(=O)-N), 1626 (NHC(=O)NH and NH urea) 1569 (Ar C=C), 1250 & 1150 (C-O) and 728 (FA C-H) cm^{-1}.

Synthesis of the telechelic polyurethane bismaleimides

Maleimide-terminated PU prepolymers were synthesised in a similar manner, a typical procedure is as follows: Polyol (either PCL for PCL-M and PBD for PBD-M) (77.96 g, 39 mmol) was loaded into a 4-

necked 250 mL flange flask, equipped with an overhead mechanical stirrer, gas inlet and digital thermometer. Vacuum was applied for 1 hour at 90 °C with a stirring rate of 90 rpm. Vacuum was removed and MDI (19.52 g, 78 mmol) was added at 110 °C under nitrogen flow with stirring increased to 180 rpm. After 15 minutes the vacuum was reapplied for 1 hour to allow MDI to react with hydroxyl groups. Vacuum was again removed, and 2-Hydroxyl ethyl maleimide (12.28 g, 87 mmol) was added at 110 °C to react with terminal isocyanate groups. ATR-IR spectroscopy showed disappearance of the isocyanate band after approximately 1.5-2 hours. The reaction was then switched off and the mixture was decanted while hot to give either maleimide-terminated poly(ε-caprolactone urethane) (PCL-M, 100.03g, 91% yield) or maleimide-terminated poly(1,4-butadiene urethane) (PBD-M, 97.86g, 89% yield).

PCL-M: **SEC** ($CHCl_3$): M_n = 8.0 kDa, M_w = 16.2 kDa, $Đ_M$ = 2.0. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ =7.30 (m, Ar), 7.10 (d, $^3J_{\text{H-H}}$ = 8.3 Hz, Ar),6.71 (s, C=OC*H*CH (HEMI)), 6.62 (s, N*H*), 6.58 (s, N*H*), 4.32 (t, $^3J_{\text{H-H}}$ = 5.2 Hz, NCH$_2$C*H*$_2$O (HEMI)), 4.14 (t, $^3J_{\text{H-H}}$ = 6.4 Hz, C*H*$_2$OC=O), 4.06 (t, $^3J_{\text{H-H}}$ = 6.7 Hz, C*H*$_2$OC=O), 3.89 (s, MDI CH$_2$Ar), 3.89 (s, NPG C*H*$_2$O), 3.85 (t, $^3J_{\text{H-H}}$ = 5.2 Hz, NC*H*$_2$CH$_2$O (HEMI)), 2.30 (t, $^3J_{\text{H-H}}$ = 7.5 Hz, C*H*$_2$C=OO), 0.98 (d, $^3J_{\text{H-H}}$= 9.4 Hz, NPG C*H*$_3$), 1.65 and 1.38 (all remaining protons) ppm. ATR-FTIR: v_{max} = 3341 (N-H), 2944- 2865 (C-H), 1722 and 1709 (C=O), 1597 (C-N), 1532 (Ar C=C), 1295 and 1164 (C-O) cm^{-1} .

PBD-M: **SEC** ($CHCl_3$): M_n = 7.4 kDa, M_w = 12.4 kDa, $Đ_M$ = 1.7. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ = 7.30 (m, Ar), 7.10 (d, $^3J_{\text{H-H}}$ = 7.8 Hz, Ar), 6.71 (s, C=OC*H*CH (HEMI)), 6.50 (s, N*H*), 5.8-5.3 (m, -C*H*=(1,2) and -C*H*=C*H*-(1,4)), 5.1-4.8 (m, =C*H*$_2$(1,2)), 4.32 (t,$^3J_{\text{H-H}}$ = 5.2 Hz, NCH$_2$C*H*$_2$O (HEMI)), 4.25-3.9 (m, -C*H*$_2$-O), 3.88 (s, MDI C*H*$_2$Ar), 3.83 (t, $^3J_{\text{H-H}}$ = 5.2 Hz, NC*H*$_2$CH$_2$O (HEMI)), 2.25-1.7 (m, -C*H*$_2$-(1,4) and -C*H*-(1,2)), 1.7-1 (m, -C*H*$_2$-(1,2)). ATR-FTIR: v_{max} = 3332 (N-H), 3070 (C=C $_{\text{stretch 1,2}}$), 3050-2780 (C-H), 1702 (C=O), 1595 (C-N), 1521 (Ar C=C), 995 (C=C $_{\text{bending 1,2}}$), 965 (C=C $_{\text{bending 1,4 trans}}$), 907 (C=C $_{\text{bending 1,2}}$) and 696 (C=C B_1) cm^{-1}.

Synthesis of DDNs

The DDNs were synthesised *via* initial solvent casting PCL-M or PBD-M prepolymers with TF-ester, TF-urethane or TF-urea multifunctional crosslinkers. The mass of reagents required to achieve 1 : 1 furan : maleimide stoichiometric ratio were calculated based on the molar masses of the cross-linkers (TF-ester = 766 g.mol^{-1}, TF-urethane = 799 g.mol^{-1} and TF-urea = 793 g.mol^{-1}) and the theoretical molar masses of the bismaleimide PU prepolymers (using OH values to determine the theoretical molar mass of polyol + the molar mass of two MDI units + the molar mass of two FA or two HEMI end units), where PCL-M = 2764 g.mol^{-1} and PBD-M = 2878 g.mol^{-1}. A typical procedure is as follows: PCL-M (10 g, 3.6 mmol) and TF-ester (1.85 g, 2.4 mmol) were added to a 50 mL glass vial followed by 20 mL of CH_2Cl_2 solvent. The components were stirred at room temperature until a homogenous solution formed after which the solution was cast into a PTFE-lined petri dish. The solvent casted network was left in the fume hood overnight so that most of the CH_2Cl_2 evaporated. Residual CH_2Cl_2 was removed in a vacuum oven at 40 °C overnight. After solvent removal the bulk PU network was compression moulded at 110 °C for 10 minutes using 3 MPa of pressure to produce a bubble-free, 1 mm elastomeric sheet which was left at 25 °C for 7 days to allow crosslinking to occur before testing. For DDNs containing TF-urea a similar procedure was used but DMF and mild heating (60 °C) were required to fully solubilise the cross-linker to achieve a homogenous solution. Samples were also placed in a vacuum oven at 80 °C for 3 days to remove residual DMF. Moreover, compression moulding was typically carried out between 120-130 °C using 3 MPa of pressure for 20 minutes.

DA(PCL-ester): ATIR-FTIR: ν_{max} = 3334 (N-H), 2997-2820 (C-H), 1775 (C=O DA), 1722 (PCL C(=O)-O and free NHC(=O)N), 1693 (N-C(=O)-N and H-bonded NHC(=O)N), 1597 (C-N),1531 (Ar C=C), 1216 & 1155 (C-O) and 725 (FA C-H) cm^{-1}. DSC: T_{mPCL} = 44 °C, ΔH_{mPCL} = 17.8 J.g^{-1}, T_{rDA} = 107 & 134 °C, and ΔH_{rDA} = 11.0 J.g^{-1}.

DA(PCL-urethane): ATIR-FTIR: ν_{max} = 3334 (N-H), 2997-2820 (C-H), 1774 (C=O DA), 1722 (PCL C(=O)-O and free NHC(=O)N), 1695 (N-C(=O)-N and H-bonded NHC(=O)N), 1598 (C-N), 1532 (Ar C=C), 1224 & 1157 (C-O) and 734 (FA C-H) cm^{-1}. DSC: T_{mPCL} = 44 °C, ΔH_{mPCL} = 20.0 J.g^{-1}, T_{rDA} = 115 & 146 °C, and ΔH_{rDA} = 10.8 J.g^{-1}.

DA(PCL-urea): ATIR-FTIR: ν_{max} = 3337 (N-H), 2997-2810 (C-H), 1771 (C=O DA), 1728 (PCL C(=O)-O and free NHC(=O)N), 1697-1630 1695 (N-C(=O)-N, H-bonded NHC(=O)N and H-bonded NHC(=O)NH), 1595 (C-N),1528 (Ar C=C), 1242 & 1156 (C-O) and 726 (FA C-H) cm^{-1}. DSC: T_g = -43 °C, T_{mPCL} = 36 & 43 °C, ΔH_{mPCL} = 6.1 J.g^{-1}, T_{rDA} = 115 & 143 °C, and ΔH_{rDA} = 10.4 J.g^{-1}.

DA(PBD-ester): ATIR-FTIR: ν_{max} = 3328 (N-H), 3070 (C=C$_{\text{stretch 1,2}}$), 3050-2780 (C-H), 1775 (C=O DA), 1735 (TF-ester C(=O)-O and free NHC(=O)N), 1692 (N-C(=O)-N, H-bonded NHC(=O)N), 1640 (C=C$_{\text{stretch}}$) 1597 (C-N), 1528 (Ar C=C), 995 (C=C$_{\text{bending 1,2}}$), 965 (C=C$_{\text{bending 1,4 trans}}$), and 907 (C=C$_{\text{bending 1,2}}$) cm^{-1}. DSC: $T_{g\,lower}$ = -29 °C, $T_{g\,upper}$ = 41 °C, T_{rDA} = 129 °C, and ΔH_{rDA} = 12.4 J.g^{-1}.

DA(PBD-urethane): ATIR-FTIR: ν_{max} = 3327 (N-H), 3070 (C=C$_{\text{stretch 1,2}}$), 3050-2780 (C-H), 1775 (C=O DA), 1735 (free NHC(=O)N), 1700 1640 (C=C$_{\text{stretch}}$) 1597 (C-N), 1528 (Ar C=C), 995 (C=C$_{\text{bending 1,2}}$), 965 (C=C$_{\text{bending 1,4 trans}}$), and 907 (C=C$_{\text{bending 1,2}}$) cm^{-1}. DSC: $T_{g\,lower}$ = -29 °C, $T_{g\,upper}$ = 54 °C, T_{rDA} = 137 °C, and ΔH_{rDA} = 11.2 J.g^{-1}.

DA(PBD-urea): ATIR-FTIR: ν_{max} = 3327 (N-H), 3070 (C=C$_{\text{stretch 1,2}}$), 3050-2780 (C-H), 1775 (C=O DA), 1740 (free NHC(=O)N), 1700-1660 (N-C(=O)-N, H-bonded NHC(=O)N and H-bonded NHC(=O)NH), 1640 (C=C$_{\text{stretch}}$), 1597 (C-N), 1532 (Ar C=C), 995 (C=C$_{\text{bending 1,2}}$), 965 (C=C$_{\text{bending 1,4 trans}}$), and 907 (C=C$_{\text{bending 1,2}}$) cm^{-1}. DSC: $T_{g\,lower}$ = -29 °C), $T_{g\,upper}$ = 55 °C, T_{rDA} = 136 °C, and ΔH_{rDA} = 9.6 J.g^{-1}.

Instrumental methods

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker AV or AVIIIHD 400 MHz spectrometer at room temperature with approximately 10 mg of sample fully dissolved in deuterated chloroform ($CDCl_3$) or DMSO-d$_6$. Chemical shifts were recorded in parts per million (ppm) relative to the reference peak of chloroform solvent at δ = 7.26 ppm or dimethyl sulfoxide solvent at δ = 2.50 ppm. Spectra were analysed on MestReNova v6.0.2. **Carbon nuclear magnetic resonance (^{13}C NMR)** spectra were recorded at 125 MHz using approximately 40 mg of sample. Chemical shifts were recorded in parts per million (ppm) relative to a reference peak of chloroform solvent at δ = 77.16 ppm or DMSO solvent at δ = 39.51 ppm. **Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)** spectra were collected on a PerkinElmer FT-Infra-red spectrometer equipped with a UATR Two accessory. Eight scans were taken in the range of 4000 – 400 cm^{-1}. Analysis was performed on PerkinElmer Spectrum software. **Size Exclusion Chromatography (SEC)** 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. Approximately 20 mg of sample was dissolved in HPLC grade chloroform eluent (2 mL) containing 0.25 %w/w triethylamine (NEt_3) and filtered through 0.45 µm PTFE filters. The flow rate was set at 1.0 mL.min^{-1}. RI and UV detectors were calibrated using a series of near-monodisperse poly(methyl methacrylate) standards. **Differential scanning calorimetry (DSC)** was performed using a TA instruments Discovery DSC 25. Less than 3 mg of sample was accurately weighed on a microbalance and loaded into a T_{zero} aluminium pan. Heating and cooling ramps (from -90 °C to 200 °C) were conducted under a N_2 flow (40 $mL.min^{-1}$) at a standard rate of 10 $°C.min^{-1}$. T_g was taken as the midpoint of inflexion. T_m and T_{rDA} were measured as the temperature at the minimum heat flow of the appropriate endotherms. Analysis was performed on TRIOS v5.1.1 software. **Dynamic Mechanical Analysis (DMA)** was performed using a TA Instruments Q800 DMA using tensile clamps. Sample dimensions were typically 10 mm length by 5 mm width by 1 mm thickness. Samples were evaluated between -80 °C and 200 °C at a heating rate of 3 $°C.min^{-1}$. A deformation frequency of 1 Hz and a strain of 0.05% were used. **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. **Monotonic uniaxial extension experiments** were carried out on a Zwickiline tensometer according to ISO 527 (10 $mm.min^{-1}$ extension rate). Dumbbell specimens were cut out of approximately 1 mm thick compression moulded sheets using a ZwickRoell® knee manual cutting press ZCP 020 with cutting device for ISO 527-2 type 5B die attachment. (Length= 35 mm, gauge length = 12 mm, width = 2 mm). Before testing, the thickness of each specimen was measured using a digital calliper and recorded on the software. Five repeat specimens were tested for each material. Results were analysed on TestXpert II software. **Small-Angle (SAXS) and Wide-Angle (WAXS) X-ray Scattering** experiments were performed at ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Oxfordshire, United Kingdom on a Xenocs Nano-inxider using an X-ray wavelength = 1.541889 Å and an acquisition time = 10 min × 3.

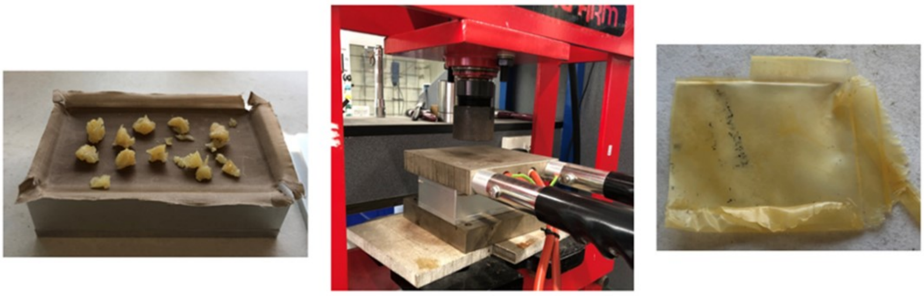
Soxhlet extraction

Approximately 0.5 g of DA-PU CAN elastomeric sheet was accurately weighed and folded into a pre-weighed piece of filter paper. A repeat sample was made up *via* the same method. A folded piece of blank filter paper containing no sample was included as a control. Samples were inserted into a 250 mL Soxhlet extractor on top of a 500 mL round-bottom flask containing THF solvent (300 mL) with a reflux condenser attached above. The solvent was heated to reflux for 24 hours. The samples were then removed and dried at 40 °C overnight in a vacuum oven to remove residual THF. Sample mass was recorded before and after extraction (dried). The sample mass difference was used to calculate the gel fraction of the material. The gel fraction is defined as the weight ratio of dried network polymer (W_2) after extraction to that of the polymer before (W_1).

$[W_2 / W_1] \times 100\% = \text{Gel fraction, }\%$

Compression moulding

5 g of each DA network (bulk material) was cut into small pieces and spread evenly into a metal compression mould lined with a thin sheet of PTFE. Another PTFE sheet was placed on top followed by the metal mould lid. The metal mould was then placed between two preheated metal plates in the temperature range of 110-130 °C, depending on TF-crosslinker used. 3 MPa of pressure was applied for ten minutes to melt and spread the material into an even film. The mould was then removed from the heated press and once cooled to room temperature, the material was removed.



The compression moulding process.

Thermal reprocessing

For thermal reprocessing pristine dumbbell samples which had been pulled apart *via* uniaxial tensile testing were combined with the rest of the original cuttings, so the total mass was 5 g, and the sample was evenly spaced into a metal compression mould lined with a thin sheet of PTFE. Another PTFE sheet was placed on top followed by the metal mould lid which was then positioned between two preheated metal plates at 110-130 °C. 3 MPa of pressure was applied for ten minutes to melt and spread the material into an even film. The mould was then removed from the heated plates and once cooled to room temperature, the material was carefully removed. Rubber sheets were conditioned for 7 days at ambient temperature to allow crosslinking to occur, before re-cutting of dumbbell specimens using the ZwickRoell® knee manual cutting press and remeasurement of tensile properties *via* uniaxial tensile testing (R1). This process was repeated a further two times (R2, R3) with the same materials to determine any change in mechanical properties.

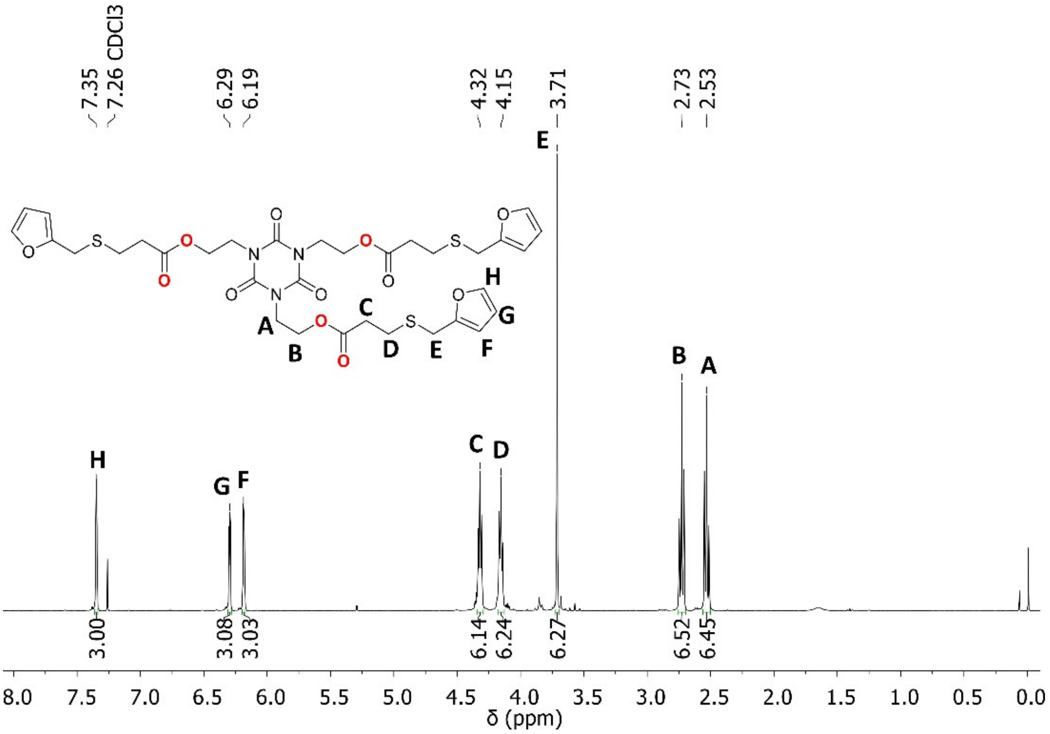


Figure S1. *^{1}H NMR spectrum of TF-ester crosslinker (400 MHz, 298 K, $CDCl_3$). Chemical shifts labelled at the top and integration values at the bottom.*

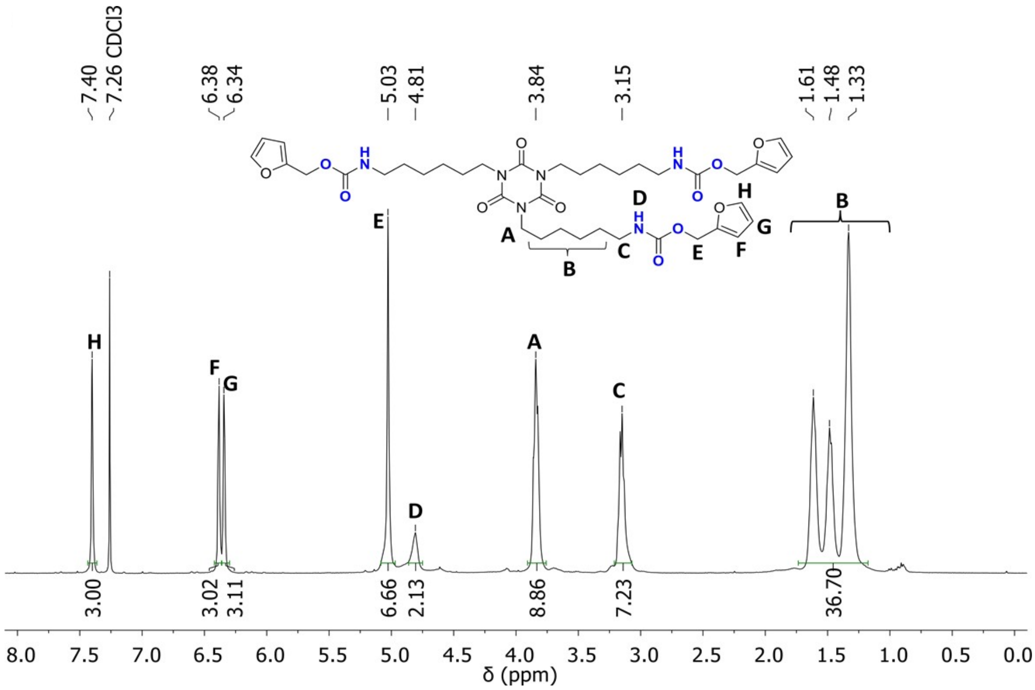


Figure S2. *^{1}H NMR spectrum of TF-urethane crosslinker (400 MHz, 298 K, $CDCl_3$). Chemical shifts labelled at the top and integration values at the bottom.*

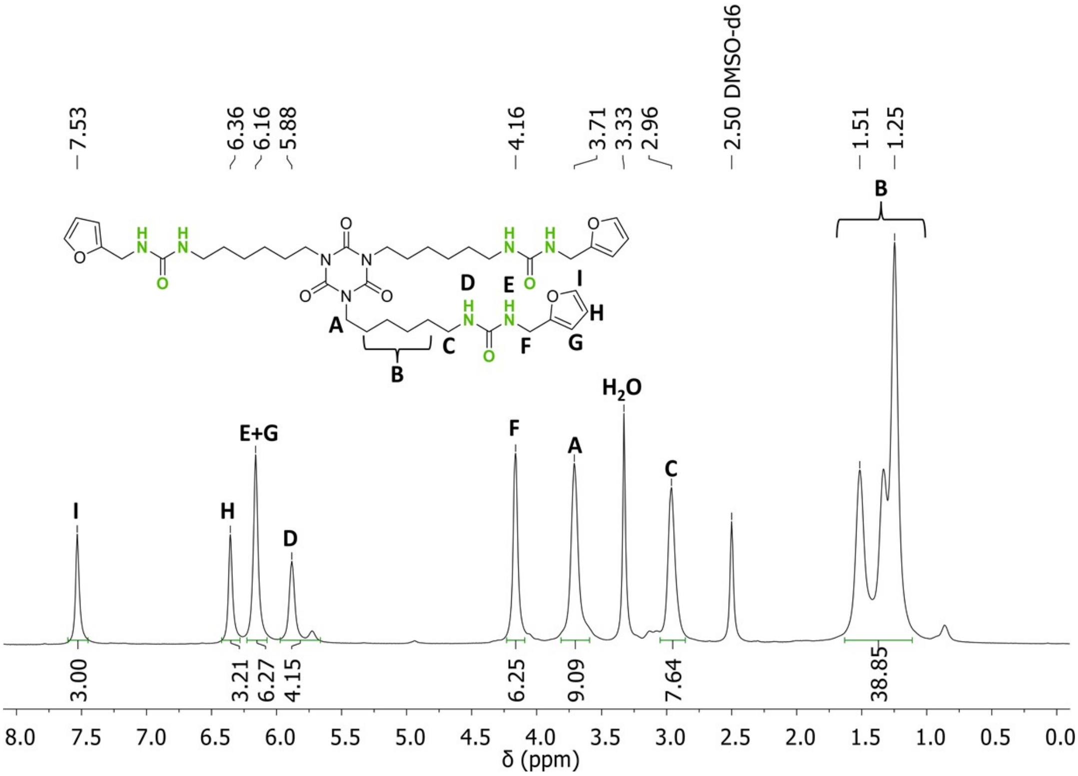


***Figure S3**. ^{1}H NMR spectrum of TF-urea crosslinker (400 MHz, 298 K, DMSO-d_6). Chemical shifts labelled at the top and integration values at the bottom.*

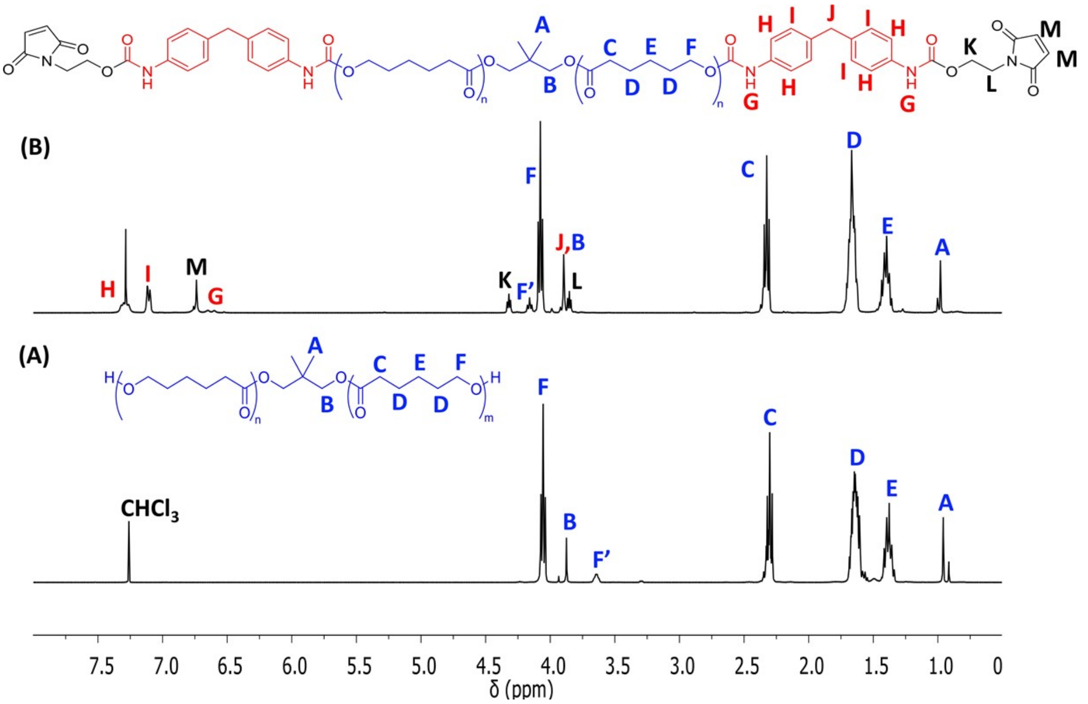


Figure S4. *^{1}H NMR spectra of (A) PCL polyol and (B) PCL-M prepolymer. (400 MHz, 298 K, $CDCl_3$).*

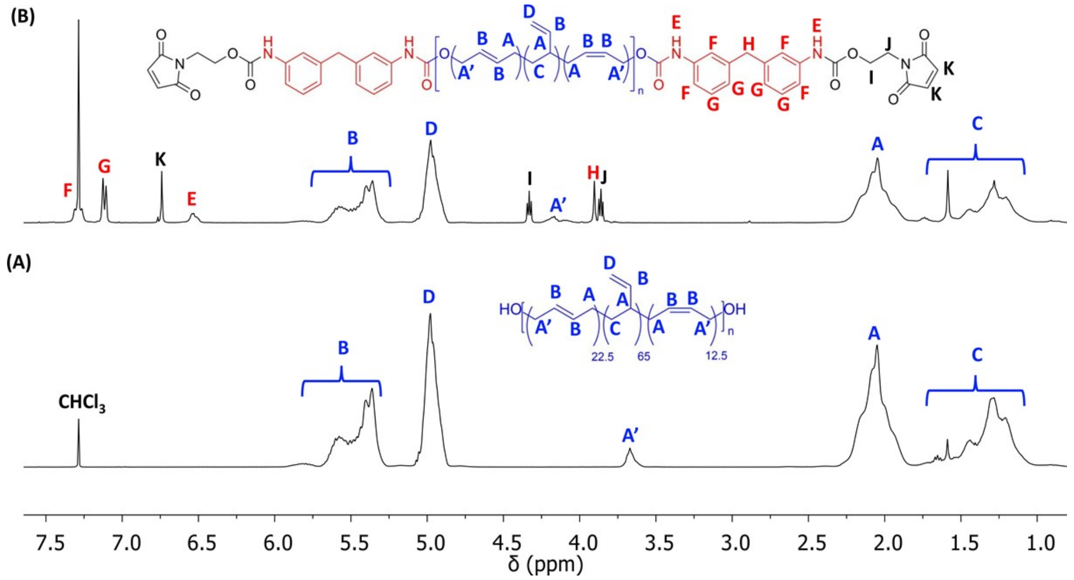


Figure S5. *^{1}H NMR spectra of (A) PBD polyol and (B) PBD-M prepolymer. (400 MHz, 298 K, $CDCl_3$).*

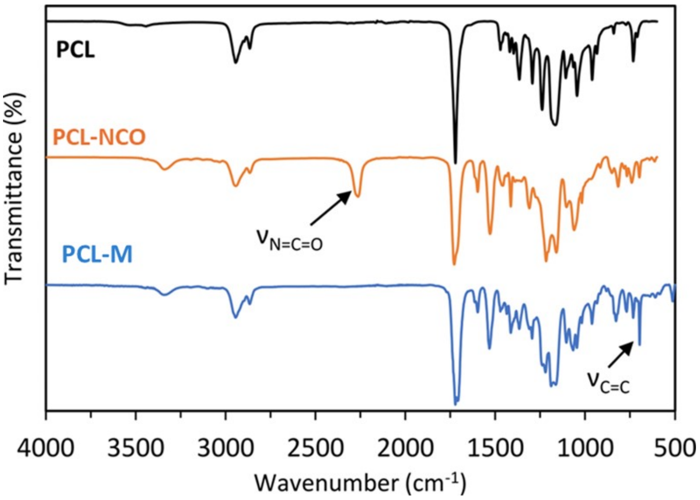


Figure S6. *ATR-FTIR spectra of PCL polyol, NCO-terminated intermediate (PCL-NCO) and maleimide-terminated PCL prepolymer (PCL-M).*

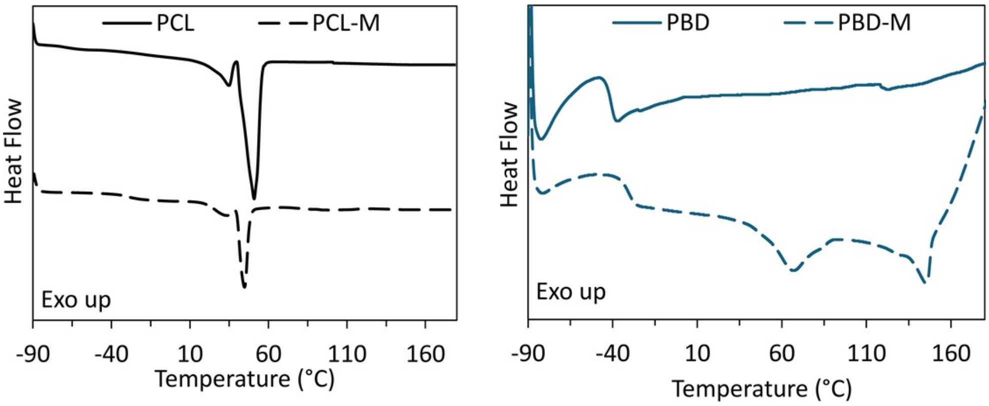


Figure S7. *DSC thermograms (1st heating cycles) of maleimide-terminated prepolymers compared to corresponding polyols. 10 °C.min^{-1} heating rate.*

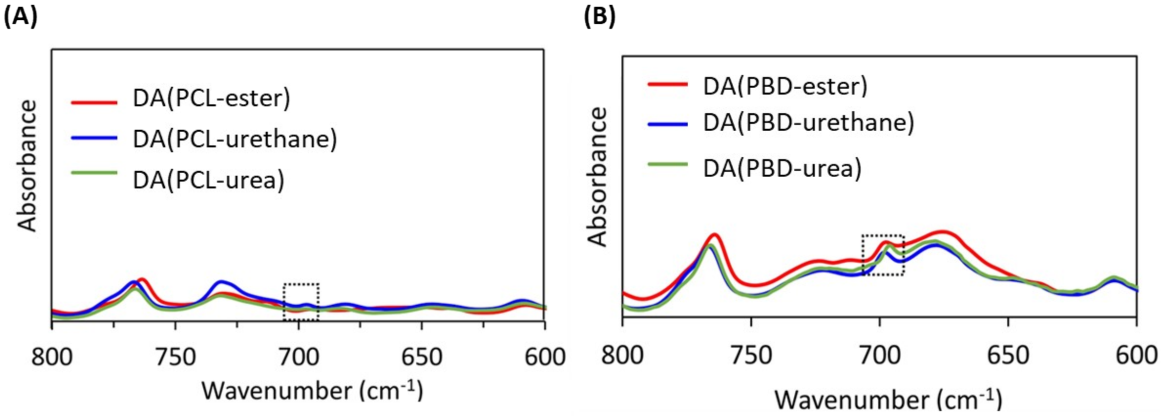


Figure S8. *ATR-FTIR spectra of (A) DDNs based on PCL and (B) DDNs based on PBD with different crosslinkers between 800-600 cm^{-1}. Dashed boxes highlight low maleimide absorption at 696 cm^{-1}.*

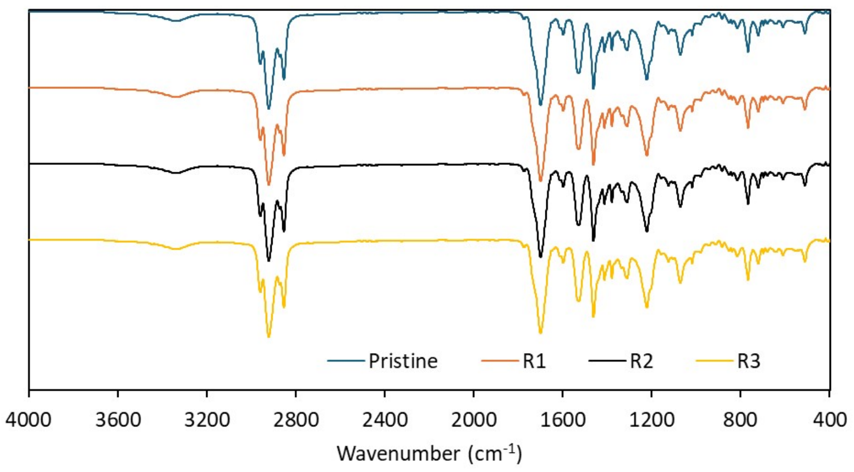


Figure S9. *ATR-FTIR spectra before recycling DA(PBD-urethane) (pristine) and after three reprocessing cycles showing no changes to the chemical structure.*

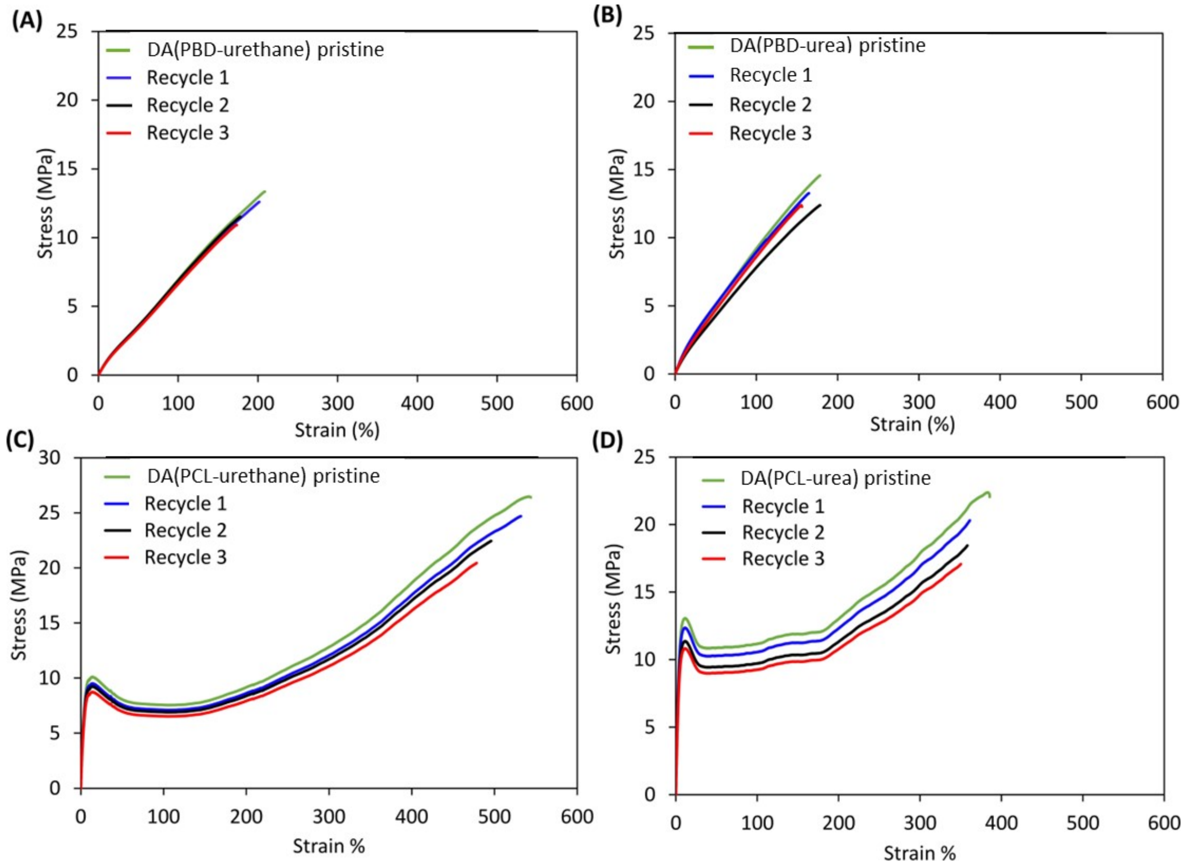


Figure S10. *Representative stress-strain curves of (A) DA(PBD-urethane), (B) DA(PBD-urea), (C) DA(PCL-urethane) and (D) DA(PCL-urea) DDNs before recycling (pristine) and after 3 mechanical reprocessing cycles.*

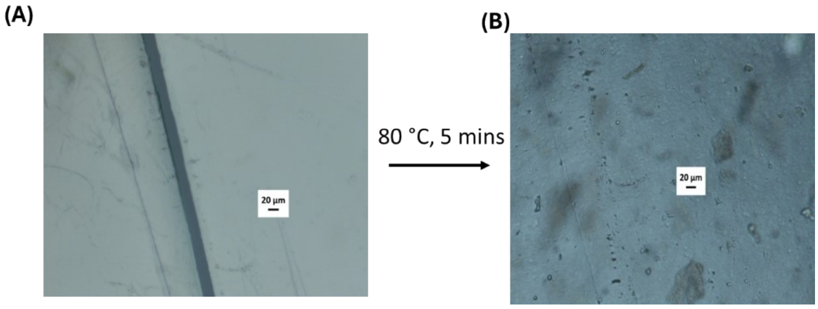


Figure S11. *Optical microscopy images of (A) DA(PCL-ester) with a 20 µm defect and (B) the same sample after heating to 80 °C for 5 minutes with the defect fully healed.*

Table S1*. Characterisation data of PCL and PBD polyols compared to corresponding maleimide-terminated prepolymers.*

Sample	M_n [a] (g.mol^{-1})	M_w [a] (g.mol^{-1})	$Đ_M$ [a]	T_g [b] (°C)	$T_{m\ PCL}$ [b] (°C)	$T_{m\ HS}$ [b] (°C)	$\Delta H_{m\ PCL}$ [b] (J.g^{-1})	$\Delta H_{m\ HS}$ [b] (J.g^{-1})
PCL	1,900	6,000	2.6	-67	53	-	83	-
PCL-M	8,000	16,200	2.0	-30	32/45	-	35	-
PBD	3,000	3,300	1.1	-42	-	-	-	-
PBD-M	7,400	12,400	1.7	-31	-	66/146	-	9.0/5.4

[a] Determined by SEC analysis, molecular weights determined against PMMA standards in $CHCl_3$ eluent, [b] determined from DSC analysis using the 1st heating cycle.

Table S2. *Thermal data for DDNs obtained via DMA using a heating rate of 3 °C.min^{-1}.*

DDN	T_g [a] (°C)	E' @ 20 °C [b] (MPa)	T_{mPCL} [c] (°C)	T_{gel} [d] (°C)
DA(PCL-ester)	-	671	45	96
DA(PCL-urethane)	-	961	45	117
DA(PCL-urea)	-28	574	41	130
DA(PBD-ester)	-16	17	-	108
DA(PBD-urethane)	-15	18	-	130
DA(PBD-urea)	-14	24	-	150

[a] Measured as onset of tan δ peak. [b] Storage modulus measured at 20 °C. [c] Measured as the onset of modulus reduction. [d] Measured as viscous flow where step drop in E' occurs.

Table S3*. Mechanical properties of pristine DDNs.*

DDN	$E_y{}^a$ (MPa)	$\sigma_b{}^a$ (MPa)	$\varepsilon_b{}^a$ (%)	$U_T{}^a$ (MJ/m^3)
DA(PCL-ester)	136 ± 8	16.2 ± 0.4	690 ± 65	80.6 ± 12.3
DA(PCL-urethane)	219 ± 12	26.5 ± 1.1	540 ± 42	75.7 ± 10.4
DA(PCL-urea)	299 ± 10	22.1 ± 1.3	390 ± 40	55.6 ± 9.8
DA(PBD-ester)	8.8 ± 1.3	11.7 ± 0.5	350 ± 27	26.2 ± 4.0
DA(PBD-urethane)	9.9 ± 1.0	13.3 ± 0.7	210 ± 40	14.8 ± 3.0
DA(PBD-urea)	15.3 ± 0.9	14.6 ± 0.4	180 ± 42	14.4 ± 2.9

[a] *determined by uniaxial tensometry using an extension rate 10 mm.min^{-1}. Mean values ± standard deviation from measurements conducted independently on 5 specimens.*

***Table S4**. Stress recovery values of DDNs after each thermal reprocessing cycle.*

DDN	[a] Recovery ratio R1 (%)	[a] Recovery ratio R2 (%)	[a] Recovery ratio R3 (%)
DA(PCL-urethane)	93	85	77
DA(PCL-urea)	92	83	77
DA(PBD-urethane)	95	87	82
DA(PBD-urea)	90	85	84

[a] *calculated as a percentage based on the ratio of the average stress at break for the pristine materials and the same materials after each reprocessing cycle (R1, R2, R3).*

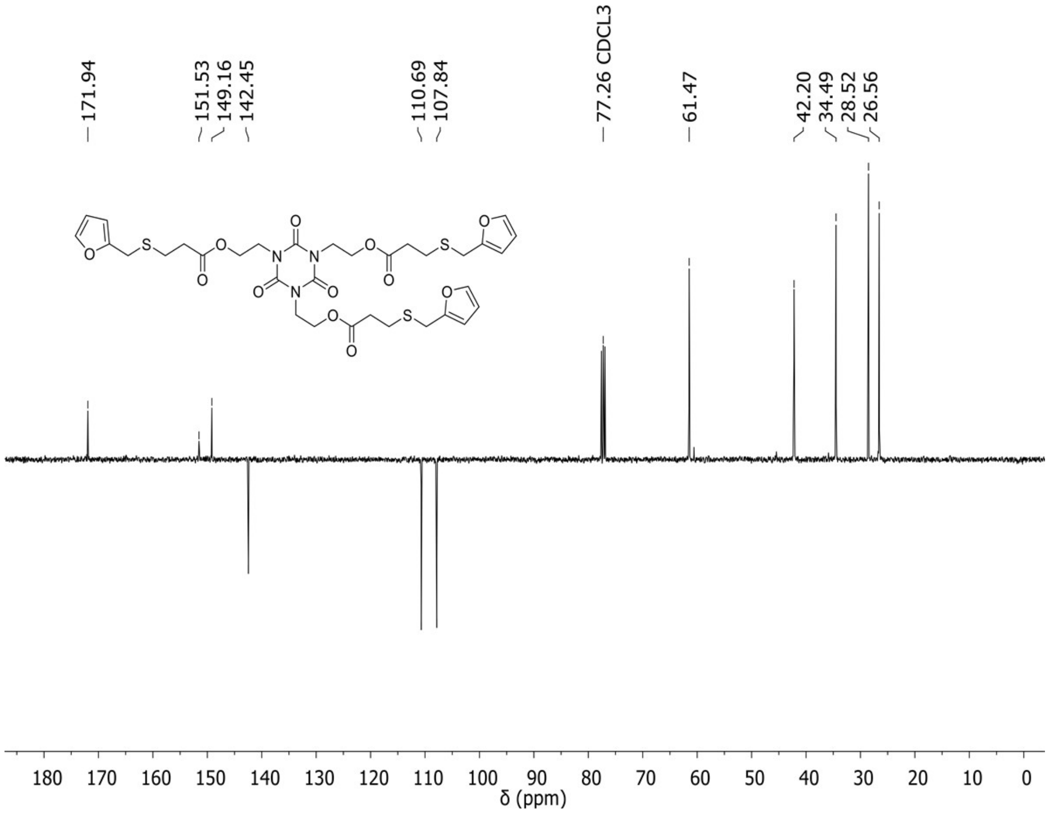


***Figure S12.** ^{13}C NMR spectrum of TF-ester crosslinker (125 MHz, 298 K, CDCl$_3$).*

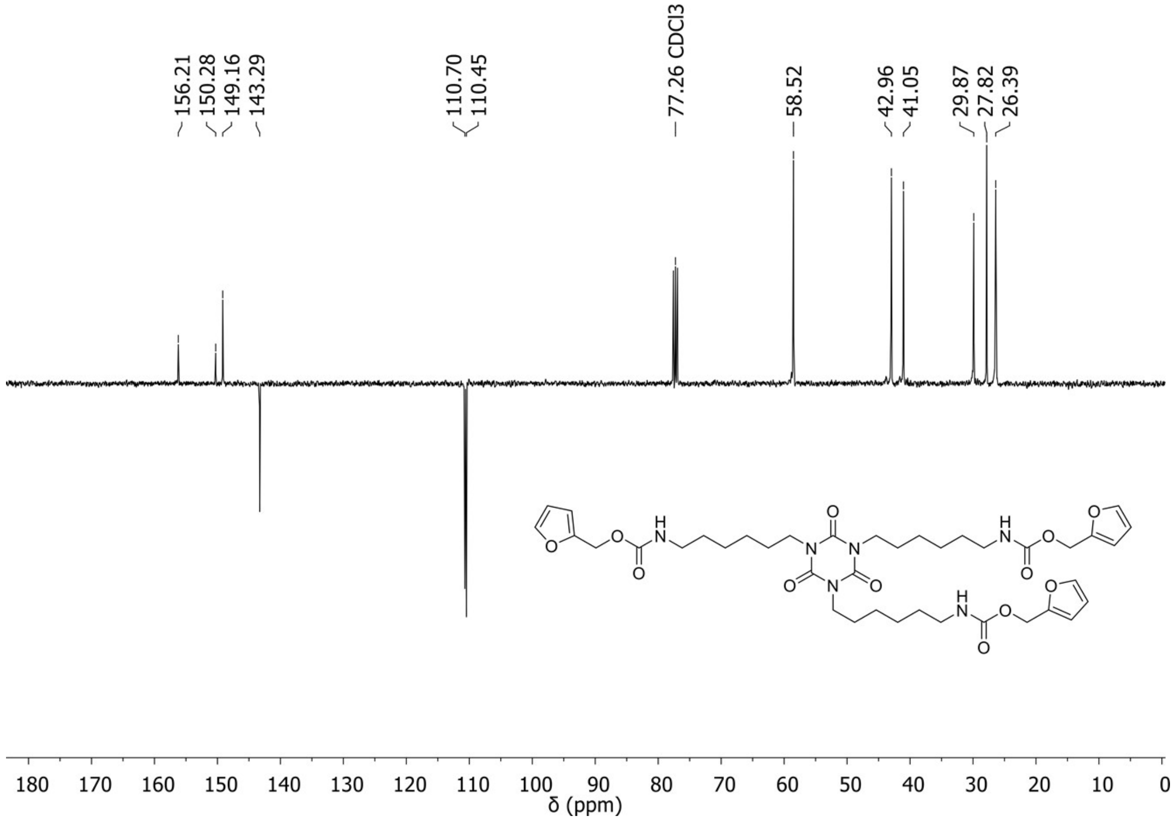


Figure S13. *^{13}C NMR spectrum of TF-urethane crosslinker (125 MHz, 298 K, $CDCl_3$).*

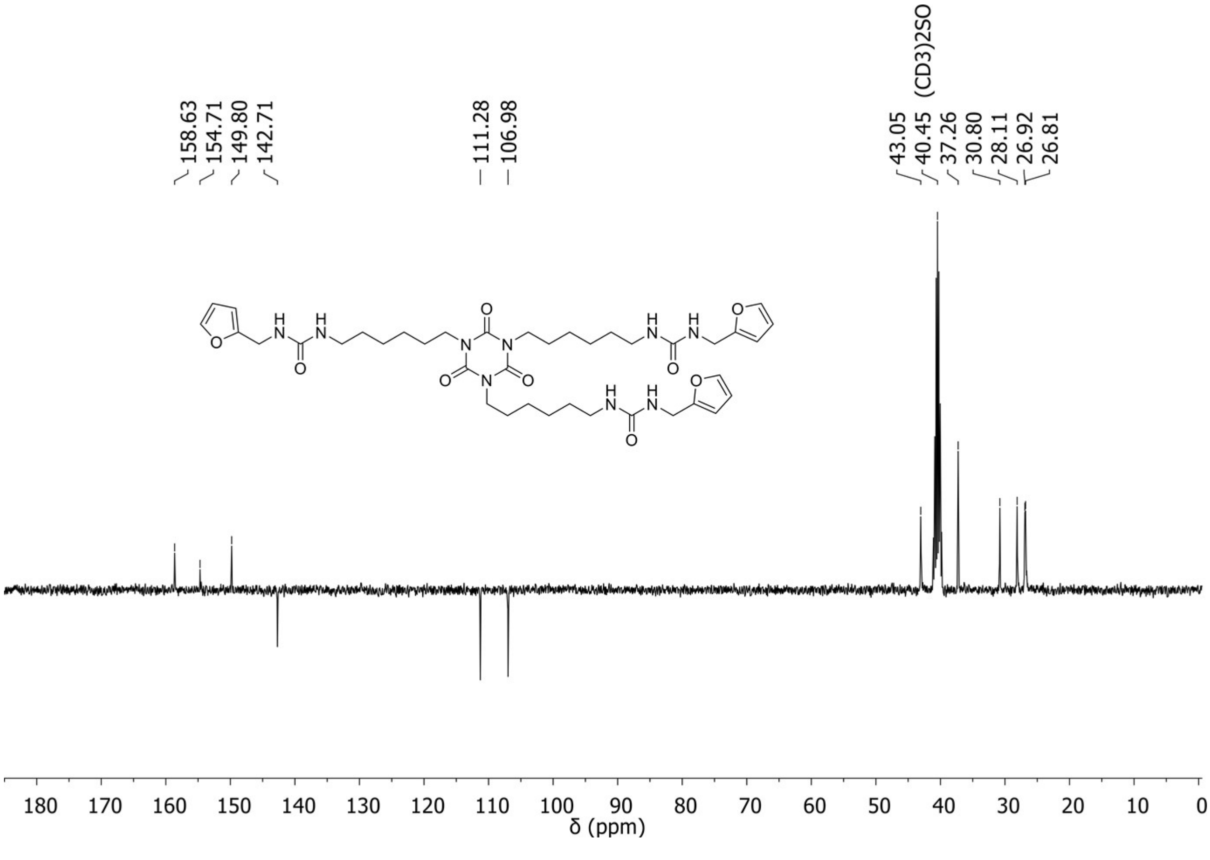


Figure S14. *^{13}C NMR spectrum of TF-urea crosslinker (125 MHz, 298 K, DMSO d6, $(CD_3)_2SO$).*

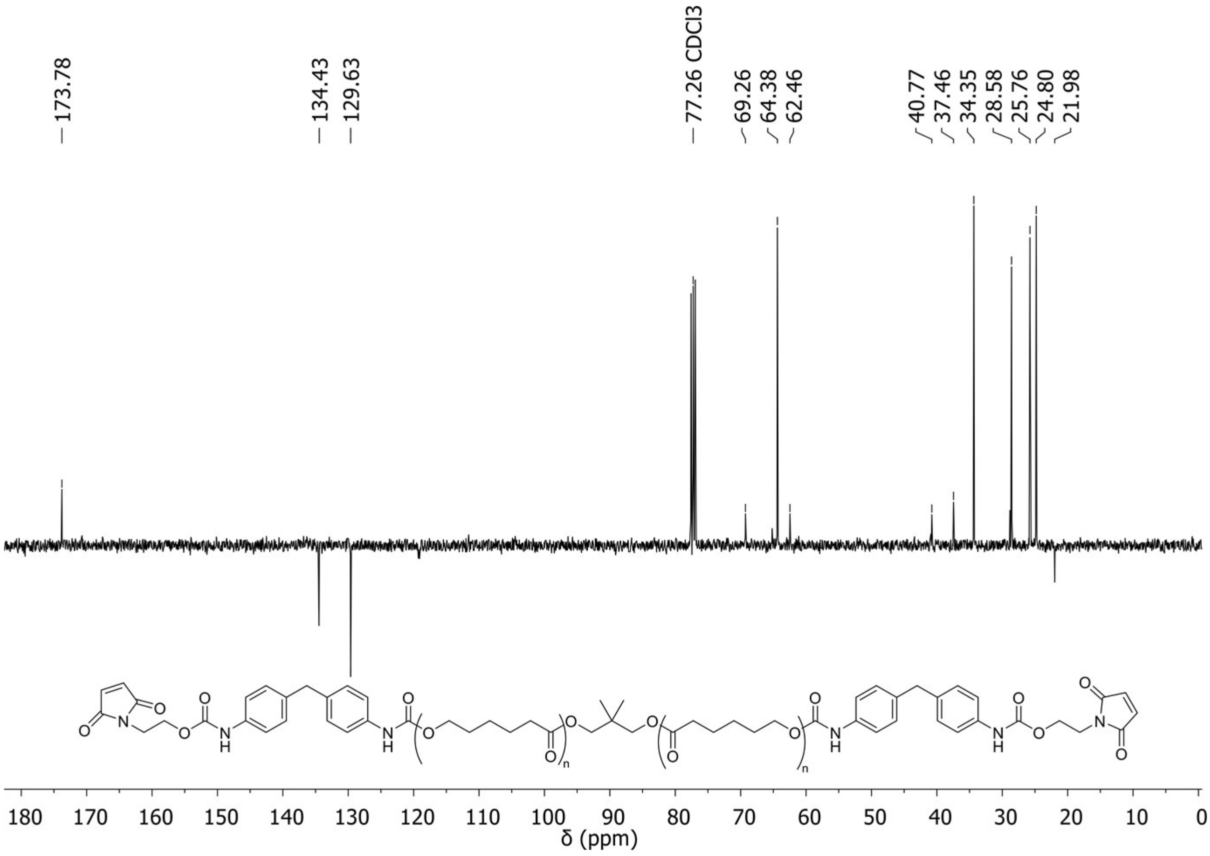


Figure S15. *^{13}C NMR spectrum of PCL-M maleimide telechelic prepolymer (125 MHz, 298 K, $CDCl_3$).*

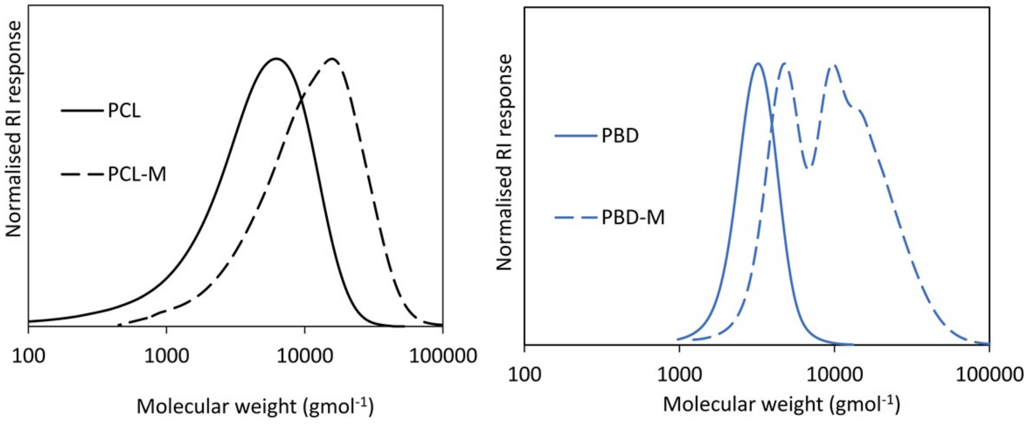


Figure S16. *SEC chromatograms of maleimide-terminated prepolymers compared to corresponding polyols. Molecular weights determined against PMMA standards using $CHCl_3$ as eluent.*