Supporting Information: ***Fluoride degradable and thermally debondable polyurethane based adhesive.***

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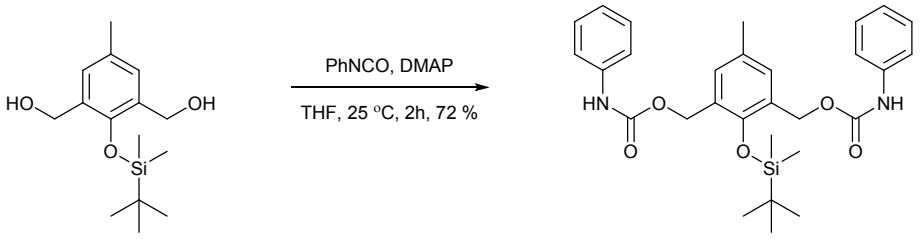
Supplementary Data

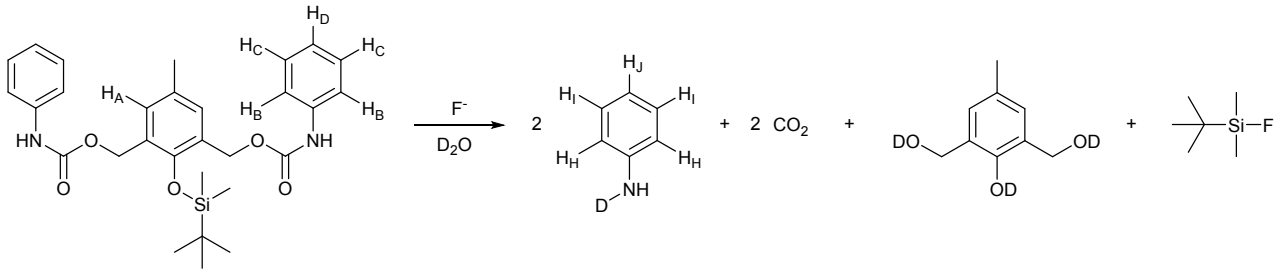
S1 – Synthesis and degradation tests of a model biscarbamate compound containing the degradable unit (DU).

Synthesis of SI 1 was achieved using a modification of the methods described by Shabat[1] and Akkaya and co-workers.[2] Inspired by this work, we synthesised novel bisurethane **SI-2** by the addition of two equivalents of phenyl isocyanate (Scheme S1).



Scheme S1 *Synthesis of the model biscarbamate compound (**2**).*

Initial degradation tests were carried to verify that the carbamate linkages were susceptible to fluoride initiated degradation. This was achieved by the addition of a fluoride source (tetra-butylammonium fluoride, TBAF) to a solution of **SI-2** in DMSO followed by deuterium oxide. Degradation was readily observed by the loss of the singlet resonance signal (7.12 ppm) from the aromatic protons H_A on the cresol linker within one minute of the addition of TBAF (compare spectra A and B, Figure S1). Spectra B does show some complete degradation observed by the appearance of H_H, H_I, and H_K from the released aniline group; which is a result of the consumption of any water from the TBAF·$3H_2O$ and/or DMSO solvent. Addition of deuterium oxide was required to drive the reaction to completion, with the formation of aniline (Scheme S2).



Scheme S2 *Proposed degradation of biscarbamate* ***SI-2*** *upon treatment of fluoride ions, followed by D_2O.*

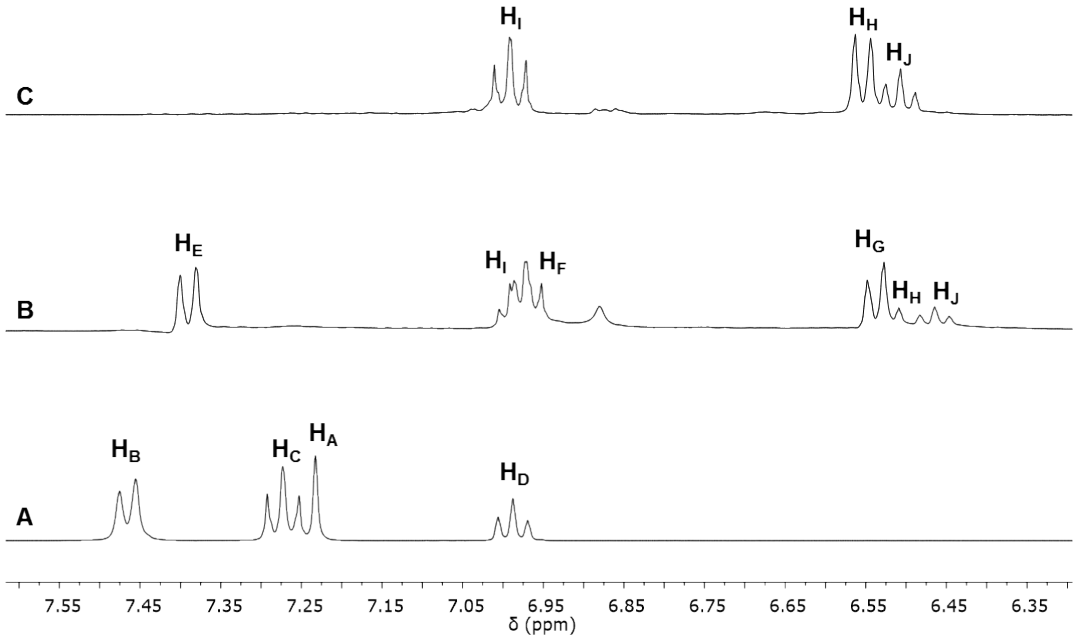


Figure S1 *^{1}H NMR spectra showing the two step degradation of the model compound (A) after addition of TBAF (B), followed by addition of deuterium oxide (C). ^{1}H NMR spectroscopy carried out in DMSO.*

The fluoride selective degradation of **SI-1** was investigated by addition of either tetra-butylammonium chloride (TBAC), tetra-butylammonium bromide (TBAB) or tetra-butylammonium iodide (TBAI) to model compound **SI-2**. As evident in Figure S2 , only the reaction containing fluoride ions underwent degradation followed by ^{1}H NMR spectroscopy (Figure S1) of **SI-2** acquired after 24 exposure to each halide ion, confirming the selectivity to fluoride ions.

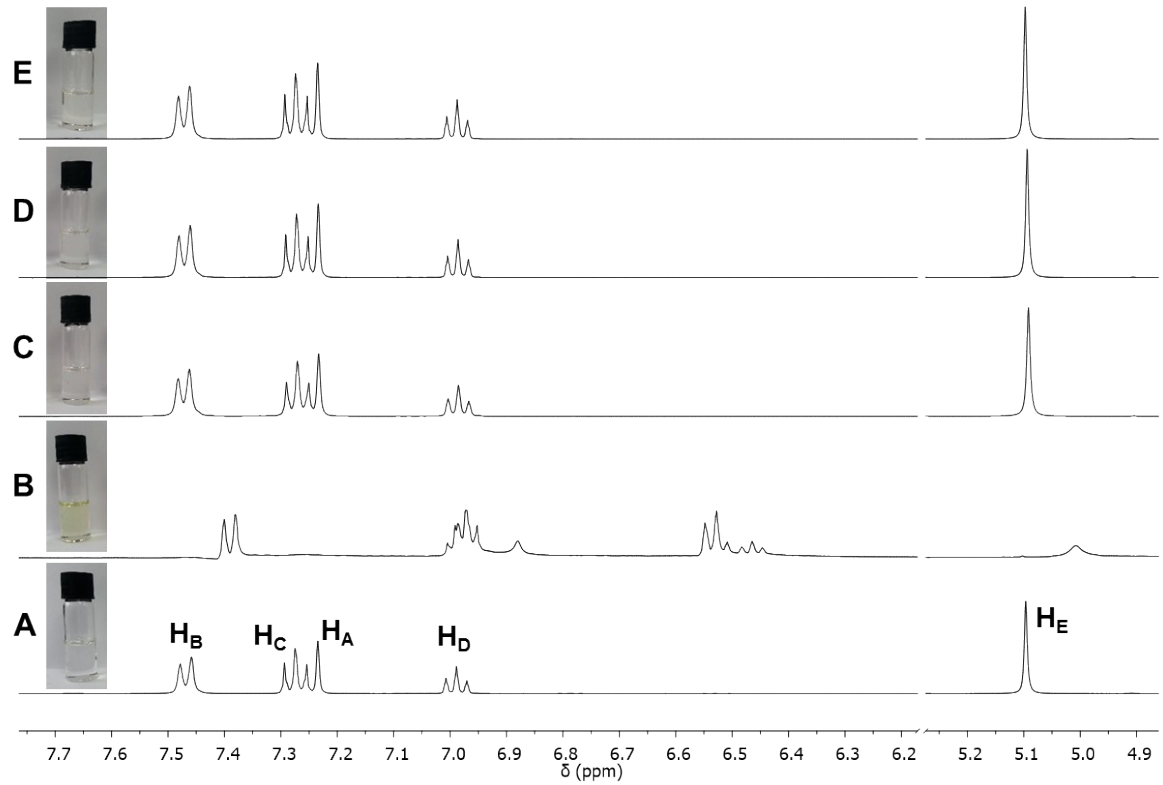
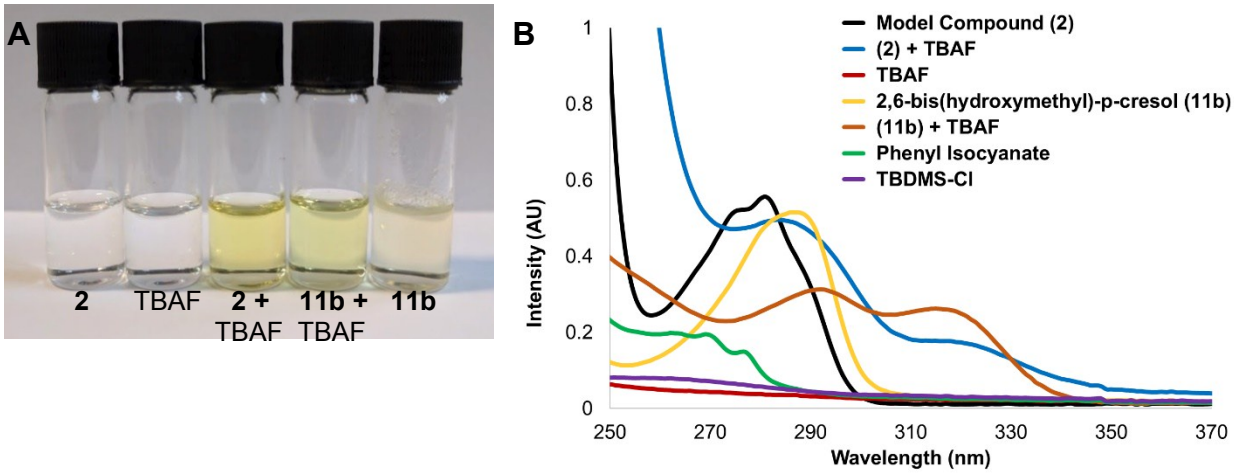


Figure S2 *Selectivity of the silyl group to the fluoride ion as determined by ^{1}H NMR spectroscopy. (A)* ***2****, (B)* ***2*** *+ TBAF, (C)* ***2*** *+ TBAC, (D)* ***2*** *+ TBAB, and (E)* ***2*** *+ TBAI. Photos show colour change from addition of TBAF and not from other tetra-butylammonium salts.*

As evident from the photos in Figure S1, a color change from colorless to yellow was seen on addition of fluoride ions to **SI-2**. This color change is attributed to the release of the cresol (Figure S2). This was proven by UV-visible spectroscopy. Samples of 0.01 mg/mL of the model compound (**SI-2**), 2,6-bis(hydroxymethyl)-*p*-cresol, phenyl isocyanate and TBDMS-Cl were prepared and added to 0.02 mg/mL of TBAF solution in chloroform. Samples before and after addition of TBAF were recorded (Figure S3).



C

	λ_{max} (nm)
Model Compound **2**	275, 281
2 + TBAF	285, 321
TBAF	-
2,6-bis(hydroxymethyl)-*p*-cresol **11b**	287
11b + TBAF	292, 317
Phenyl isocyanate	263, 270, 277
TBDMS-Cl	-

Figure S3 *(A) Addition of TBAF to model compound (**SI-2**) causes a yellow solution to form; which is a result of the formation of cresol interacting with excess TBAF salt. (B) UV-visible spectra of the model compound and its constituents before and after addition of TBAF. (C)* λ_{max} *values taken from the UV-visible spectra.*

The UV-visible spectroscopic data shows that on addition of TBAF to model compound **SI-2**, the breakdown forms the cresol core unit **11b**, which interacts with the TBAF salts to produce a vibrant yellow mixture; evidenced by the similar λ_{max} values of **2** + TBAF and **11b** + TBAF.

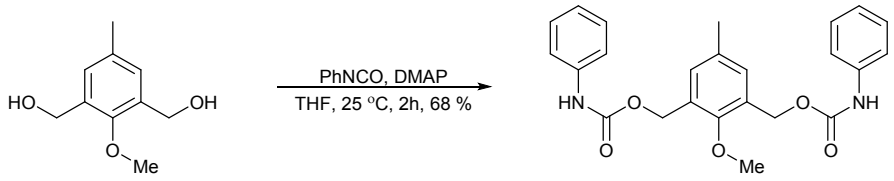
Synthesis of model bisurethane compound SI-2

To a solution of SRTU **1** (250 mg, 0.885 mmol) in anhydrous tetrahydrofuran (20 mL) was added 4-dimethylaminopyridine (10 mg, 0.09 mmol), triethylamine (0.49 mL, 3.54 mmol) and phenyl isocyanate (0.49 mL, 3.54 mmol) and allowed to stir at ambient temperature for 4 hours. The mixture was diluted into ethyl acetate (30 mL) and washed with saturated NH_4Cl (30 mL) and brine (30 mL). The organic solution was dried over $MgSO_4$, filtered and concentrated to afford the crude product solid, which was purified by column chromatography over silica gel eluting with 20 % ethyl acetate in hexane to afford a yellow oil (331 mg, 72 %). ν_{max} (thin film,

cm^{-1}) 3309, 2928, 2855, 1699, 1600, 1442, 1205, 883, 748, 690. δ_H (400 MHz, $CDCl_3$, ppm) 7.40 (4H, m, Ar-H), 7.31 (4H, m, Ar-H), 7.18 (2H, s, Ar-H), 7.07 (2H, m, Ar-H), 6.67 (2H, br, N-H), 5.20 (4H, s, Ar-CH_2), 2.30 (3H, s, Ar-CH_3), 1.05 (9H, $C(CH_3)_3$), 0.23 (6H, $Si(CH_3)_2$). δ_C (100 MHz, $CDCl_3$, ppm) 153.3, 149.1, 137.8, 131.4, 130.9, 129.1, 126.9, 123.5, 118.7, 62.5, 58.5, 25.9, 20.6, 18.7, 18.5, 0.0, -3.7. (m/z) 543.23 Da ($C_{29}H_{36}O_5N_2NaSi$), calculated 543.23 Da ($C_{29}H_{36}O_5N_2NaSi$).

S2 - Synthesis and degradation studies of Methoxy Analogue of DU

A methoxy analogue **SI-7** of the DU was synthesised as previously reported, and used to produce a second model compound **SI-8** (Scheme S3) to determine if the cresol core linker or the carbamate groups or the aniline reporter groups were affected by the addition of TBAF.



SI-7 **SI-8**

Scheme S3 *Synthesis of a methoxy analogue model compound to show that TBAF reacts with the silyl group, not the other functional groups.*

^{1}H NMR spectroscopy was carried out on both **SI-7** and **SI-7** before and after addition of TBAF (Figure S4). On addition of TBAF to **SI-7**, no shifts in resonances were recorded proving that TBAF does not affect the core cresol group. However, on addition of TBAF to **SI-8**, the aromatic resonances shifted and a small loss in resonance was observed. This is a result of the deprotonation of the urethane proton from the strong fluoride base. This does not result in breakdown of the molecule; and hence proves that fluoride ions only affect the silyl group.

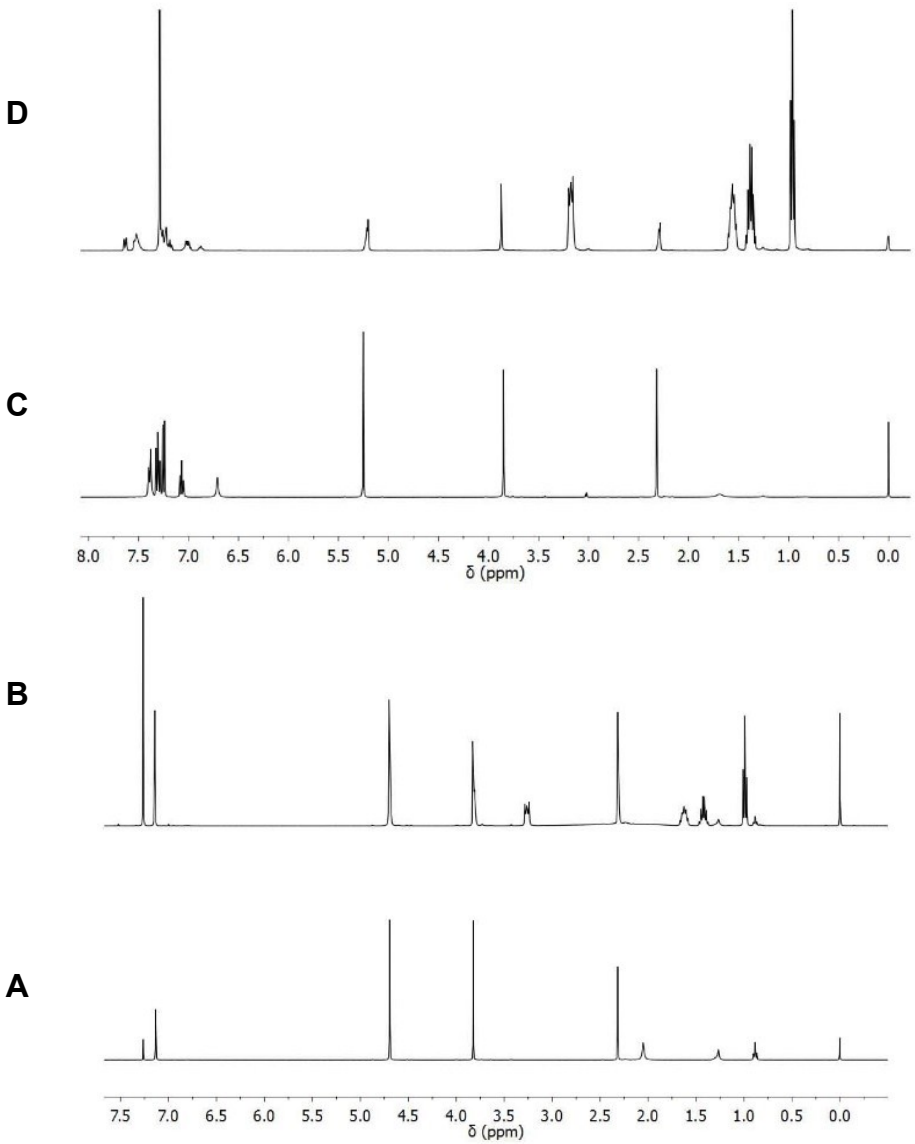


Figure S4 *^{1}H NMR spectra representing (A)* ***SI-1****, (B)* ***SI-1*** *+ TBAF, (C)* ***SI-2****, and (D)* ***SI-2*** *+ TBAF.*

Synthesis of SI-7

2,6-bis(hydroxymethyl)-*p*-cresol (5.00 g, 29.73 mmol) and sodium hydroxide (1.78 g, 44.59 mmol) was dissolved in deionised water (40 mL) at 25 °C. Dimethyl sulfate (1.69 mL, 2.25 g, 17.84 mmol) was added dropwise over 1 h while keeping the reaction mixture below 40 °C, and left to stir overnight. The white precipitate was filtered off *in vacuo*, and dimethyl sulfate (0.56 mL, 0.75 g, 5.95 mmol) was added to the filtrate, and left to stir for 5 days at 25 °C. The reaction was filtered *in vacuo* to afford a cream solid product **3** (1.46 g, 27 %). δ_H (400 MHz, $CDCl_3$, ppm) 7.13 (s, 2H, Ar-H), 4.69 (s, 4H, Ar-C$\underline{H_2}$OH), 3.82 (s, 3H, Ar-OC$\underline{H_3}$), 2.32 (s, 3H, Ar-C$\underline{H_3}$), 2.05 (s, br, 2H, Ar-CH$_2$O$\underline{H}$). δ_C (101 MHz, $CDCl_3$, ppm) 154.0, 134.3, 133.6, 129.5, 62.2, 61.0, 31.6, 22.7, 20.8, 14.1, 0.00. (m/z) 205.08 Da ($C_{15}H_{26}O_3NaSi$)

Synthesis of SI-8

Phenyl isocyanate (0.45 mL, 0.490 g, 4.12 mmol) was added to a stirred solution of **3** (0.30 g, 1.65 mmol) and 4-dimethylaminopyridine (20 mg, 0.16 mmol) in dry THF (20 mL) under a nitrogen atmosphere and left to stir for 4 h at room temperature. The mixture was diluted in ethyl acetate (30 mL), and washed with sat. ammonium chloride (30 mL) and sat. brine (30 mL). The ethyl acetate was extracted, dried over $MgSO_4$, filtered and the filtrate was concentrated i*n vacuo* to give a white solid product **5** (0.47 g, 68 %). δ_H (400 MHz, $CDCl_3$, ppm) 7.38 (m, 4H, Ar-H), 7.32 (m, 4H, Ar-H), 7.24 (m, 2H, Ar-H), 7.07 (m, 2H, Ar-H), 6.71 (s, br, 2H, N-H), 5.25 (s, 4H, Ar-C$\underline{H_2}$OH), 3.85 (s, 3H, Ar-OC$\underline{H_3}$), 2.32 (s, 3H, Ar-C$\underline{H_3}$). δ_C (101 MHz, $CDCl_3$, ppm) 155.1, 153.3, 137.7, 134.2, 131.6, 129.2, 129.1, 123.6, 120.5, 118.7, 63.0, 62.1, 20.8. (m/z) 443.16 Da ($C_{15}H_{26}O_3NaSi$).

S3 – Differential Scanning Calorimetry

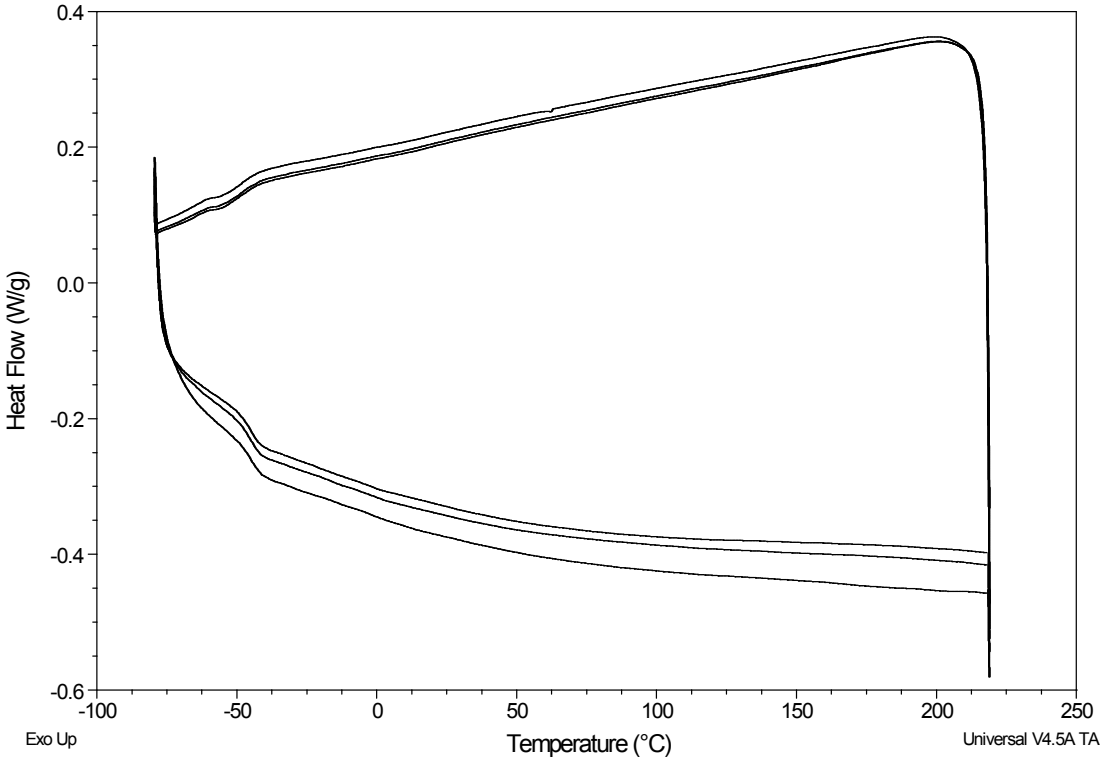


Figure S5 *Differential scanning calorimetry curves showing three heat-cool cycles as taken from the experiment.*

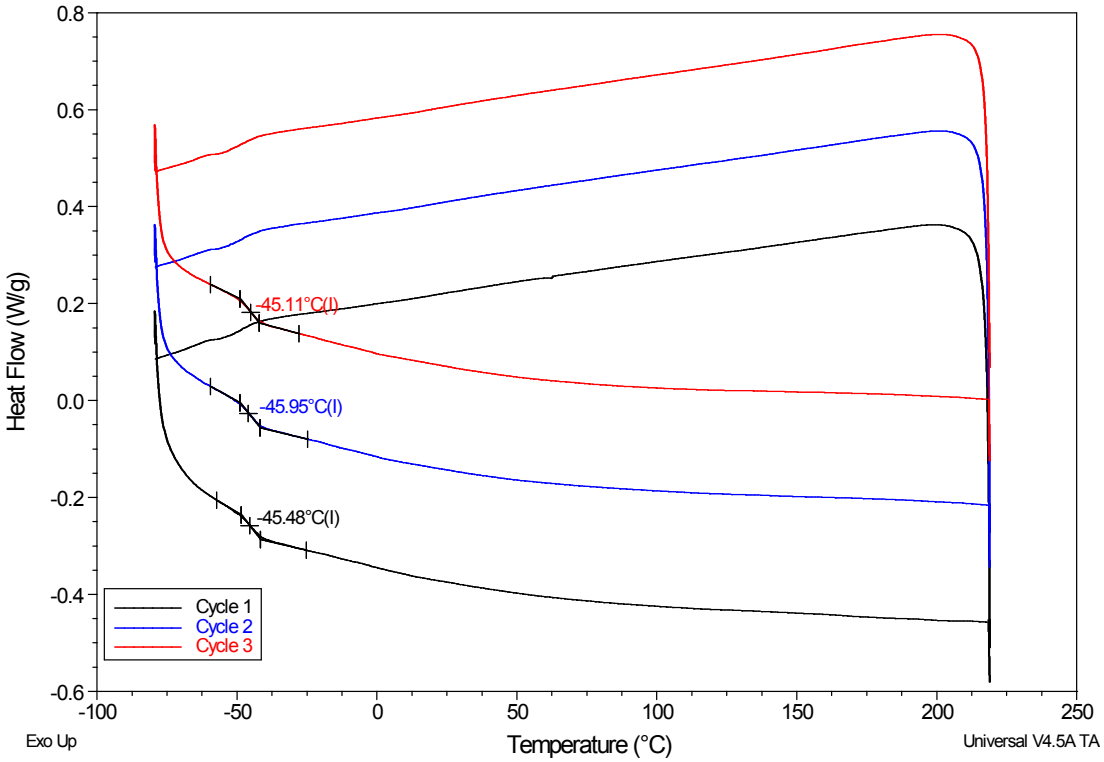


Figure S6 *Differential scanning calorimetry curves showing three heat-cool cycles separated to show the similarities in the glass transition temperature, T_g, between the three cycles.*

S4 – Rheometric Analysis and Dynamic Mechanical Analysis

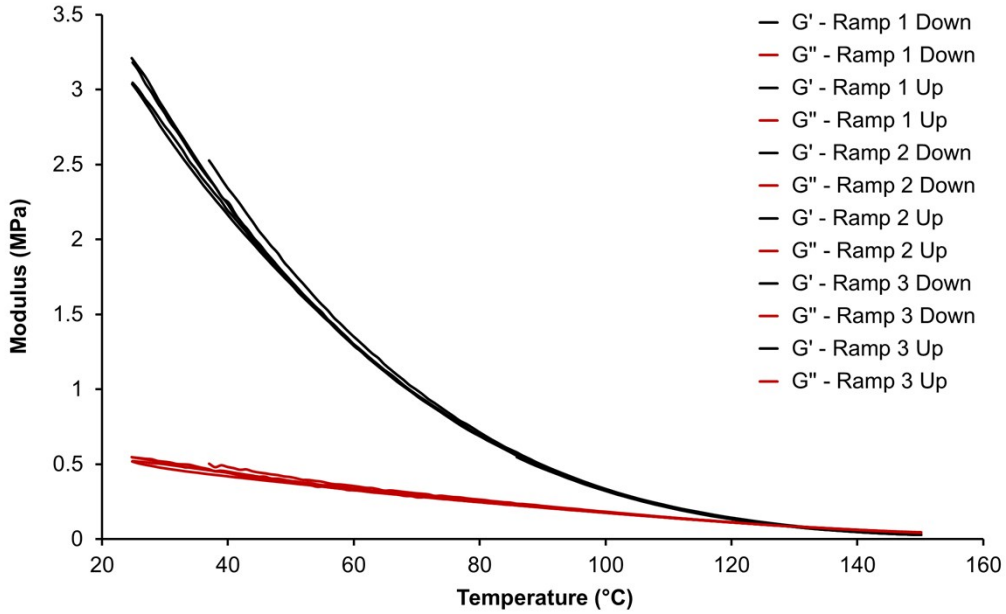


Figure S7 *Full rheometric analysis of the polymer over three cool-heat cycles showing the storage (G') and loss (G'') modulus.*

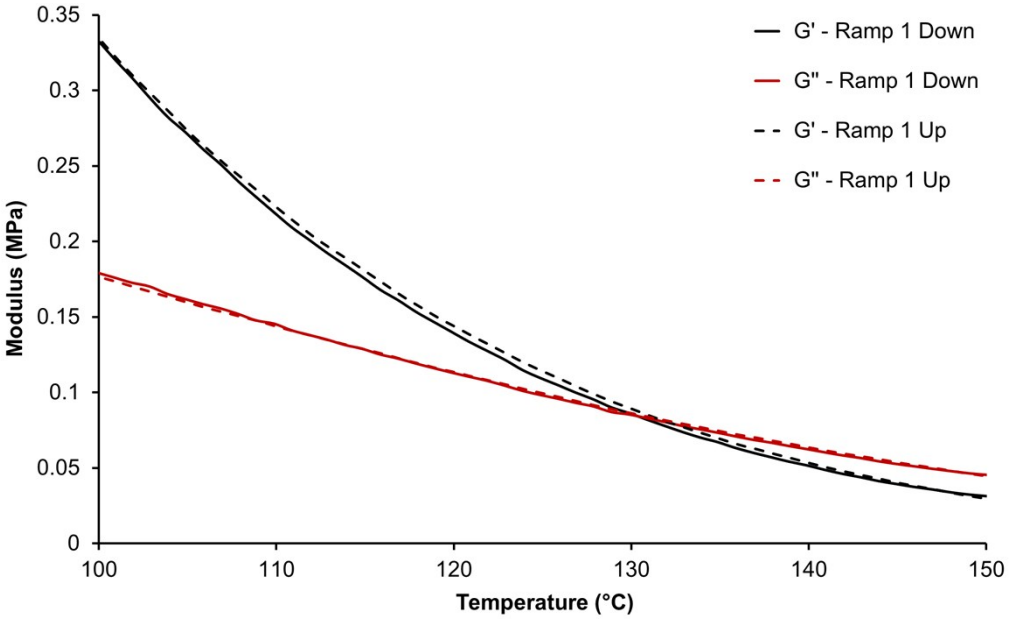


Figure S8 *First cool-heat cycle from the rheometric analysis, scaled to show the crossover of storage (G') and loss (G'') modulus.*

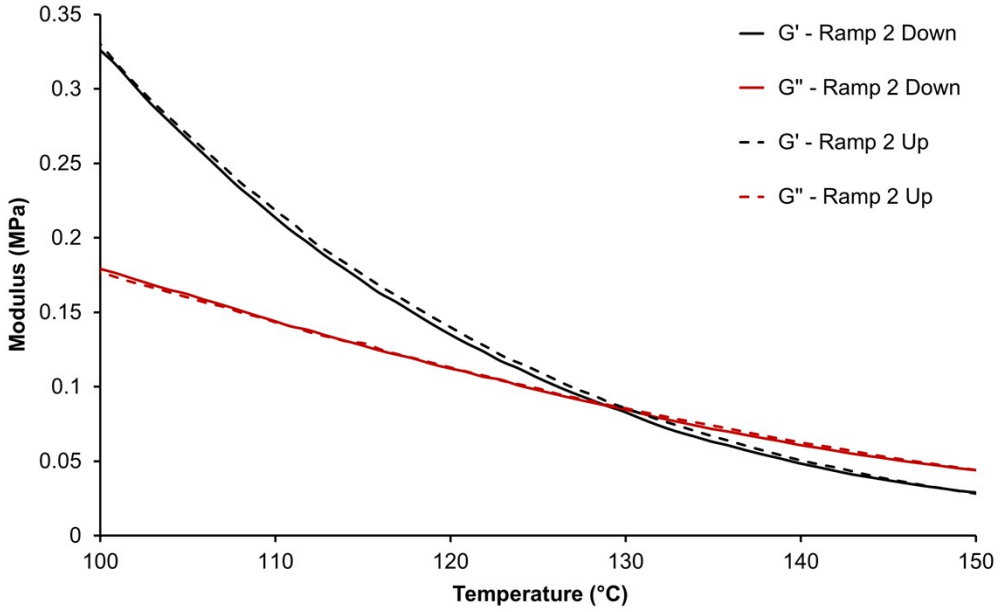


Figure S9 *Second cool-heat cycle from the rheometric analysis, scaled to show the crossover of storage (G') and loss (G'') modulus.*

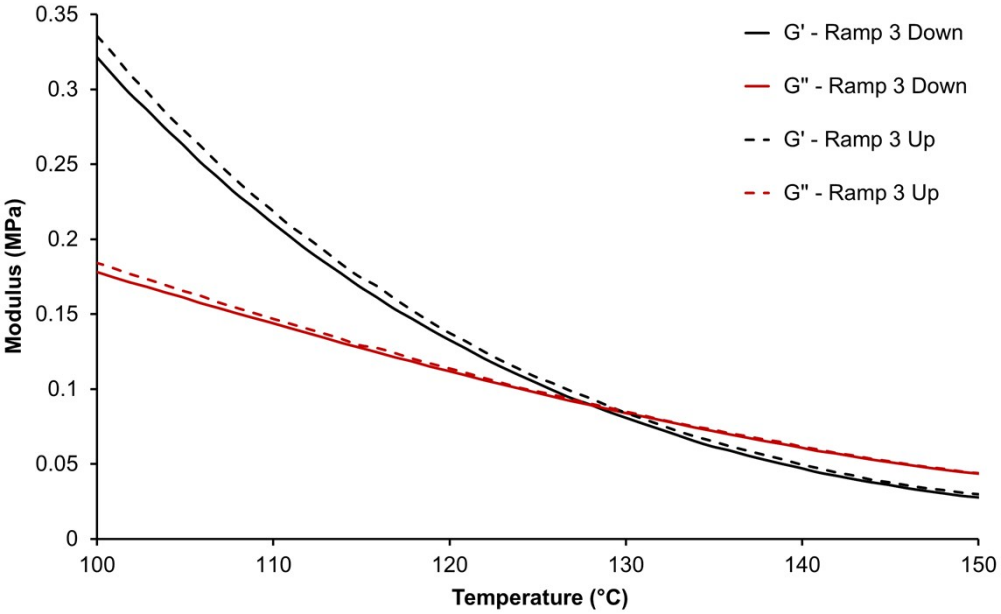


Figure S10 *Third cool-heat cycle from the rheometric analysis, scaled to show the crossover of storage (G') and loss (G'') modulus.*

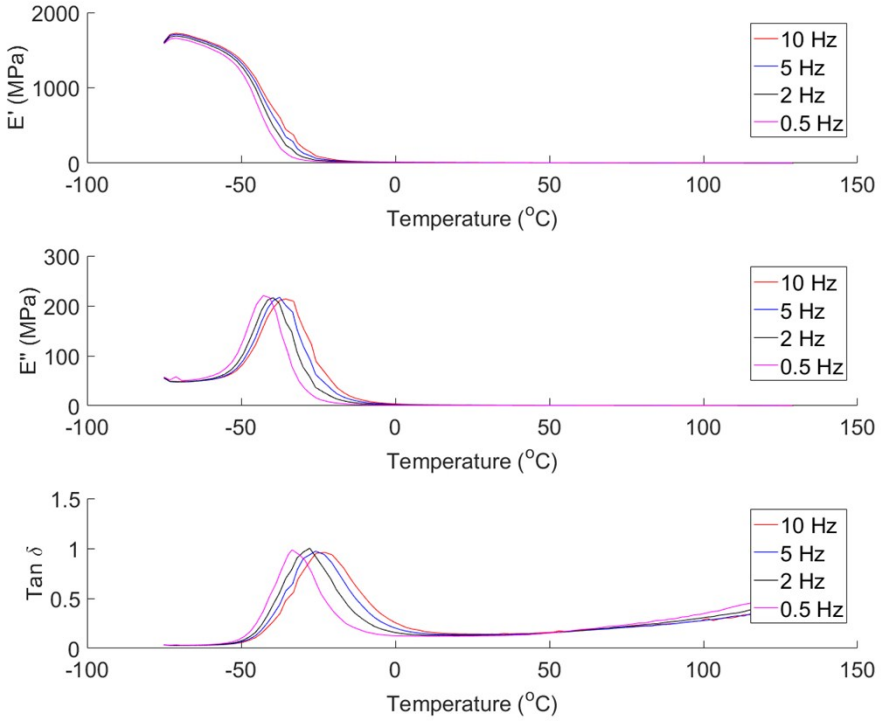


Figure S11 *Raw data from dynamic mechanical analysis of polymer **7** showing storage modulus (E'), loss modulus (E'') and Tan δ as a function of temperature, taken at different frequencies.*

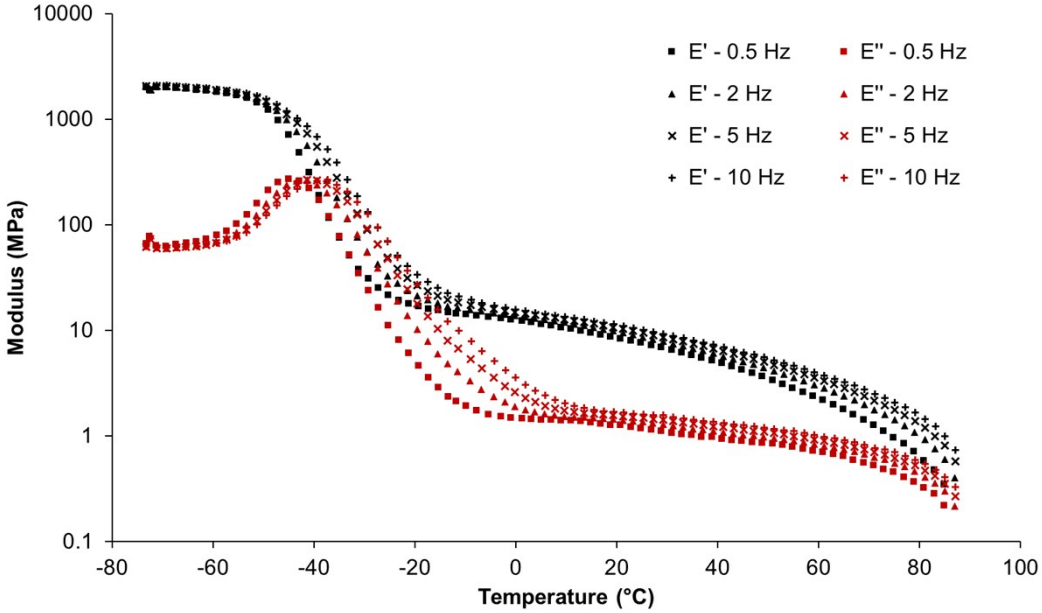


Figure S12 *Raw data of storage (E') and loss (E'') moduli superimposed taken at different frequencies, as a function of temperature.*

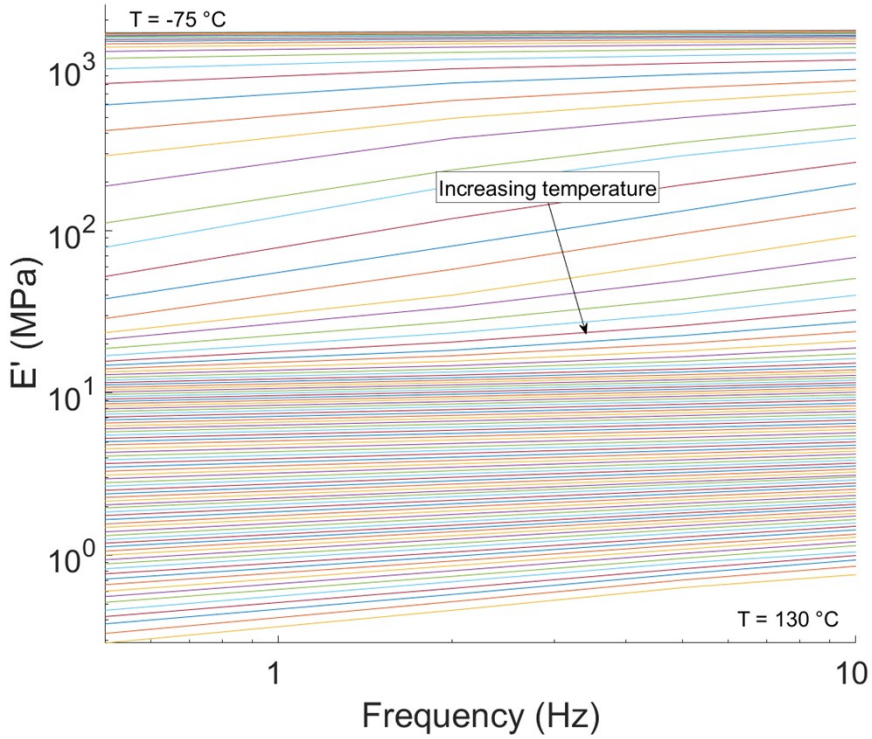


Figure S13 *Storage modulus of polymer **7** as a function of frequency for different temperatures.*

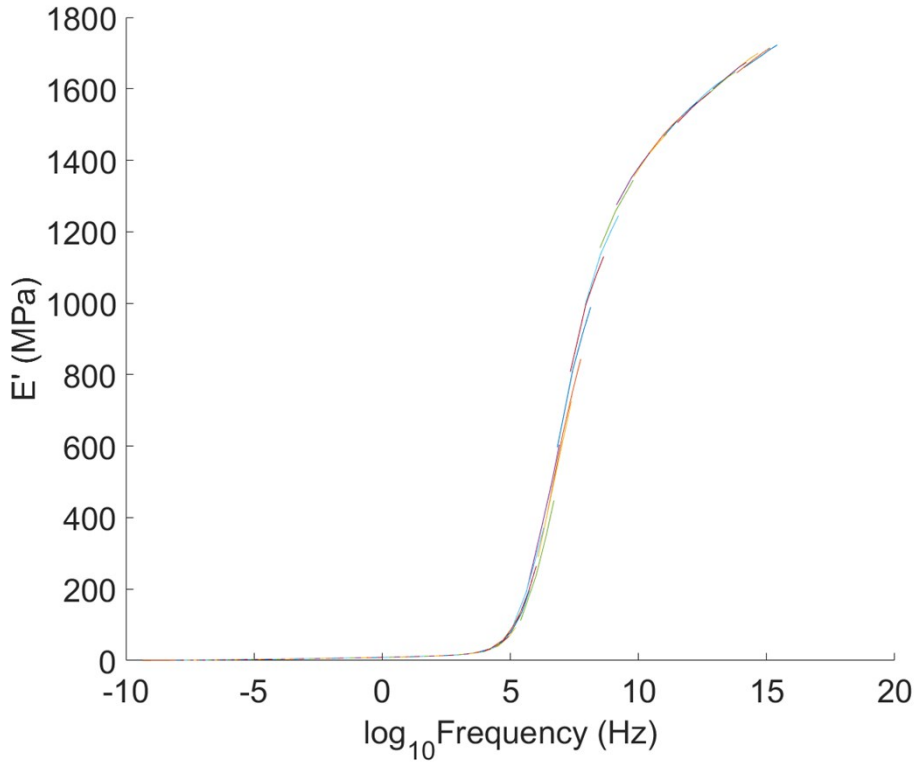


Figure S14 *Shifting the curves in Figure S13 by the calculated shift factors (see Figure S16) to form the master curve for the storage modulus. The same is done for loss modulus.*

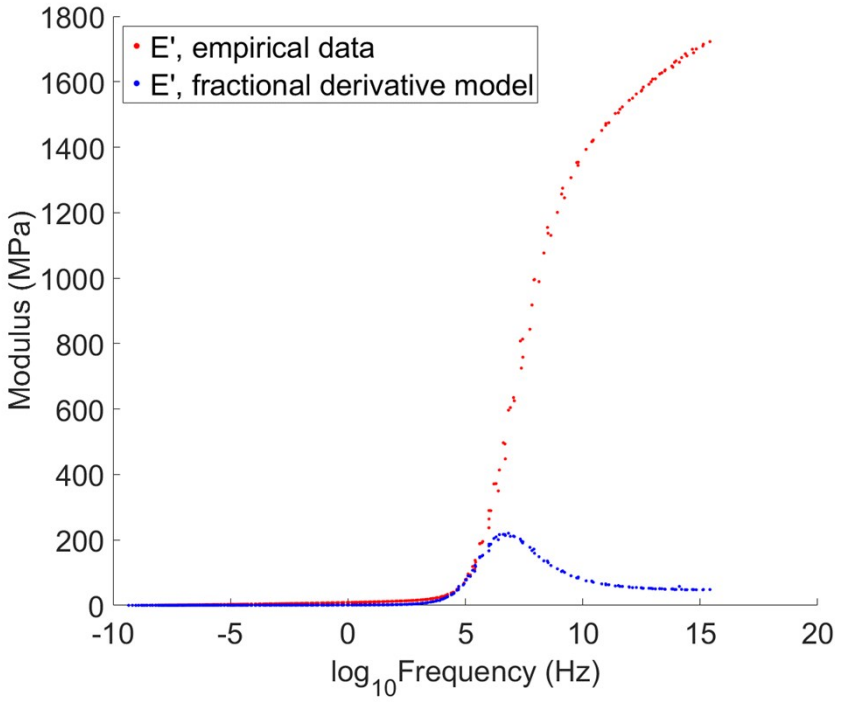


Figure S15 *Dynamic mechanical analysis of polymer **7** showing the change in storage (red) and loss (blue) moduli as a function of frequency.*

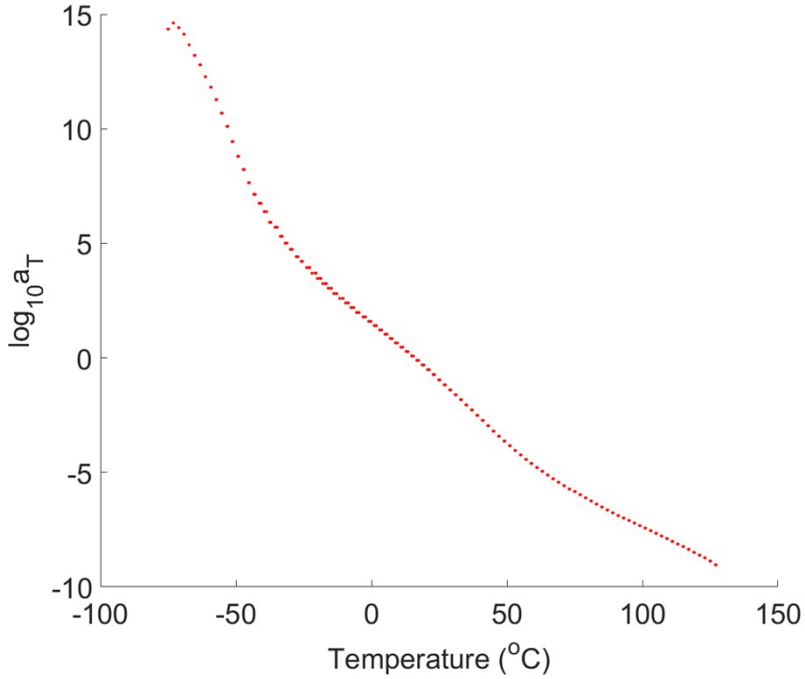


Figure S16 *Dynamic mechanical analysis of polymer **7** showing the shift factor required at each temperature to form master curves of the storage and loss moduli.*

S5 – Temperature dependant adhesive bond strengths

Samples were bonded between two steel nails and clamped together using "bulldog" clips (Figure S15) and heated at different temperatures for 30 minutes. Samples left at 80 °C fell apart as soon as the clips were removed, and hence no force to break was recorded for those samples. Samples left at 120 °C weakly bonded as the material had not completely melted after 30 minutes. The strongest samples were the ones left at 160 °C for 30 mins. The force to break the samples for each temperature dependant test are recorded in Figure S16.

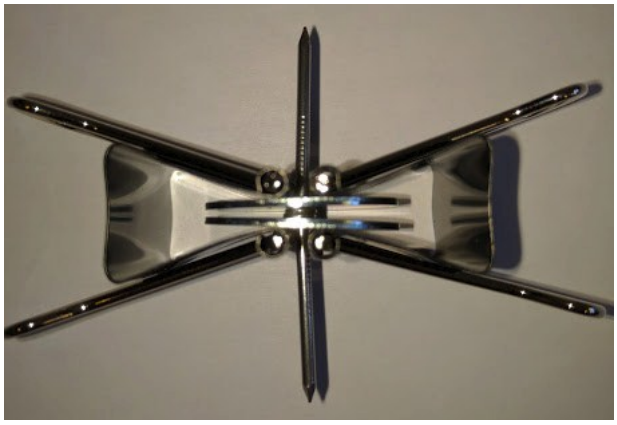


Figure S17 *Adhesion samples between two steel nails were prepared by clamping them head to head with 1.58 mm diameter circle sample between them. Washers were used to allow for larger surface area for the clips to clamp on to.*

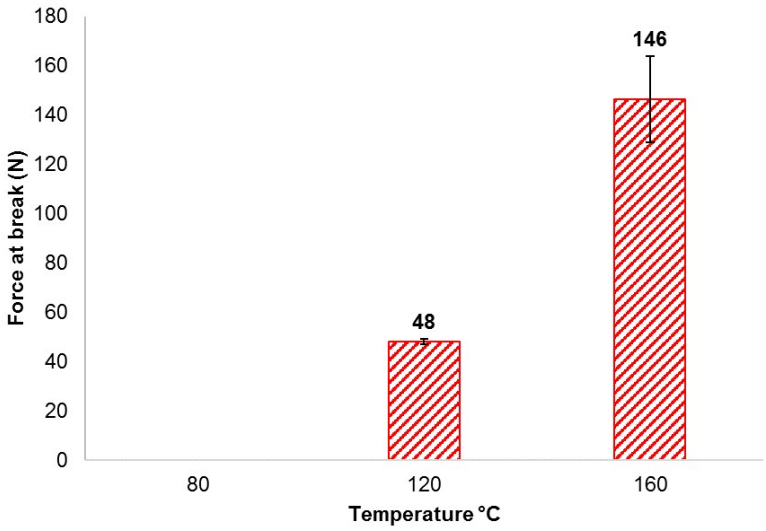


Figure S18 *Bond strengths as a function of bonding temperature.*

NMR spectra for characterisation

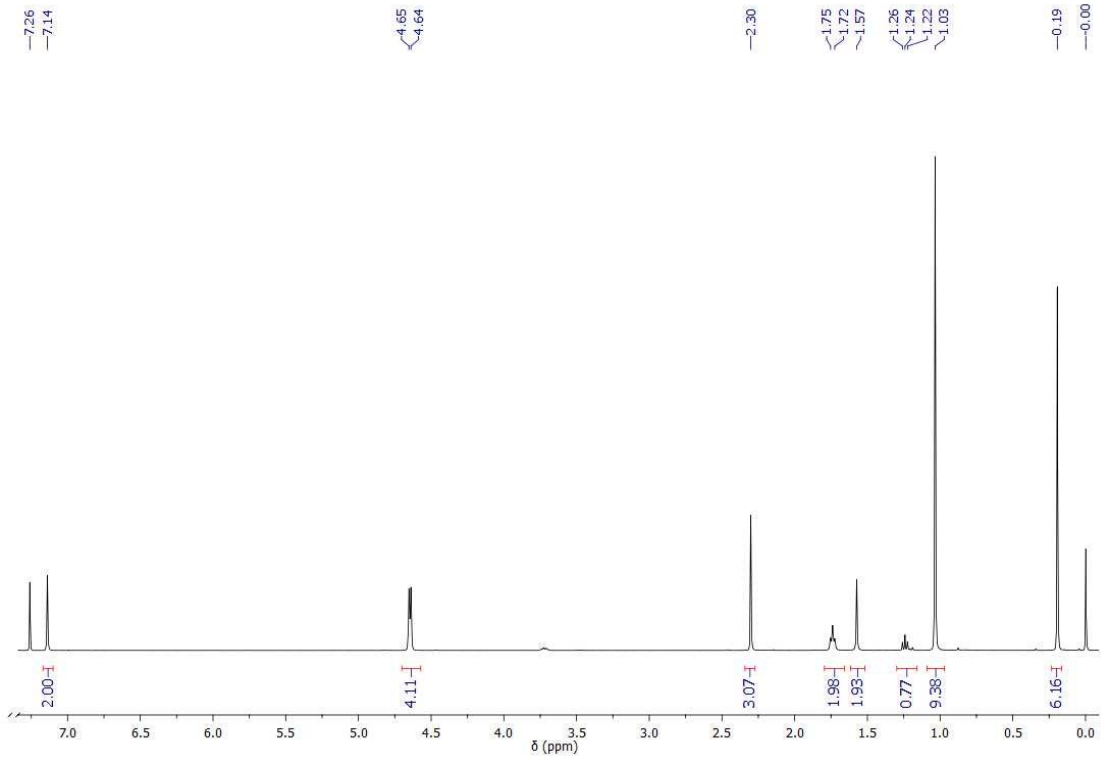


Figure S19 *^{1}H NMR spectrum of DU **1**.*

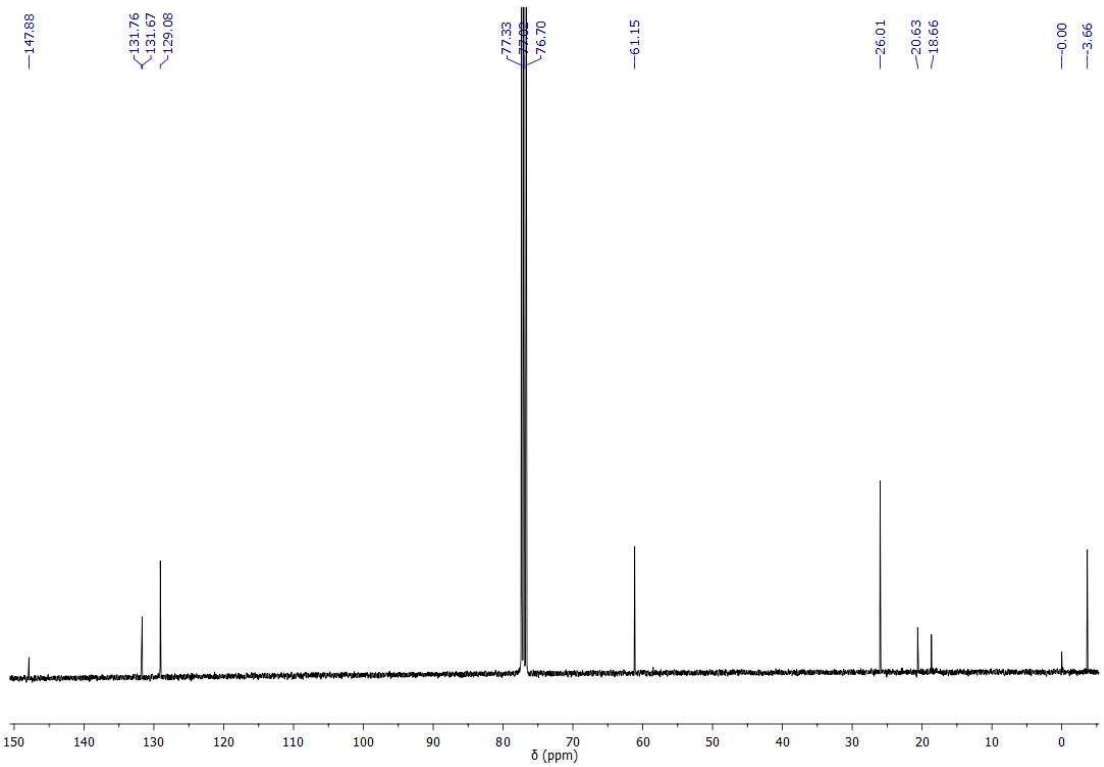


Figure S20 *^{13}C NMR spectrum of DU **1**.*

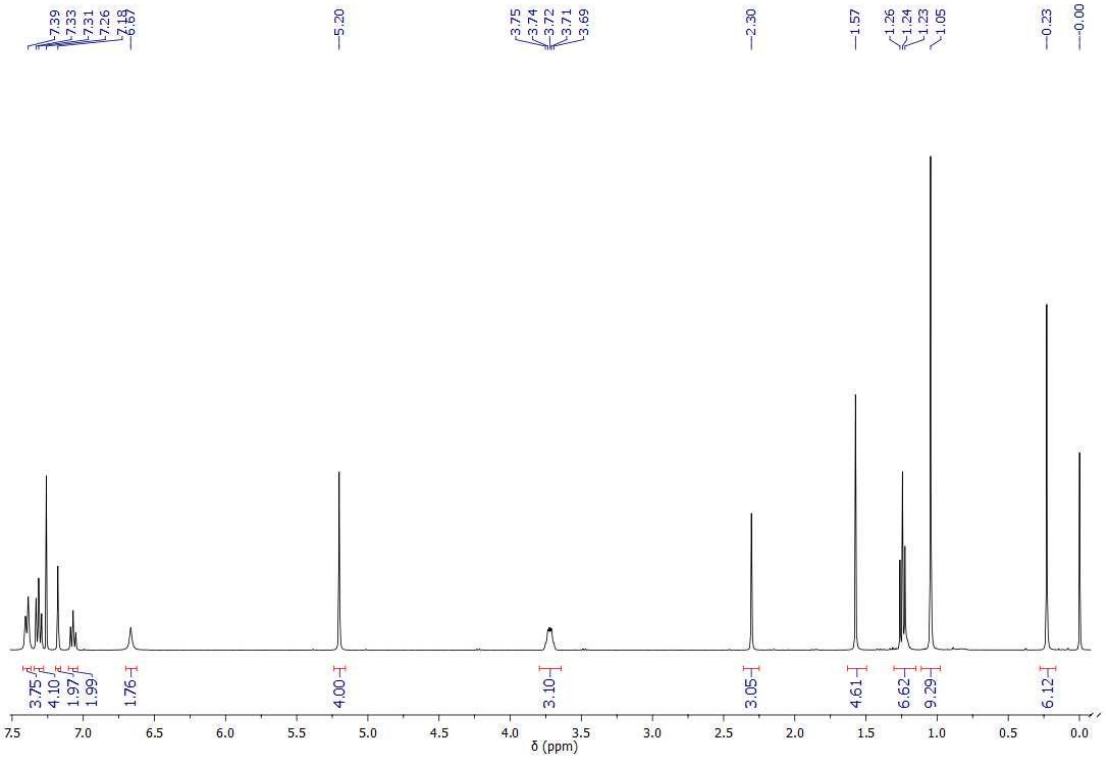


Figure S21 *^{1}H NMR spectrum of the model bisurethane compound **3**.*

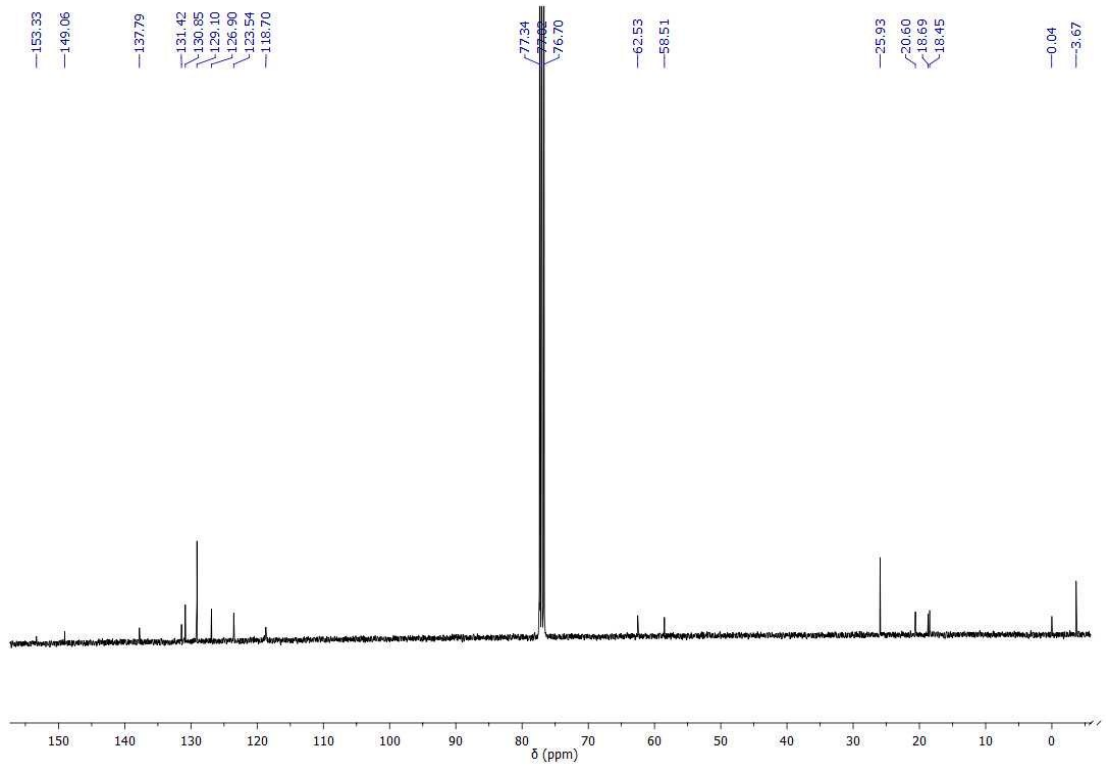


Figure S22 *^{13}C NMR spectrum of the model bisurethane compound **3**.*

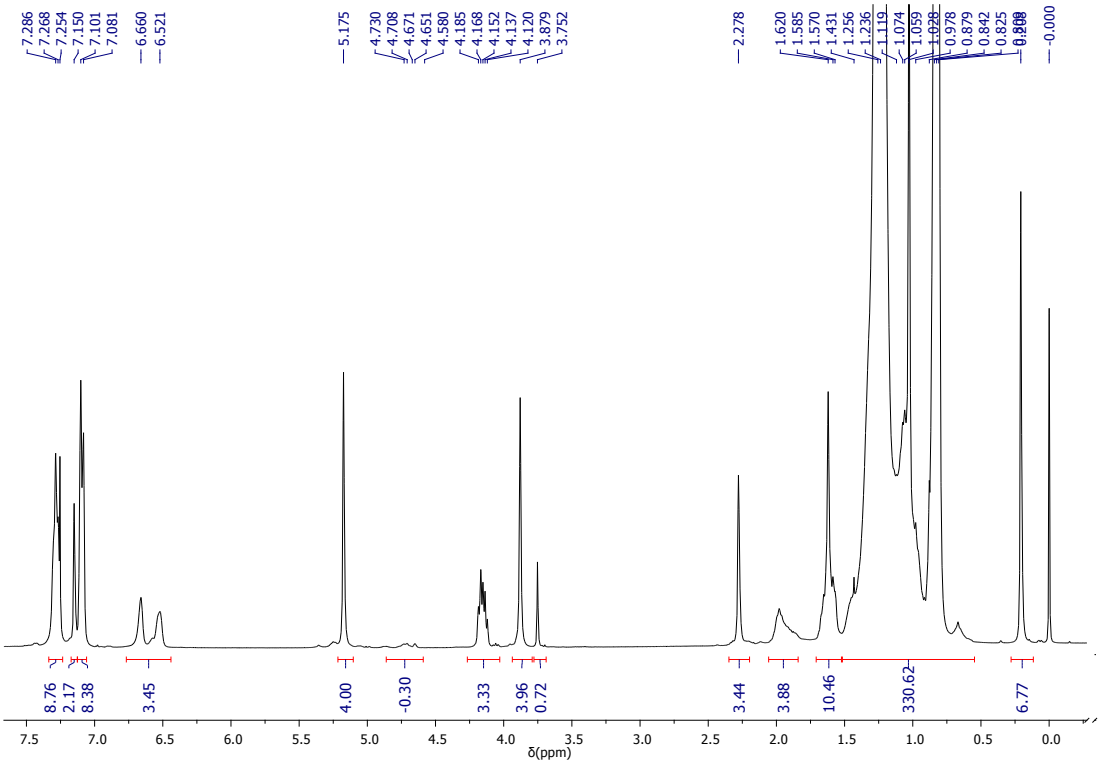


Figure S23 *^{1}H NMR spectrum of Polymer **7**.*

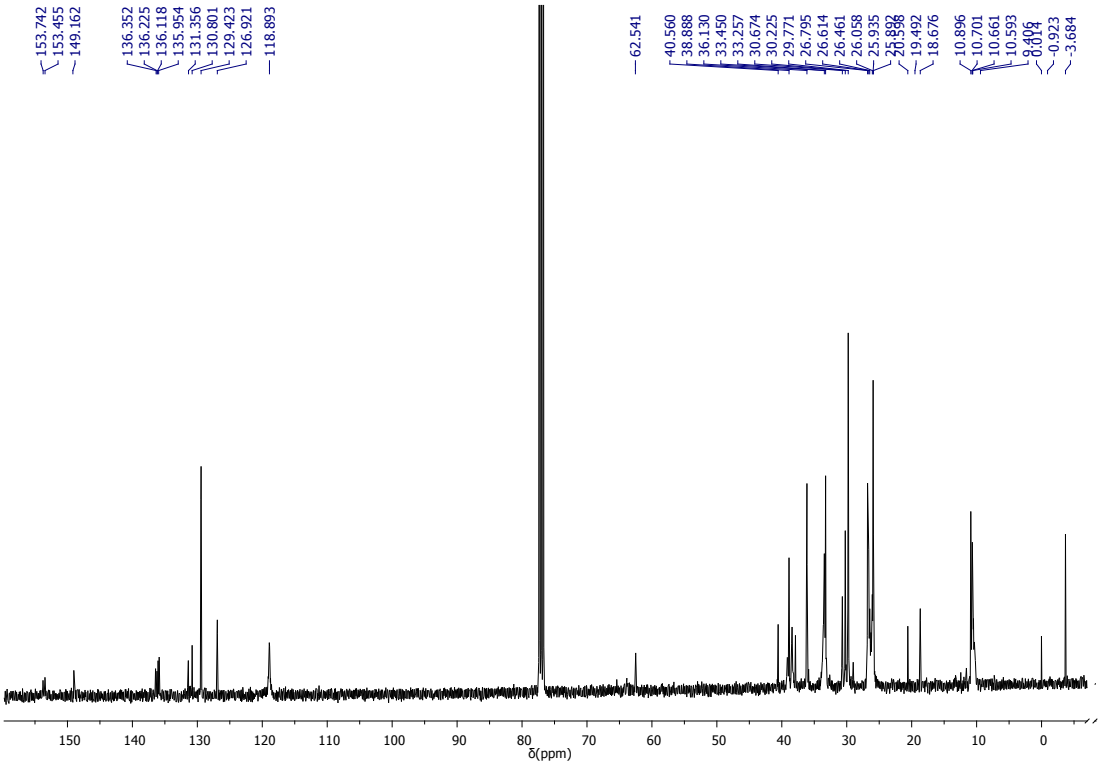


Figure S24 *^{13}C NMR spectrum of Polymer **7**.*

References:

(1) M. Shamis, H. N. Lode, D. Shabat. *J. Am. Chem. Soc.* 2004, **126**, 1726-1731
(2) I. S. Turan, E. U. Akkaya, *Org. Lett.* 2014, **16**, 1680–1683.