Electronic Supplementary Material

A Dynamic Supramolecular Polyurethane Network whose Mechanical Properties are Kinetically Controlled

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Experimental details

Sample preparation

Thin films of polyurethane **1** were produced for mechanical testing via a solution casting procedure. The polyurethane was dissolved in THF and the solution poured into a flat, PTFE-coated, mould. After a short period of air-drying, this was subsequently placed in a vacuum oven at 70 ºC with a pressure of approximately 0.6 to 0.8 bar for a duration of 16 hours. Thus producing a polyurethane film of uniform thickness between 200 and 500 μm without residual solvent.

To produce the quenched polyurethane **1** (QPU) sample, solution cast polyurethane **1** film, as described above, was completely melted at a temperature of 180 ºC, and then placed onto the flat surface of a cold metal, which acts as a heat reservoir to cool the melt quickly. Careful monitoring of the temperature showed that the molten polyurethane cooled to room temperature within three minutes. Thus, the obtained quenched polyurethane **1** was used for tensile testing, for peel test sample preparation, and tack tests. All of the annealing was carried out using the quenched polyurethane **1**.

To prepare the peel test specimen, quenched polyurethane **1** was placed between an aluminium plate (80 mm in length) and aluminium foil (with a foil thickness of 0.15 mm and width of 20 mm), and then the obtained sandwich structure was placed in a hot press under setting temperature, as indicated in the graphs in Figure 8, with a pressure of 0.5 MPa. The thickness of the polyurethane **1** was controlled by a spacer with a thickness of 0.1 mm. An image of the prepared peel test specimen can be found in Figure S14. Finally, excess polyurethane **1** was removed using a knife-blade, and the peel joints were tested within one day of manufacture.

Materials and characterisation methods

All chemicals and solvents were purchased from Sigma Aldrich and used as received. Krasol HLBH-P2000 was supplied by Cray Valley. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker Nanobay 400 or a Bruker DPX 400 spectrometer operating at 400 MHz for ^{1}H NMR or 100 MHz for ^{13}C NMR. The samples for NMR spectroscopic analysis were prepared in $CDCl_3$ (50 mg/mL) and dissolution was aided with slight heating. The data was processed using MestReNova Version 7.0.2-8636. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ_H 0.00 ppm) for ^{1}H NMR spectra and to chloroform (δ_C 77.0 ppm) for the ^{13}C NMR assignment, coupling constants (*J*) are expressed in Hertz (Hz). Differential scanning calorimetric analysis used a TA Instruments DSC 2920 and a three cycle process was carried out on the solid sample; heating from ambient to +100 ºC at a ramp rate of 10 ºC min^{-1}, followed by cooling from +100 ºC to -70 ºC at a ramp rate of -20 ºC min^{-1} and then finally by heating from -70 ºC to +200 ºC at a ramp rate of +20 ºC min^{-1}. The sample size used was 8-15 mg and the data was processed using TA Universal Analysis Version 4.7A. Infrared spectroscopic analysis employed a Perkin Elmer 100 FT-IR spectrometer equipped with a diamond ATR sampling attachment and samples were analysed in neat form. Variable temperature infrared spectra were recorded using a Specac accessory, the sample was dissolved in THF before applying a thin layer to a KBr disc, once dry another KBr disc was placed on top so that a thin film of the sample is entirely encased. This was placed into the Specac accessory holder and the temperature raised gradually in 10 °C increments. The spectra were recorded in transmission mode using 16 scans per acquisition. The infrared spectroscopic data was processed using OMNIC and Microsoft Excel 2013 software. Gel permeation chromatography (GPC) was conducted using an Agilent Technologies 1260 Infinity and the data was processed using Agilent GPC/SEC software, polystyrene was used

as the calibrant. Samples for GPC analysis were dissolved in analytical grade THF containing BHT (250 ppm) (2 mg/mL).

Testing protocols

Dynamic rheological testing: Parallel plate oscillatory shear was performed with an Anton Paar Physica MCR 301 rheometer, on circular samples (two types with diameter of 25 mm and 8 mm) that were obtained from the solution cast film using a steel punch cutter. The heat treatments, such as melting, quenching, and annealing were controlled directly on the plate of the rheometer. To carry out the quenching procedure, the maximum cooling rate was employed (with an average cooling rate of 15 ºC/min). The temperature sweep was carried out at a single frequency of 5 Hz and strain of 0.1%. For the constant shear rate test, the shear rate was 5 s^{-1}.

Tensile testing: The tensile tests were carried out using an Instron universal testing machine (model 5982) with a 100 N load cell. A constant true strain rate of 0.04 s^{-1} was used, for purposes of controlling the experiment (but not subsequent data analysis), this was calculated from the cross-head displacement. At least five samples were tested for each material type. In order to obtain accurate full-field displacement and strain data, the Digital Image Correlation technique was used. The surface of the sample was painted with both white and black spray paint in order to create a random speckle pattern. During each test, a digital camera (Point Gray GS3-U3-41C6C-C with a Micro-NIKKOR 105 mm lens), was used to record images of the specimen surface at a rate of 5 frames per second. Approximately a hundred images were thus created before specimen failure. The obtained images were analysed by commercially available image correlation software (DaVis StrainMaster Software 7.2) in order to extract displacement and strain maps on the specimen surface. The size of the test sample was 40×5×0.5 mm, which was cut directly from the solution cast polyurethane **1** film. The mean

strain was combined with force data from the Instron testing machine to generate stress-strain curves.

Modulated differential scanning calorimetry test (MDSC): Thermal characterisation was conducted using a TA Q2000 DSC with a standard heating ramp of 2 ºC min^{-1}. A modulation period of 60 s and a modulation temperature amplitude of 1 ºC min^{-1} were used.

VT-FTIR spectroscopic analysis: Variable temperature infrared spectroscopic analyses were conducted using a Perkin Elmer 100 FT-IR spectrometer equipped with a Specac variable temperature sample holder. A thin film of polyurethane **1** (~ 0.2 mm thick) was placed inside the sample holder, the temperature was equilibrated at 30 °C until stable and the first spectra acquired. Subsequently the temperature was raised in 10 °C increments and the spectra acquired once the temperature was stable (after around 5 minutes).

SAXS experiments were performed on BM26B (DUBBLE) at the ESRF. Samples were mounted in modified DSC pans and placed in a Linkam hotstage for controlled variable temperature SAXS/WAXS experiments. The sample was sandwiched in the modified DSC pans between two mica windows with a 1 mm Teflon spacer. The sample to SAXS detector distance was 3.16 m using a wavelength of 1.033 Å. A Dectris-Pilatus 1M detector was used to acquire the 2D SAXS scattering patterns and diffraction from silver behenate were used to calibrate the wavevector scale of the scattering curve. The SAXS data were normalized to the intensity of the incident beam (in order to correct for primary beam intensity fluctuations) and were corrected for absorption and background scattering. WAXS patterns were collected using a Pilatus 300 K-W (linear, 254 mm × 33.5 mm active area) with a pixel size of 172 μm^2. The wavenumber $q = 4\pi/\lambda \sin\theta$ scale calibration for WAXS experiments scale was achieved using alpha aluminium. [1,2]

Thermogravimetric analysis (TGA): Thermogravimetric analysis employed a TGA Q50 instrument by heating the solid samples (sample size *ca*. 20 mg) from ambient temperature to +300 ºC at a ramp rate of +10 ºC min^{-1}. The data was processed using TA Universal Analysis Version 4.7A.

Peel tests: The peel test was carried out at ambient conditions (20 ±2 ºC). The peel specimen was rigidly bolted to an almost frictionless sliding trolley on the crosshead of a universal testing machine, as shown below in Peel Testing Protocol. The free end of the flexible peel arm was bent to an applied peel angle of 90° and connected to the load cell via a loading rod and grip. The peel test was conducted by setting the machine in motion at a constant speed of grip separation, thus the displacement of the movable end of the test machine was equivalent to the fracture length for a peel angle of 90° with the speed of 50 mm/min. During the test, the peel force was recorded as a function of the displacement of the crosshead to initiate and propagate a peel fracture. An initiation region can be observed where the peel force rises steeply before the measured force settles to an approximately constant value during crack propagation, but in the peel tests curve, only the steady-state peel propagation region was shown. The average value of the force over this propagation region was calculated, and was used to determine the values of the adhesive fracture energy.

Tack test: The tack test was carried out using Anton Paar Physica MCR 301 rheometer with a flat surface. The default test template with the separation speed of -5 mm/s was adopted. The thickness of the test sample was 0.8 mm with the diameter of 8 mm, and during the test, the loading force and displacement were recorded.

Polyurethane 1 Synthesis

Methylene diphenyl diisocyanate (10.1 mmol, 2.52 g) was added to Krasol HLBH-P2000 (4.8 mmol, 10.06 g), and the mixture was stirred for 3 hours at 80 °C under a nitrogen atmosphere after which dry THF (80 mL) was added. The reaction was left to cool to room temperature, dibenzylamine (2.1 mmol, 2.08 g) was then added, and the mixture was stirred for 1 h at 50 °C. THF was then removed *in vacuo*, and the product was purified by multiple slow precipitation in methanol and dried *in vacuo*. The product was isolated as an elastomeric white solid (12.76 g, 89%). T_g = -43.9 °C, small T_m = 103.0 °C. FTIR (ATR) ν_{max}, cm^{-1} 3325, 2960, 2918, 2862, 2850, 1721, 1700, 1632, 1596, 1525, 1495, 1498, 1413, 1386, 1380, 1378, 1307, 1306, 1233; ^{1}H NMR (δ_H ppm; 400 MHz; $CDCl_3$) 0.66-1.98 (337H, *m*), 3.85 (4H, $_{apt}t$, $_{obs}J$ = 13.0), 4.12-4.18 (4H, *m*), 4.59 (8H, *s*), 6.25 (2H, *br*), 6.50 (2H, *br*), 6.98-7.38 (36H, *m*); ^{13}C NMR (δ_C ppm; 100 MHz; $CDCl_3$), 10.91, 25.91, 26.62, 26.80, 29.79, 30.23, 30.70, 33.26, 33.45, 36.14, 37.90, 38.42, 38.89, 40.55, 50.76, 63.78, 65.36, 118.84, 120.16, 127.34, 127.77, 128.15, 128.41, 128.97, 129.22, 129.35, 129.39, 135.97, 136.04, 136.11, 136.18, 136.33, 136.87, 136.95, 137.20, 153.727, 156.00; GPC (THF), M_w 14303, M_n 7303, $Đ_M$ 1.96.

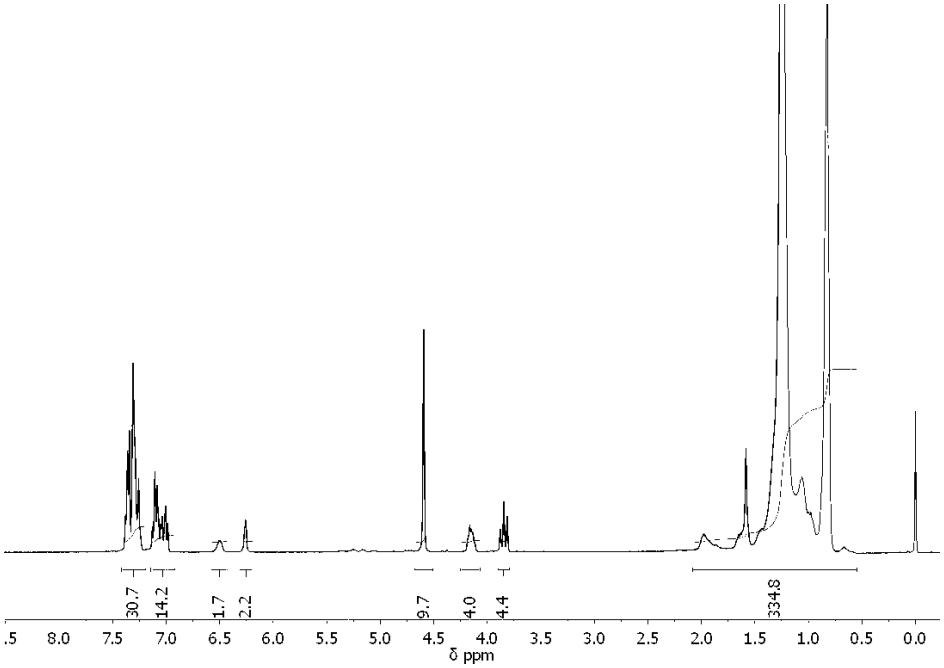

Figure S1. ^{1}H NMR of polyurethane **1** in $CDCl_3$ at 25 °C.

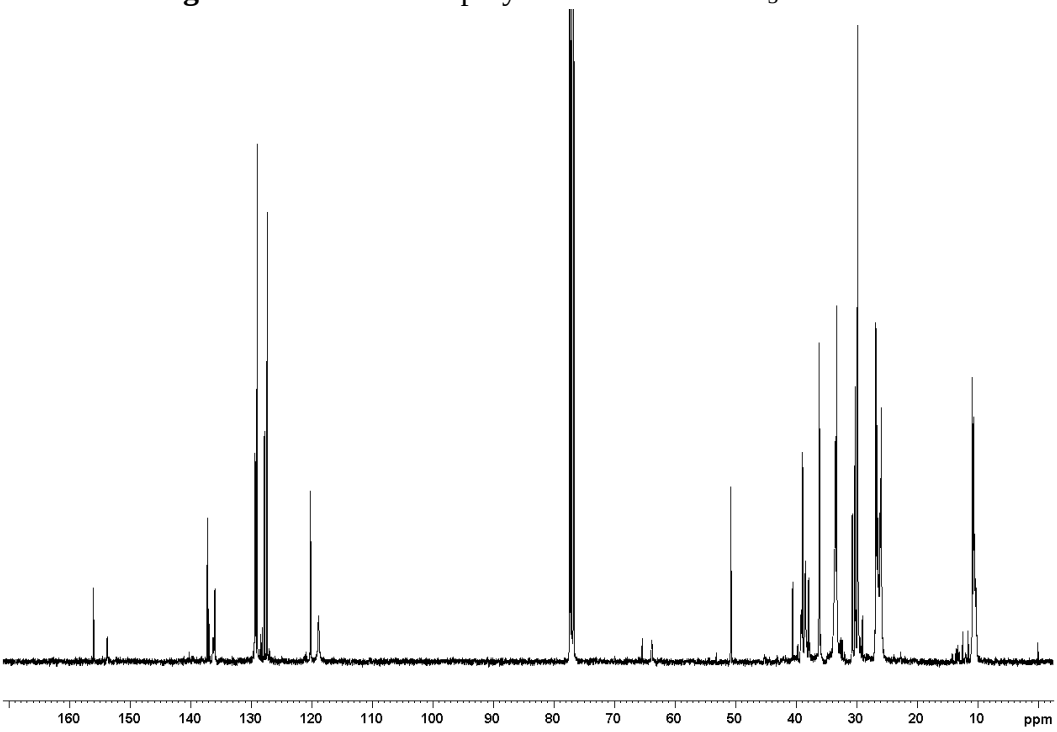

Figure S2. ^{13}C NMR of polyurethane **1** in $CDCl_3$ at 25 °C.

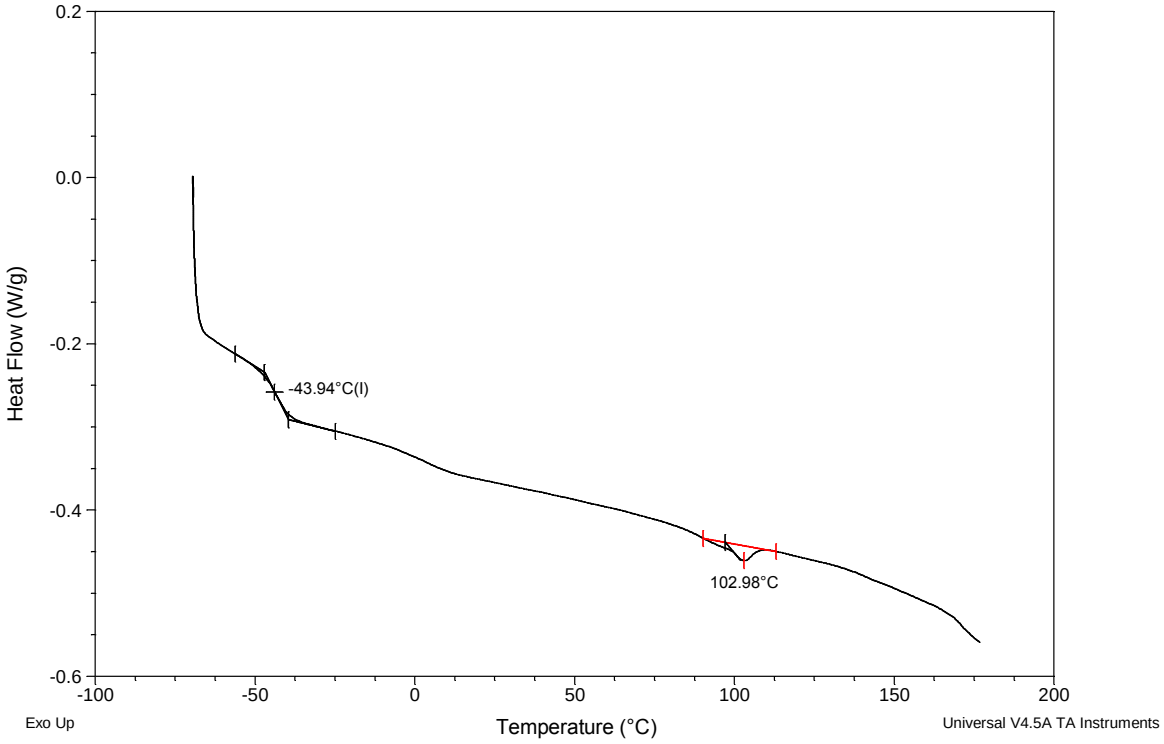

Figure S3. DSC curve of polyurethane **1**, showing the second heating ramp of a heat/cool/heat cycle.

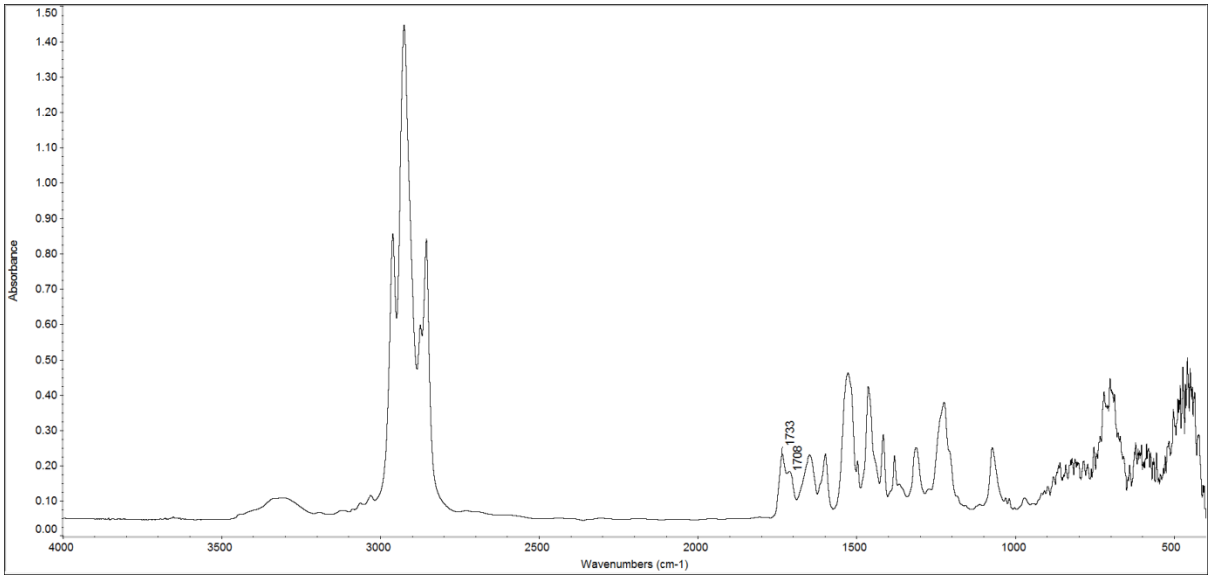

Figure S4 (a). FTIR of polyurethane **1** at 30 °C.

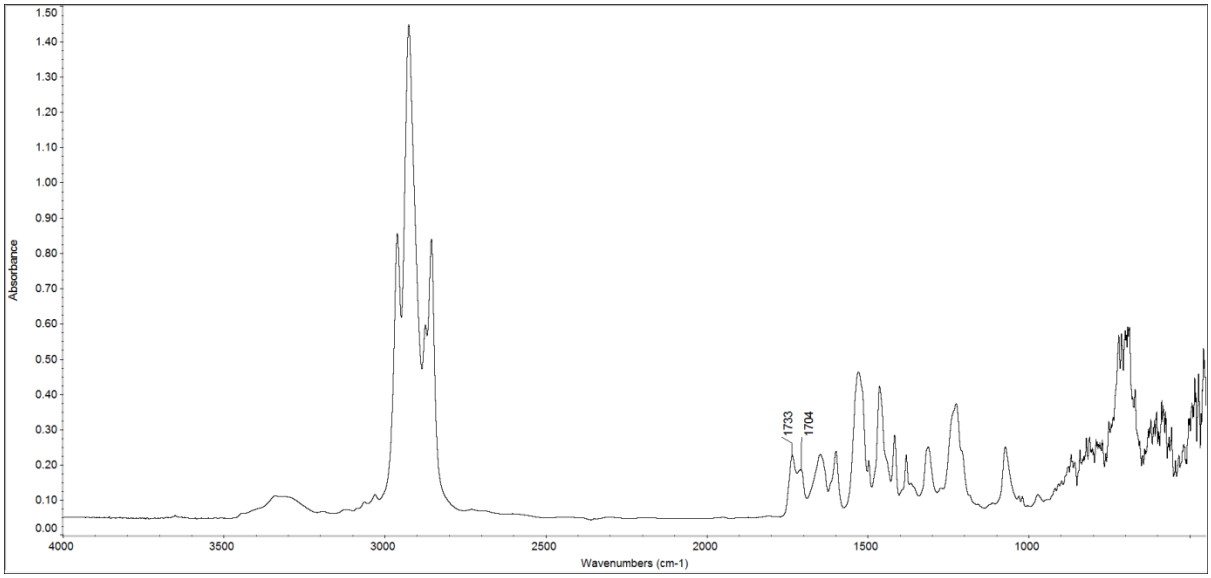

Figure S4 (b). FTIR of polyurethane **1** at 40 °C.

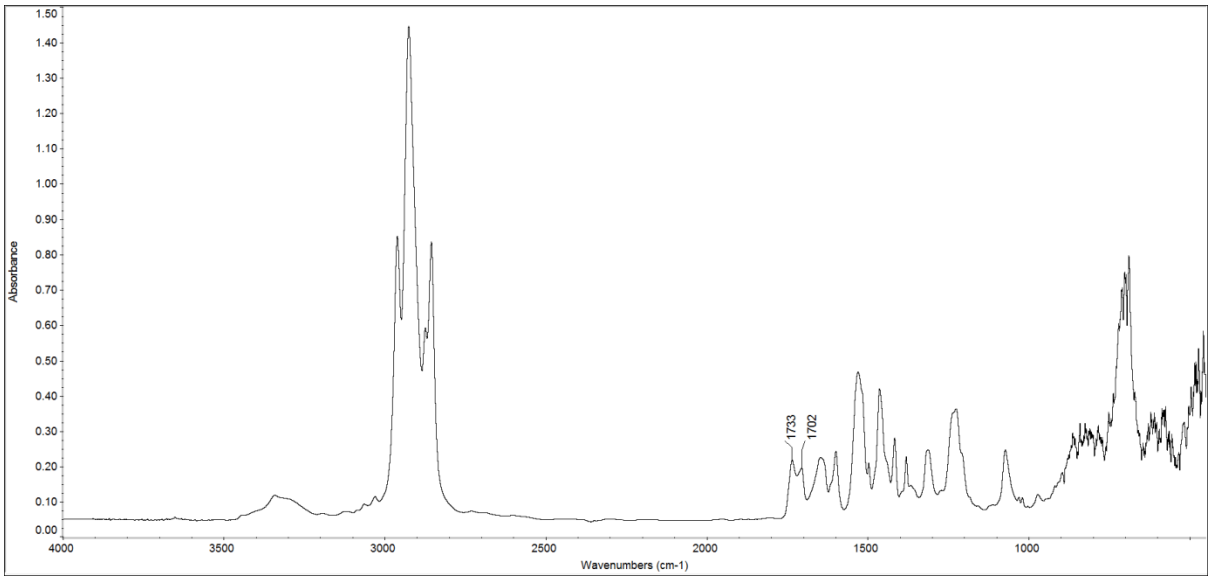

Figure S4 (c). FTIR of polyurethane **1** at 50 °C.

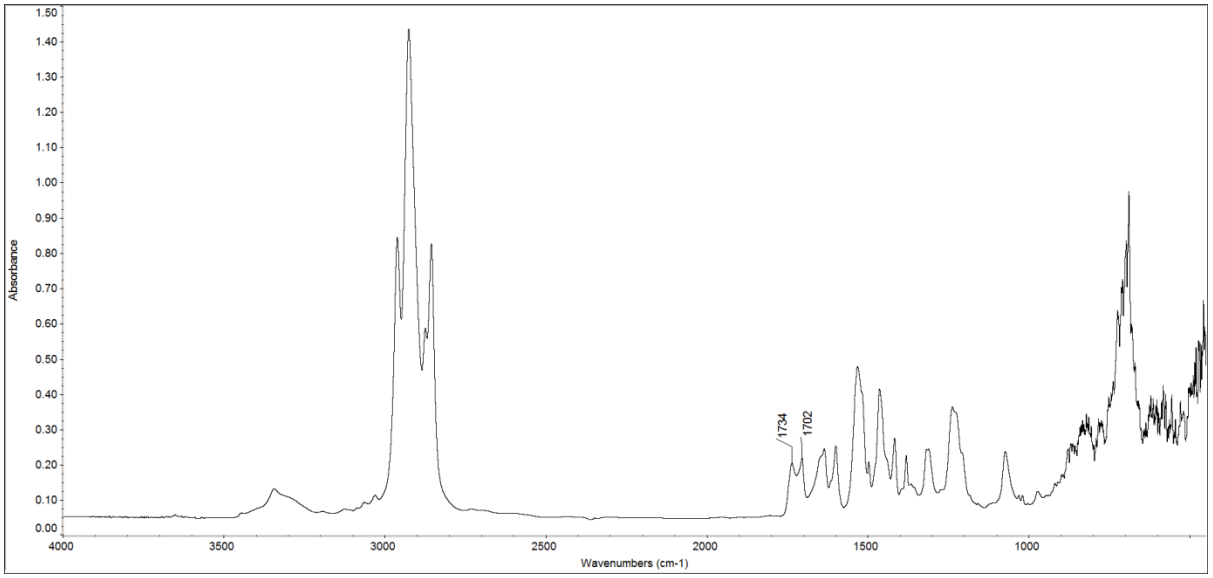

Figure S4 (d). FTIR of polyurethane **1** at 60 °C.

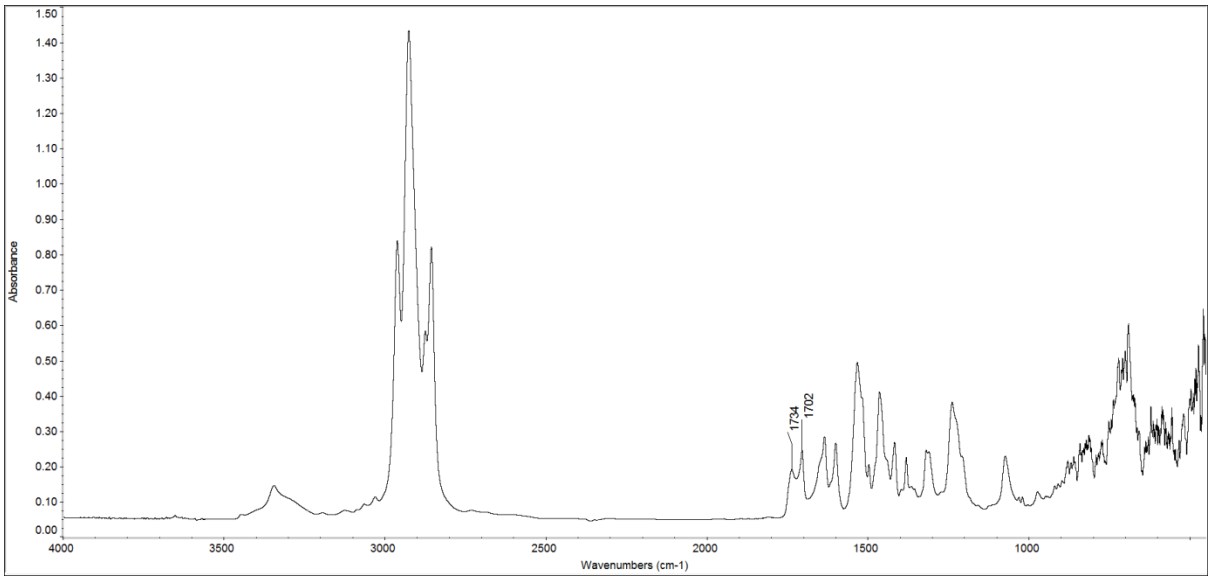

Figure S4 (e). FTIR of polyurethane **1** at 70 °C.

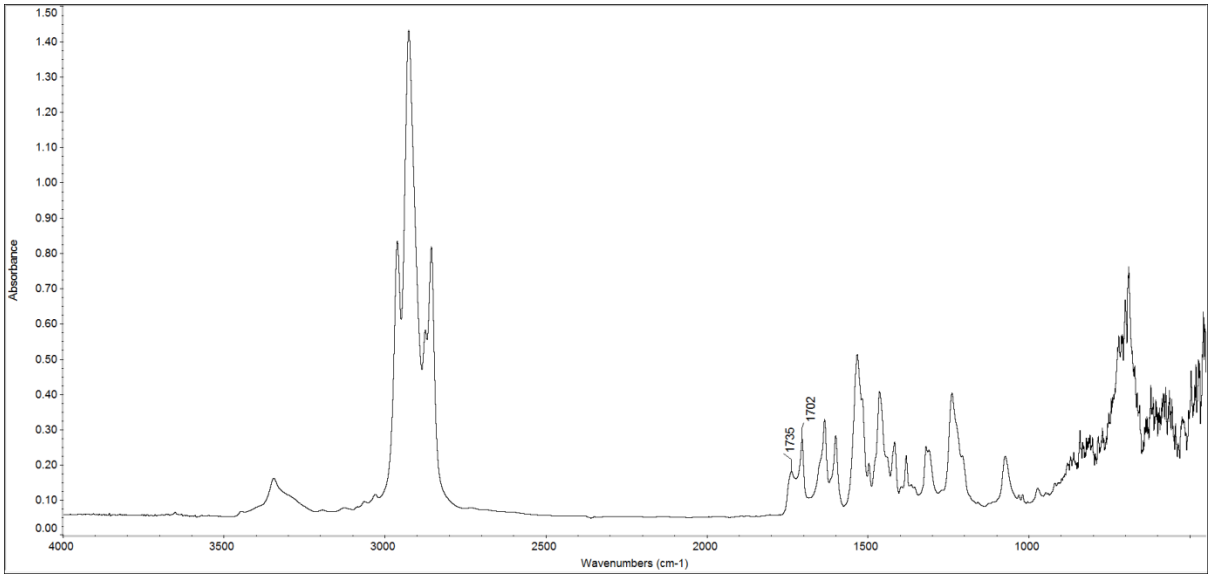

Figure S4 (f). FTIR of polyurethane **1** at 80 °C.

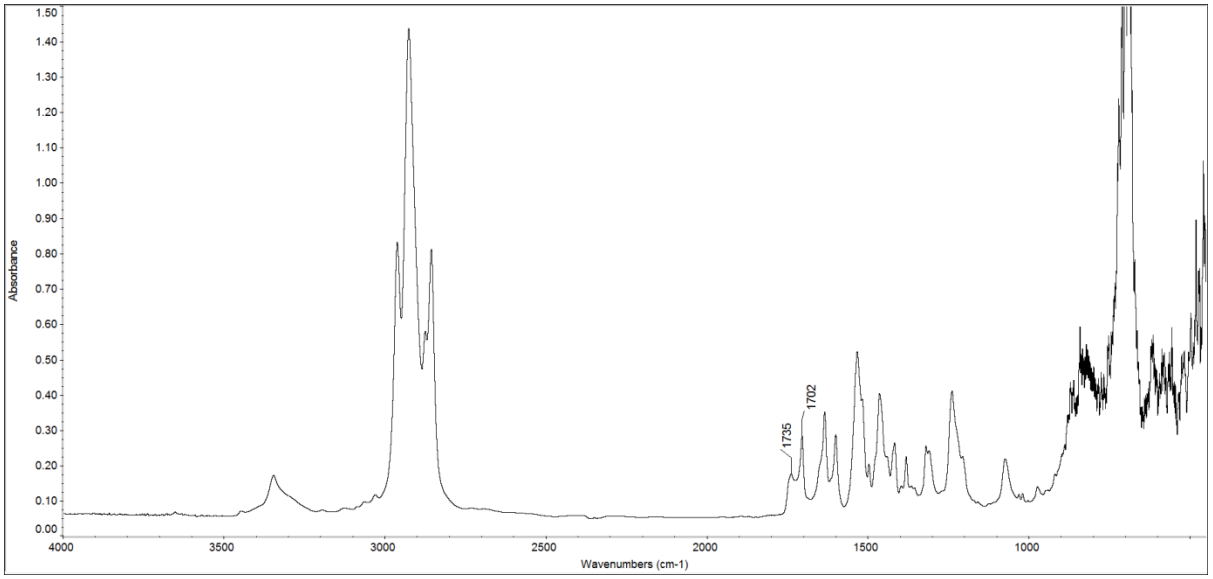

Figure S4 (g). FTIR of polyurethane **1** at 90 °C.

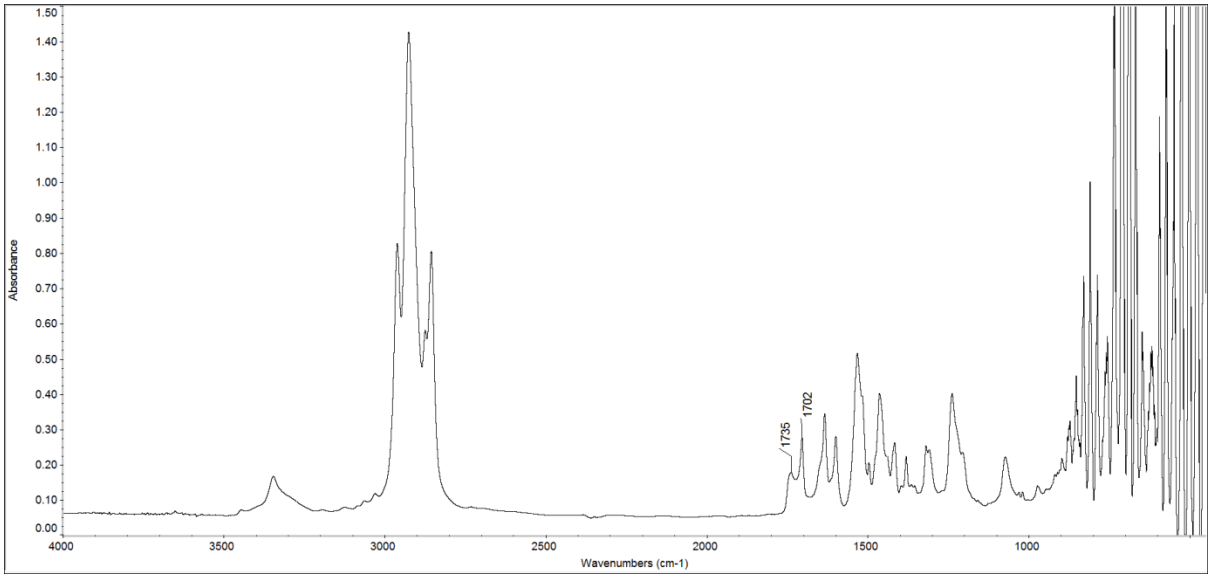

Figure S4 (h). FTIR of polyurethane **1** at 100 °C.

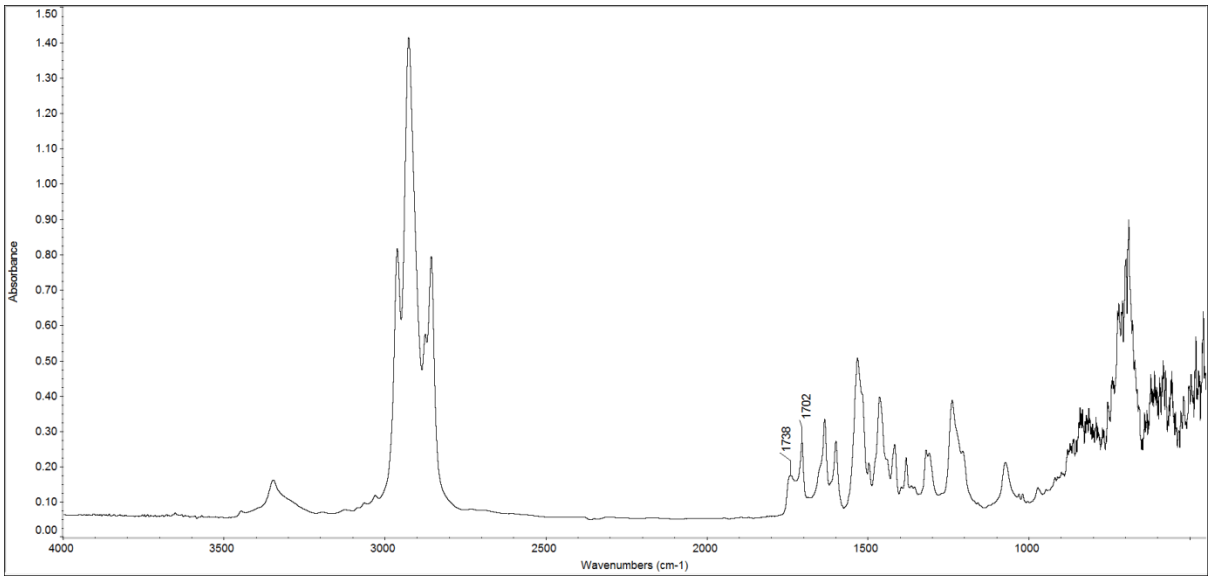

Figure S4 (i). FTIR of polyurethane **1** at 110 °C.

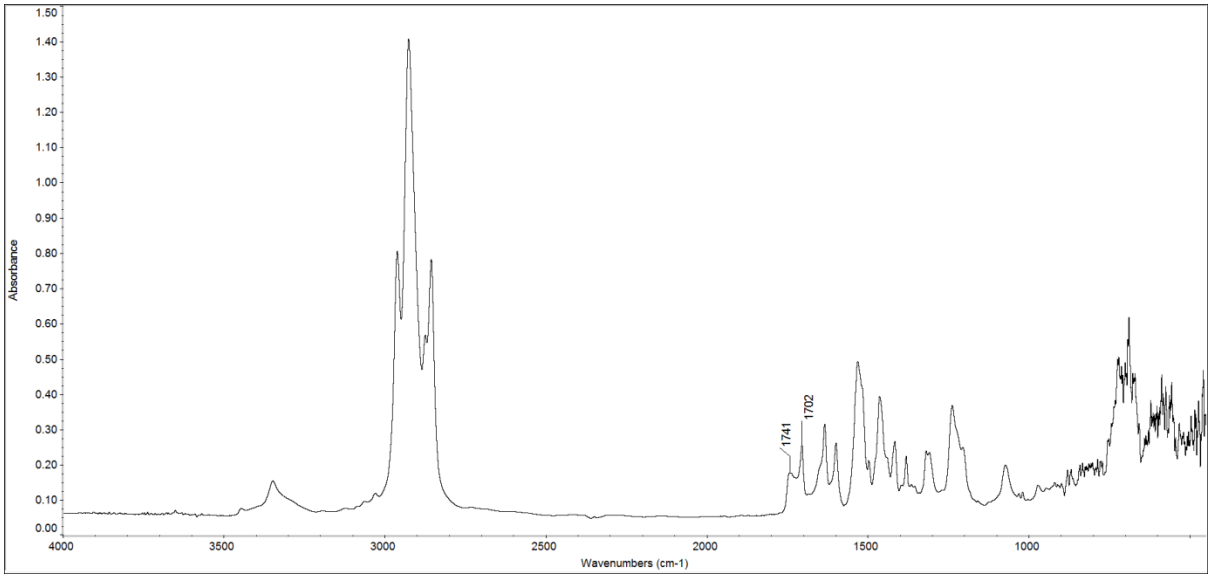

Figure S4 (j). FTIR of polyurethane **1** at 120 °C.

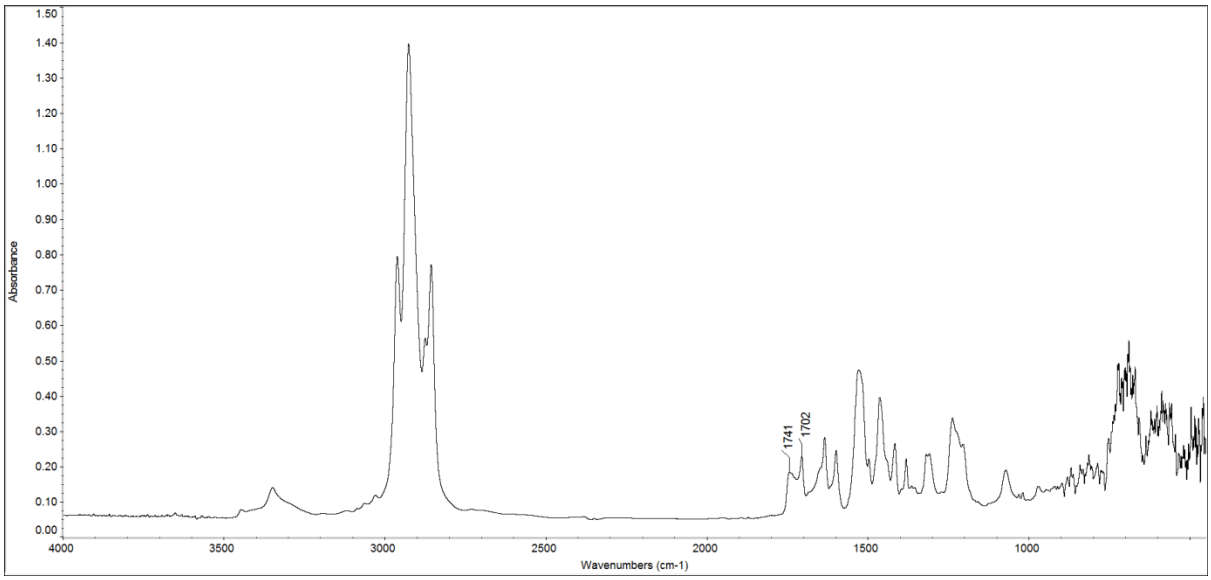

Figure S4 (k). FTIR of polyurethane **1** at 130 °C.

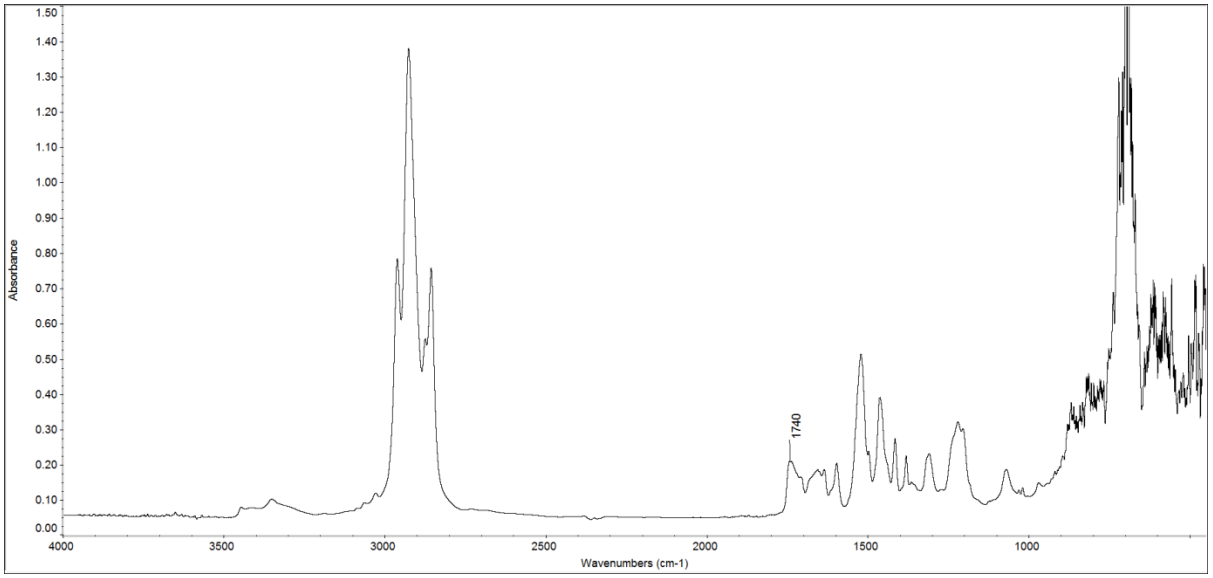

Figure S4 (l). FTIR of polyurethane **1** at 140 °C.

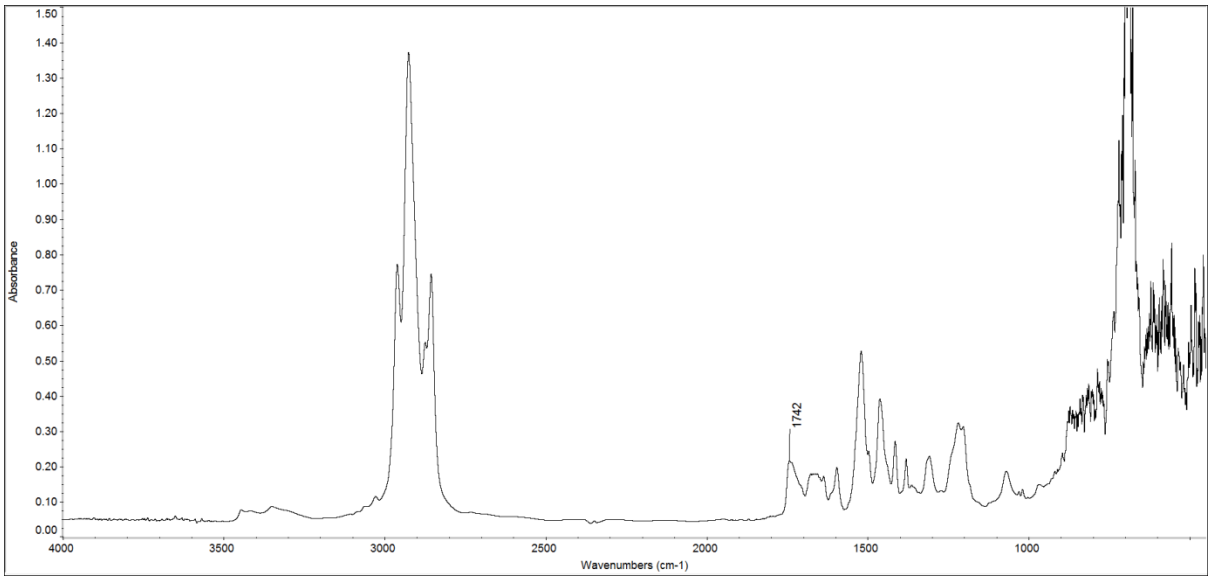

Figure S4 (m). FTIR of polyurethane **1** at 150 °C.

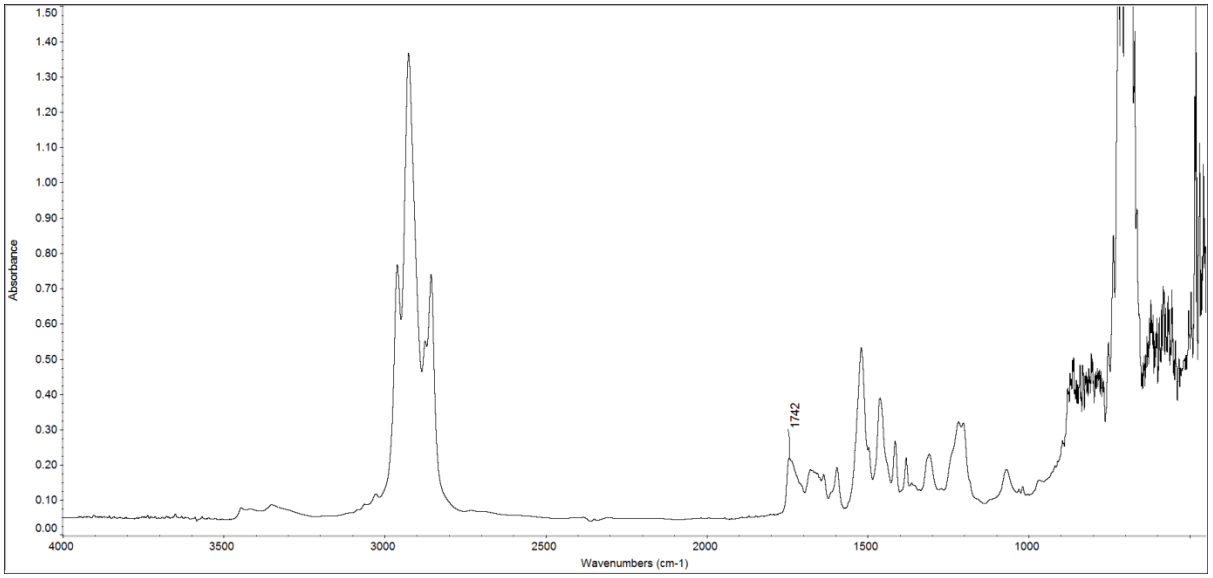

Figure S4 (n). FTIR of polyurethane **1** at 160 °C.

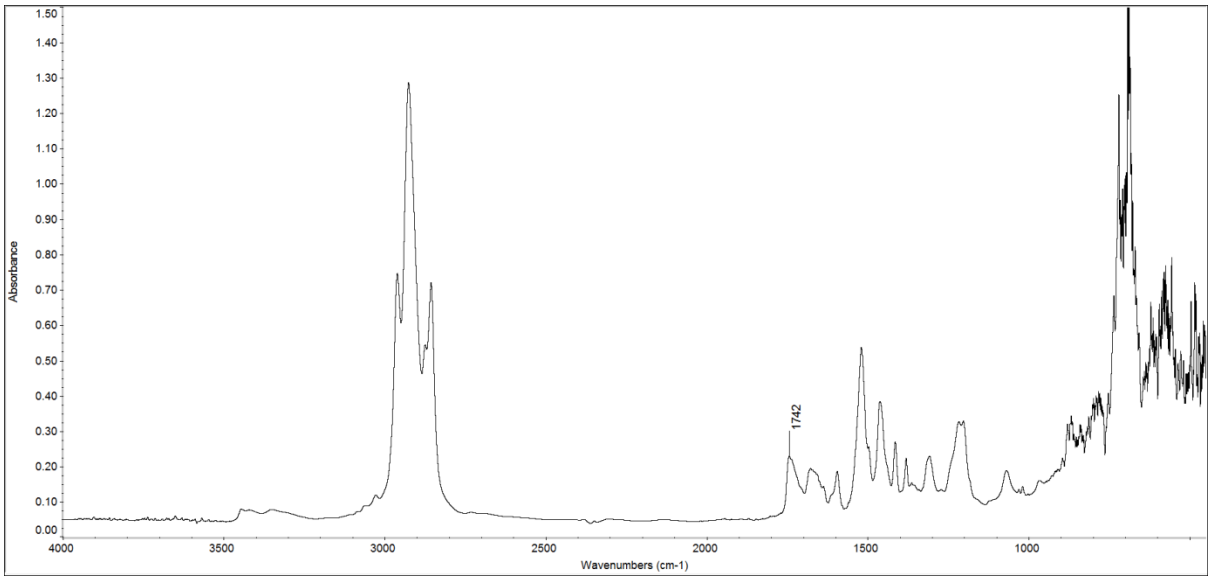

Figure S4 (o). FTIR of polyurethane **1** at 170 °C.

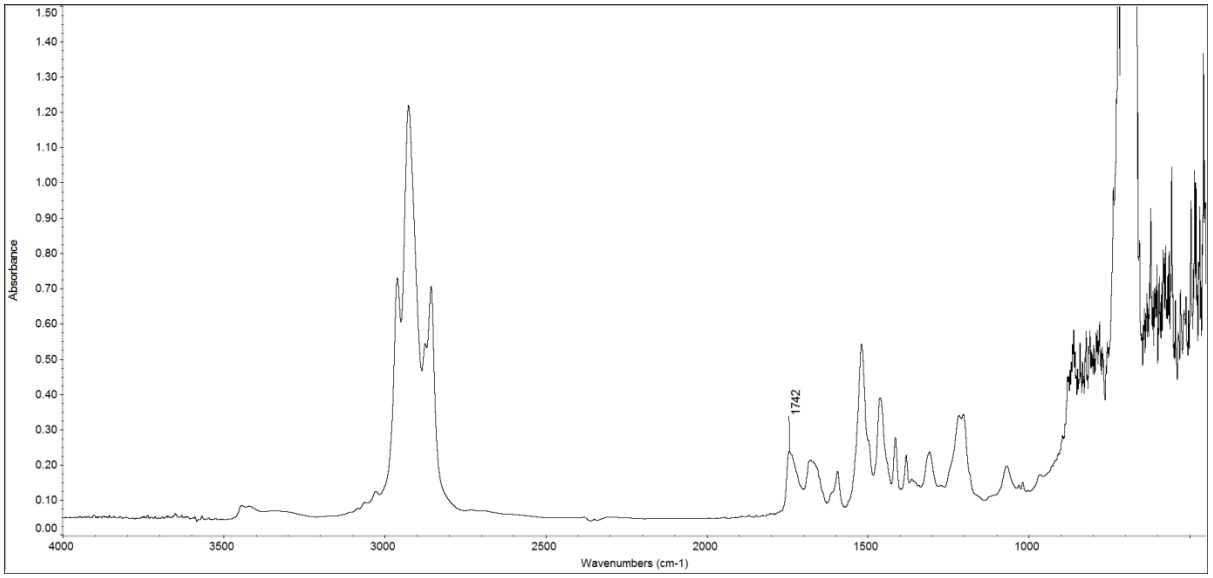

Figure S4 (p). FTIR of polyurethane **1** at 180 °C.

Figure S4. FTIR of polyurethane **1** at temperatures from 30 °C to 180 °C.

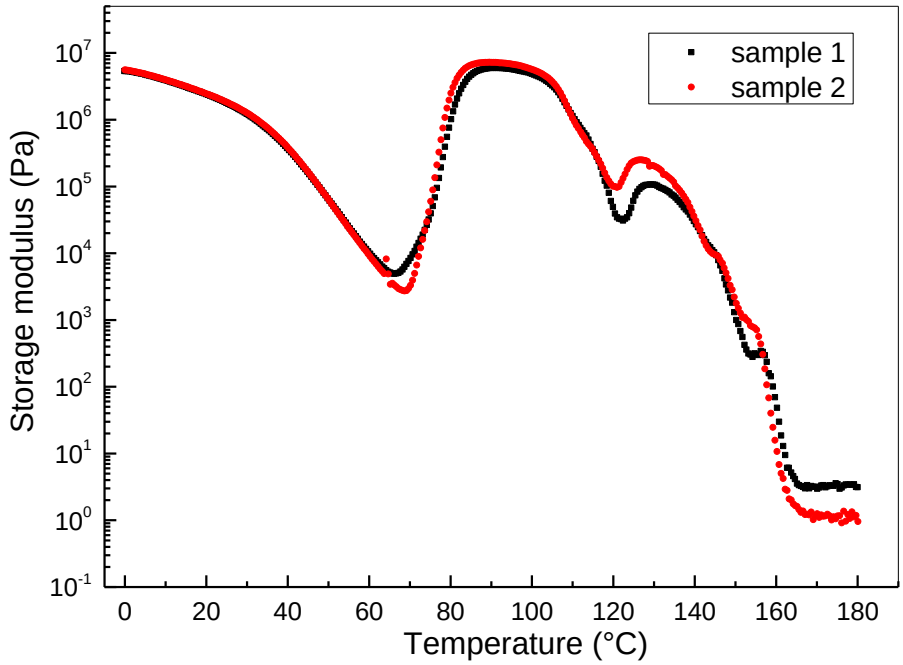

Figure S5. Rheological behaviour of two specimens of quenched polyurethane **1**

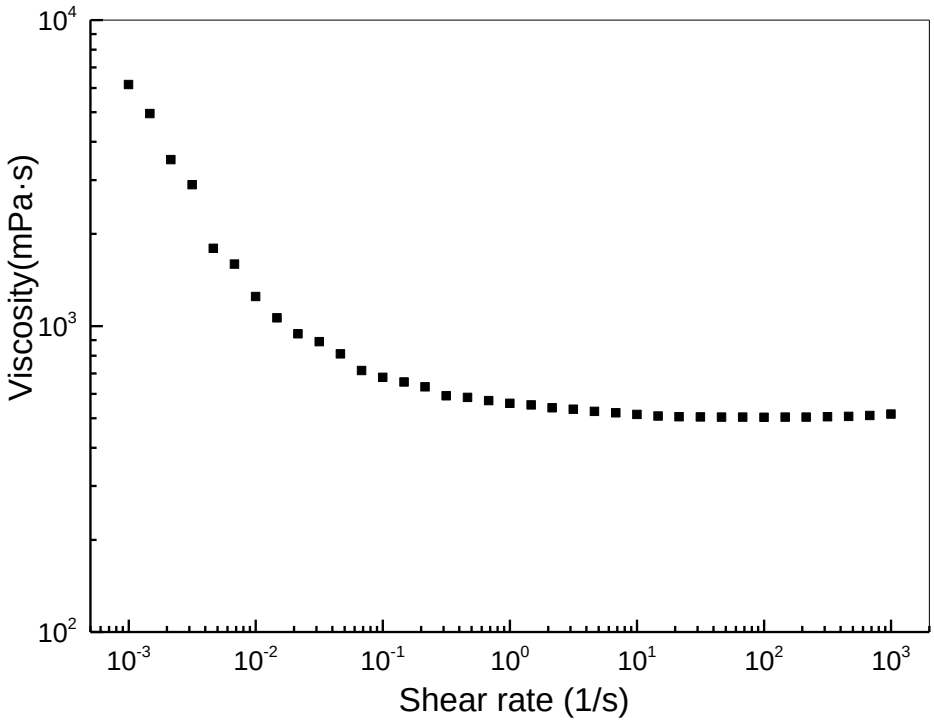

Figure S6. Flow curve for polyurethane **1** at 180°C

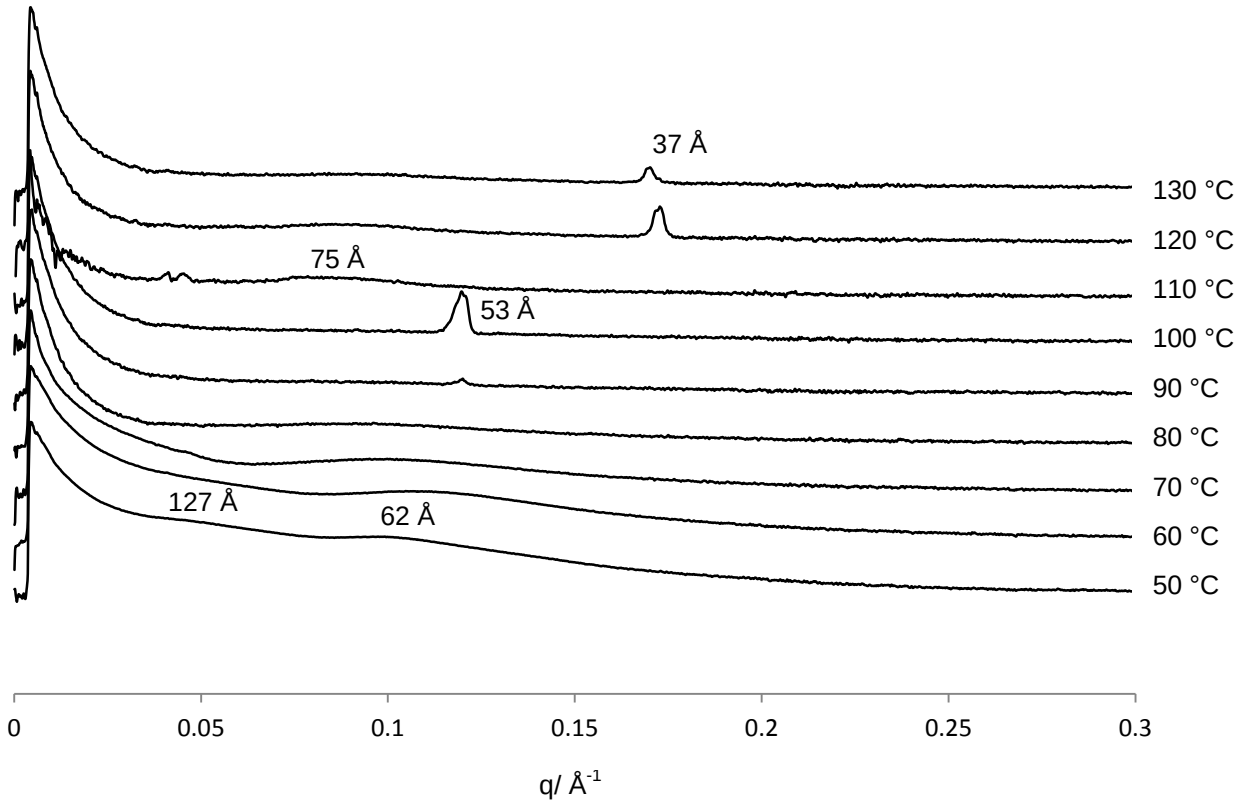

Figure S7. SAXS of quenched polyurethane **1** at a heating rate of 2 °C/min taken at 10 °C intervals.

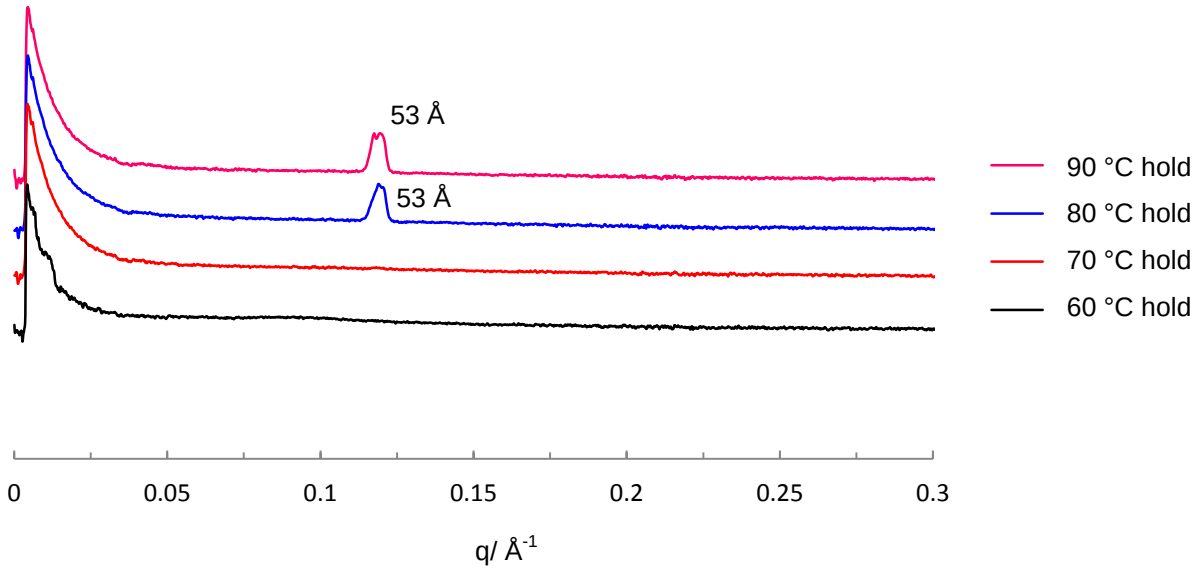

Figure S8. SAXS profiles for quenched polyurethane **1** at different temperatures, after holding at given temperature for 300 seconds. These data are analogous to those in Figure 3.

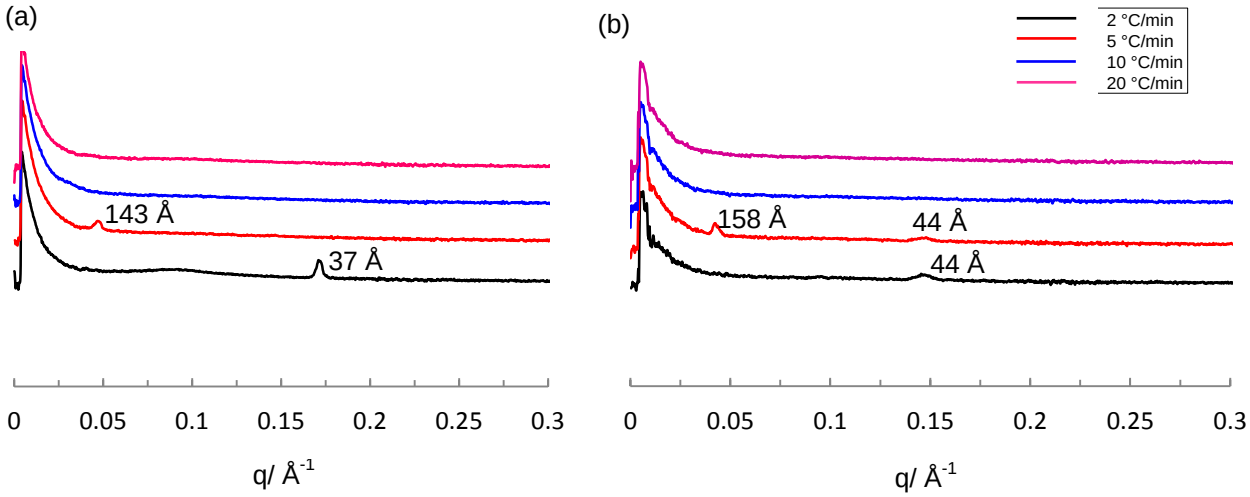

Figure S9. SAXS of quenched polyurethane **1** at different rising (a) and cooling (b) rates taken at 120 °C taking during the heat/cool cycle analogous to that shown in Figure 4.

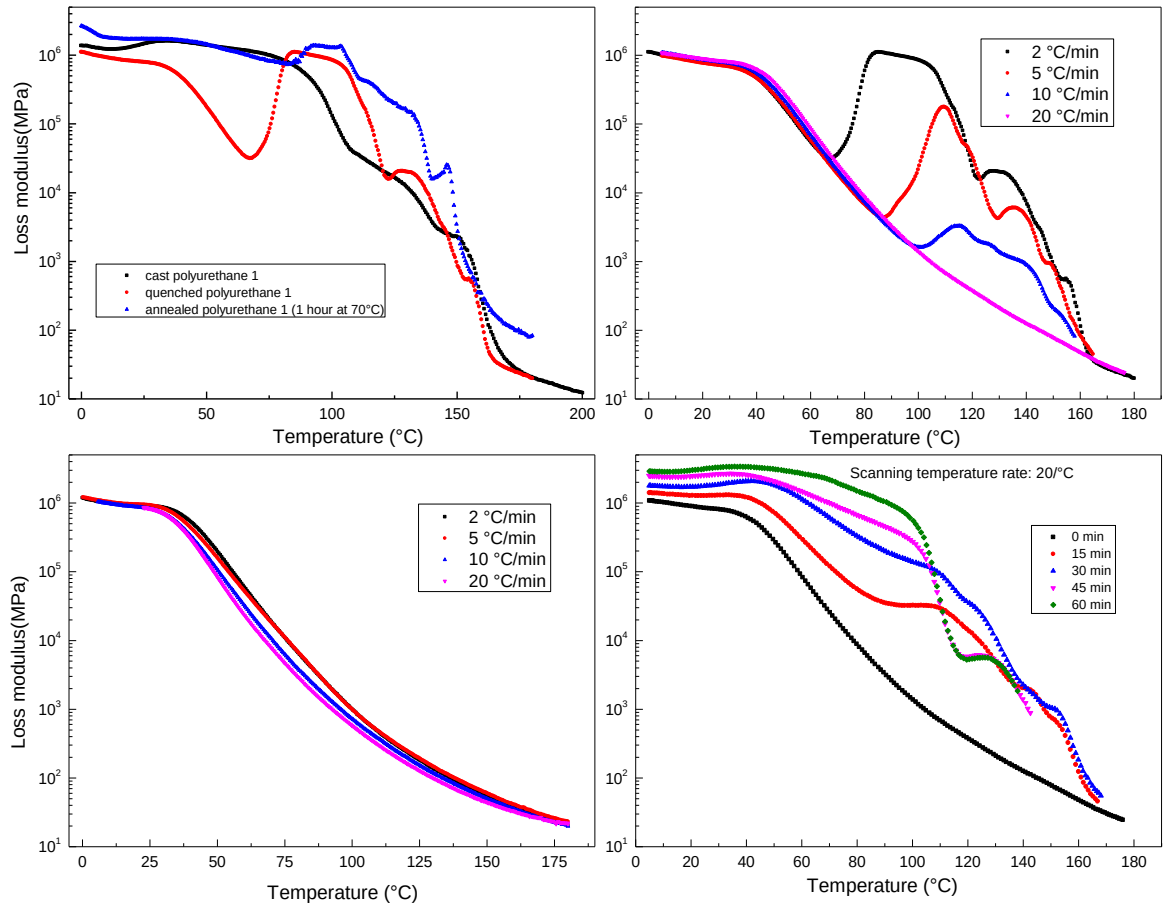

Figure S10. The corresponding loss modulus for Figure 2, 4a (b), 4b (c) and 5.

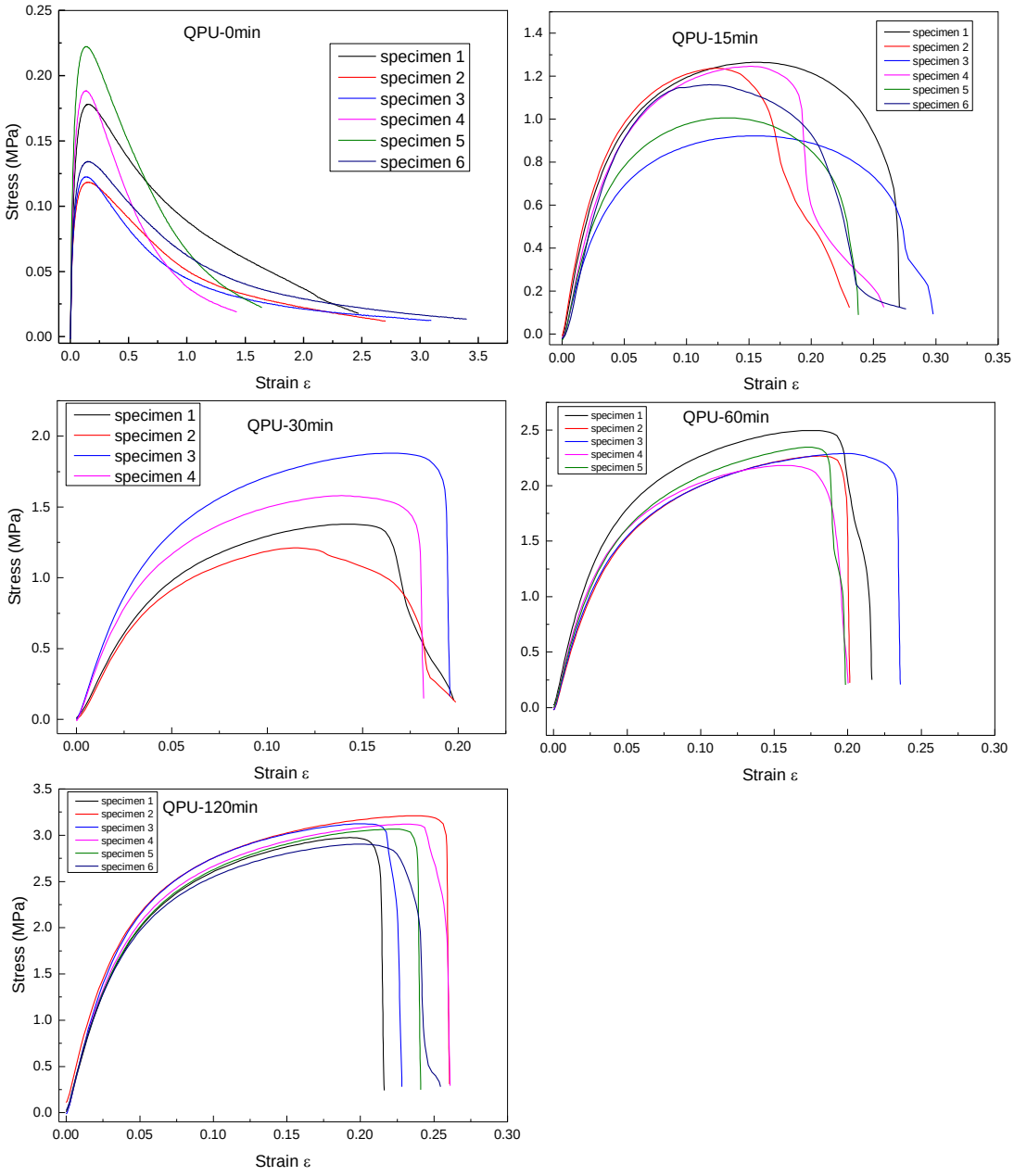

Figure S11. The original stress-strain curves for quenched polyurethane **1** after annealing for different times.

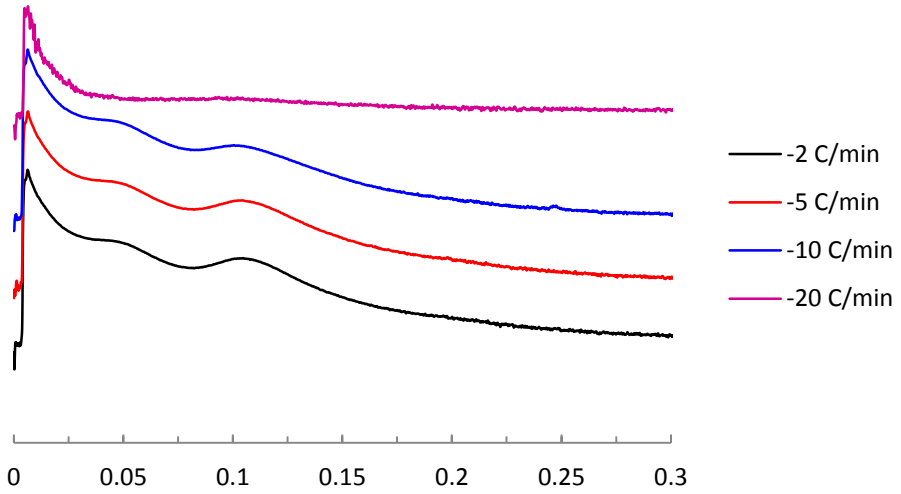

Figure S12. SAXS of polyurethane **1** after cooling to 0 ºC from annealed temperature (70 ºC) at different rates.

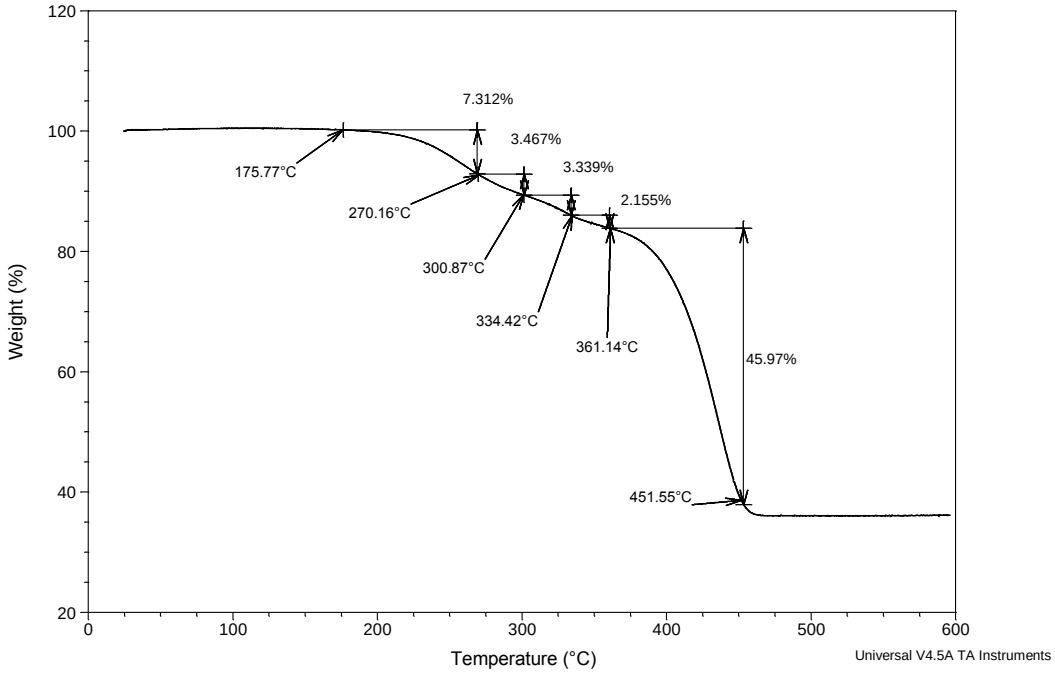

Figure S13. TGA plot of polyurethane **1**

Peel testing protocol

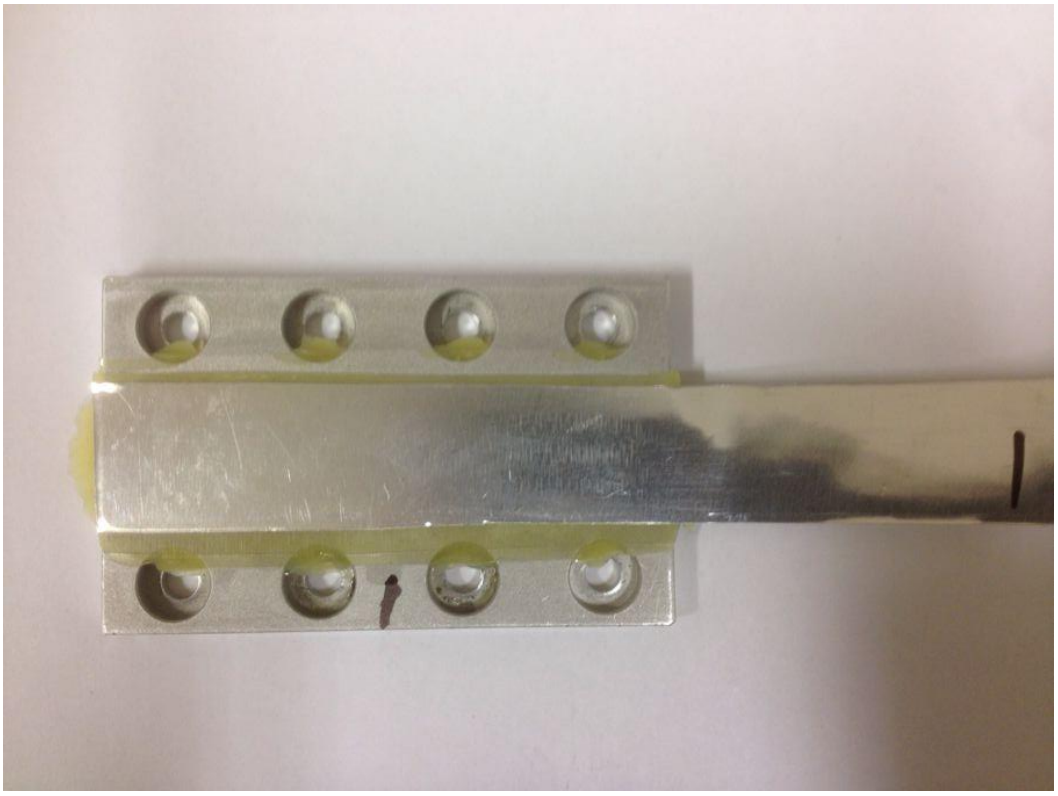

Figure S14. Peel joints: a prepared test specimen

Within the realm of destructive adhesion tests, there are two major classes: those dealing with relatively soft flexible coatings and those dealing with hard brittle coatings. By far the most common test for flexible coatings is the peel test, which are used widely for the determination of adhesive strength of flexible laminate systems in aerospace, automotive, electronic, and packaging applications. However, it is now well-recognized that the total input work: G, includes both the adhesive fracture energy, G_A, and any plastic work done in bending the peeling arm(s), G_P. [3,4] Thus, the adhesive fracture energy, G_A, is then obtained via

$$G_A = G - G_P \qquad \textbf{(Equation S1)}$$

where G_P is the energy associated with the plastic bending of the peel arm. To determine the value of G_P, a tensile test should be performed first on the peel arm material at the same equivalent test rate as the peel test, and then, the value of G_P can be determined using large displacement beam theory with the modifications for plastic bending.[5] The detail theoretical background can be found in references 1, 2.

In this work, the peel tests follows the procedures outlined in the ESIS TC 4 protocol, and data analysis was performed using the Microsoft Excel macro, 'IC Peel', which is freely available to download from the Imperial College website.[6]

Figure S20 (a) and (b) show the measured stress-strain curve for the aluminium foil peel arm used in this work with the data fitted using (a) the bi-linear model and (b) the power law model. ESIS TC 4 protocol permits either fitting technique to be used, but for the present tests, the power-law model gives the loser fit to the measured data and hence, in the manuscript, pow-law model fitting results was used. The representative peel curves can be seen in Figure S26. The calculated value for quenched polyurethane **1** and annealed polyurethane **1** can be found in Table 2 and 3.

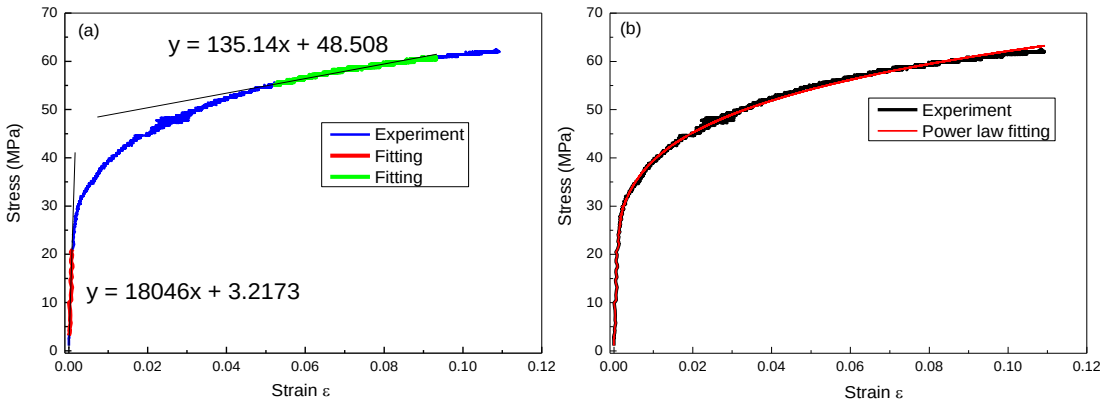

Figure S15. Measured tensile stress-strain curve for the aluminium foil peel arm: (a) fitted using the bi-linear model and (b) fitted using the power-law model.

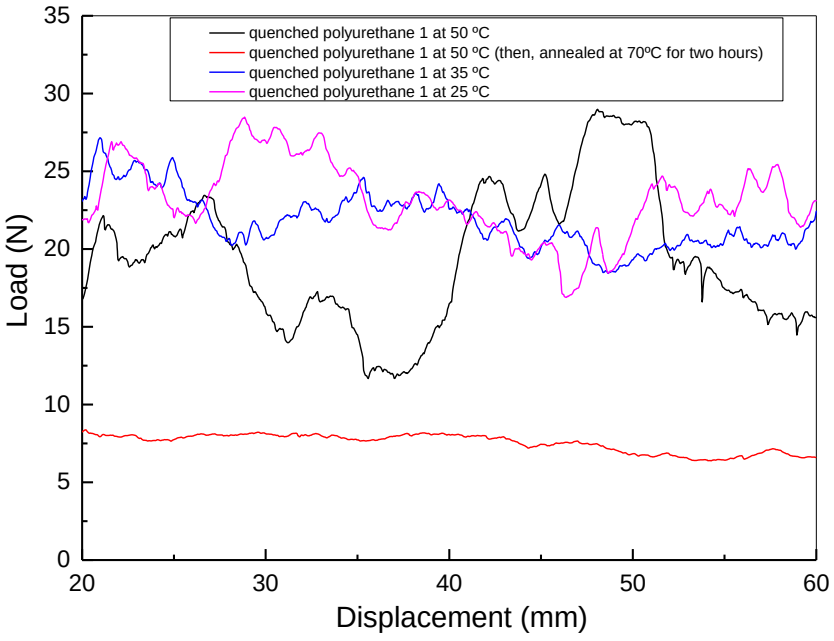

Figure S16. Peel tests for the aluminium polyurethane **1** peel joints prepared at different conditions

Table S1. Data obtained from fitting the stress-strain curve for the aluminium foil, and the resulting values of G_P and G_A for the quenched polyurethane **1**.

	Bi-linear	Power law
E1(GPa)	18.1	18.1
α	0.0075	
n		0.1976
G(J/m^2)	1125	1125
G_P(J/m^2)	300	390
G_A(J/m^2)	825	735

Table S2. Data obtained from fitting the stress-strain curve for the aluminium foil, and the resulting values of G_P and G_A for the annealed polyurethane **1**.

	Bi-linear	Power law
E1(GPa)	18.1	18.1
α	0.0075	
n		0.1976
G(J/m^2)	375	375
G_P(J/m^2)	245	260
G_A(J/m^2)	130	115

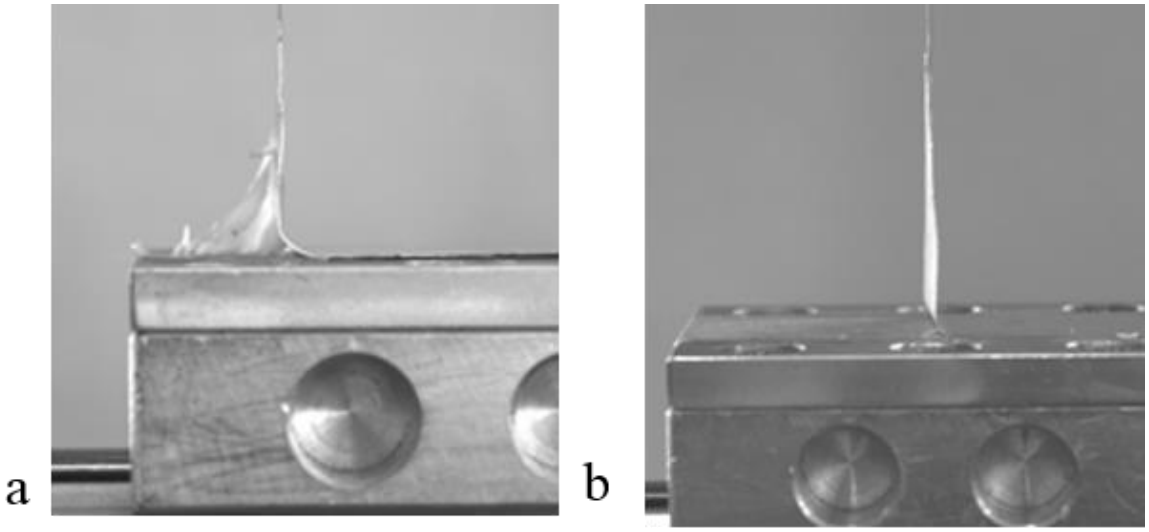

Figure S17. The recorded images of the peel tests for polyurethane **1**: a) quenched polyurethane 1, b) after quenched at the temperature of 70 ºC after two hours

References

1. Portale, G.; Cavallo, Alfonso, G. C.; Hermida-Merino, D.; van Drongelen, M.; Balzano, L.; Peters, G.W.M.; Goossens, J.G.P. ; Bras, W. Polymer crystallization studies under processing-relevant conditions at the SAXS/WAXS DUBBLE beamline at the ESRF. *J. Appl. Cryst.* **2013**, *46*, 1681-1689.
2. Bras, W.; Dolbnya, I. P.; Detollenaere, D.; van Tol, R.; Malfois, M.; Greaves, G.N.; Ryan, A. J.; Heeley, E. Recent experiments on a small-angle/wide-angle X-ray scattering beam line at the ESRF. *J. Appl. Cryst.* **2003**, *36*, 791-794.
3. I. Georgiou, H. Hadavinia, A. Ivankovic, A. J. Kinloch, V. Tropsa and J. G. Williams, Journal of Adhesion 79 (3), 239-265 (2003).
4. L. F. Kawashita, D. R. Moore and J. G. Williams, Journal of Adhesion 82 (10), 973-995 (2006).
5. B. R. K. Blackman, S. Cui, A. J. Kinloch and A. C. Taylor, International Journal of Adhesion and Adhesives 42, 1-10 (2013).
6. D. R. Moore and J. G. Williams, (Imperial College London, 2010), Vol. 2015.