Supporting Information

The effect of chiral end groups on the assembly of supramolecular polyurethanes

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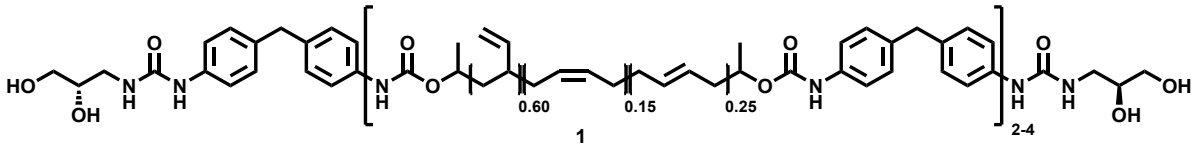
Synthesis of *S*-bis(4-(4-(3-(2,3-dihydroxypropyl)ureido)benzyl) phenylcarbamate) terminated poly(butadiene) 1



Supramolecular polyurethane **1** was synthesised via the general procedure using the direct addition approach outlined in the experimental section and 3000 g mol^{-1} hydroxy terminated poly(butadiene) as a white solid elastomer (3.92 g, 86.7 %). IR (Thin film, KBr) ν_{max}/cm^{-1} 3313, 3073, 2970, 2915, 2844, 1731, 1707, 1633, 1601, 1567, 1536, 1436, 1415; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} = 1.17-1.42 (br, $2H_n$, $(CH_2)_n$), 1.71 (br, $2H_n$, $(CH_2)_n$), 2.03 (br m, $9H_n$, (4 × cis$(CH{=}CHCH_2)_n$ + 4 × trans $(CH{=}CHCH_2)_n$ + $(CH{=}CHCH)_n$), 3.36 (br, 4H, 2 × NCH_2), 3.57 (br, 4H, 2 × CH_2OH), 3.72 (br, 2H, 2 × CHOH) , 3.88 (s, 4H, 2 × $ArCH_2Ar$), 4.07-4.16 (br, CHOC(O)N & OH), 4.95 (br, $2H_n$, (2 × $CH{=}CH_2)_n$), 5.45 (br, $2H_n$, (cis CH= CH)$_n$), 5.55 (br, $2H_n$, (trans CH= CH)$_n$), 5.80 (br, H_n, $(CH_2{=}CH)_n$), 6.51 (4 × NH), 7.08-7.10 (AA'XX' system, 8H, 8 × ArH), 7.14-7.26 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} = 24.95 (CH_3), 27.39 $(CH_2)_n$, 27.56 $(CH_2)_n$, 28.83 $(CH_2)_n$, 30.17 $(CH_2)_n$, 32.74 $(CH_2)_n$, 34.23 $(CH_2)_n$, 38.20 $(CH)_n$, 38.66-41.67 ($(CH_2)_n$ + CH_2), 43.49 ($ArCH_2Ar$), 63.63 (CH_2), 71.56 (CHO), 111.91-115.04 $(CH_2{=}CH)_n$, 119.21 (ArC), 128.14 (ArC), 129.42 cis$(CH{=}CH)_n$, 130.12 trans$(CH{=}CH)_n$, 131.23 cis(CH= CH)$_n$, 131.75 (ArC), 142.71-143.16 $(CH_2{=}CH)_n$ 153.28 (NHC(O)O), 157.60 (NHC(O)NH); GPC (THF) M_w = 11037, M_n = 6439, Đ = 1.7.

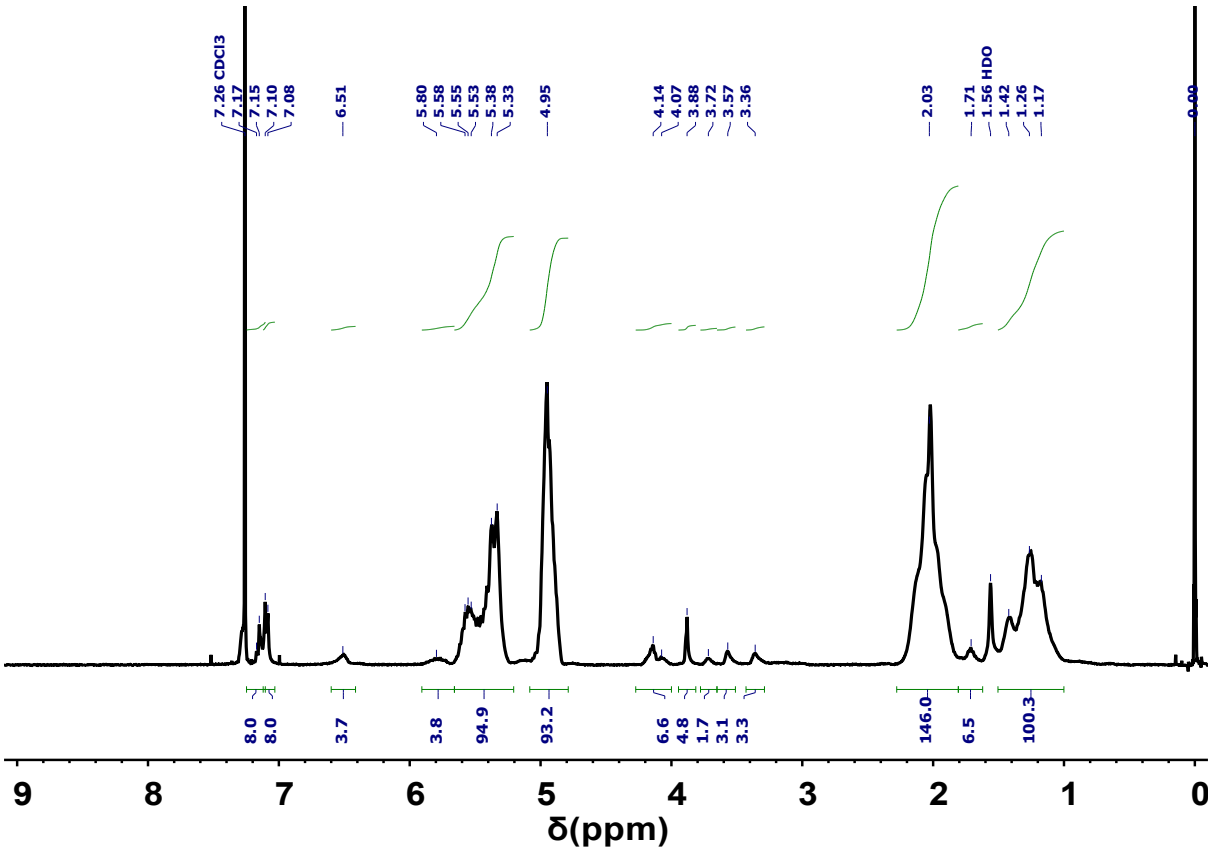


Figure S1: ^{1}H NMR spectra of SPU **1**.

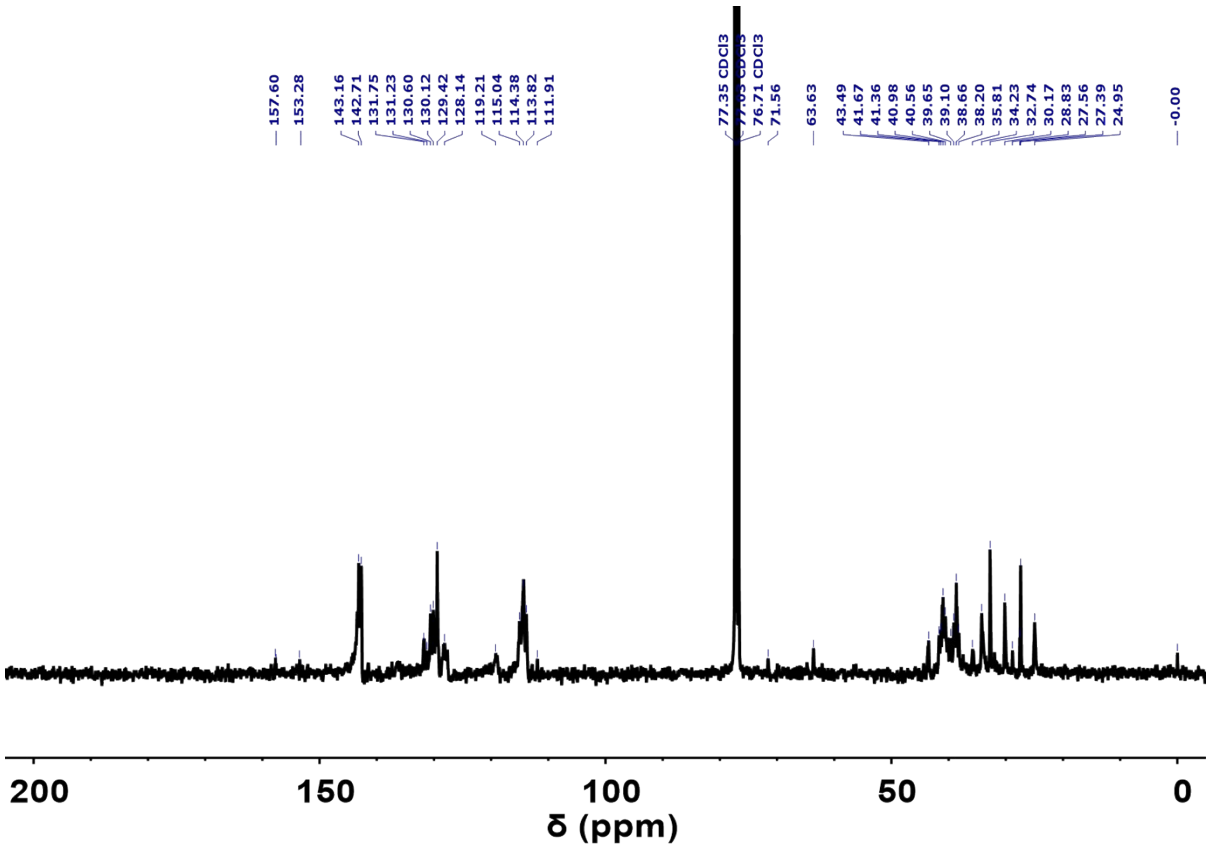
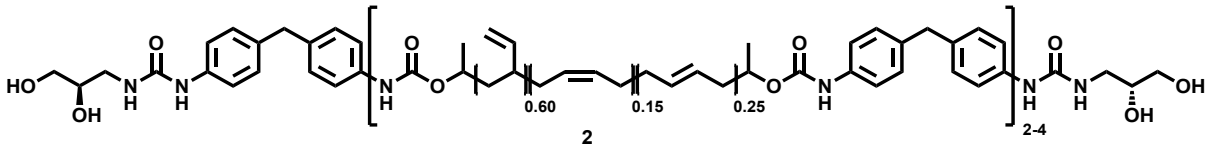


Figure S2: ^{13}C NMR spectra of SPU **1**.

Synthesis of *R*-bis(4-(4-(3-(2,3-dihydroxypropyl)ureido)benzyl) phenylcarbamate) terminated poly(butadiene) 2



2

Supramolecular polyurethane **2** was synthesised via the general procedure using the direct addition approach outlined in the experimental section and 3000 g mol^{-1} hydroxy terminated poly(butadiene) as a white solid elastomer (7.12 g, 78.9 %). IR (Thin film, KBr) ν_{max}/cm^{-1} 3312, 3072, 2970, 2916, 2843, 1706, 1634, 1601, 1568, 1523, 1431, 1415; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} = 0.97-1.50 (br, $2H_n$, $(CH_2)_n$), 2.03 (br m, $9H_n$, (4 × cis$(CH{=}CHCH_2)_n$ + 4 × trans $(CH{=}CHCH_2)_n$ + $(CH{=}CHCH)_n$), 3.38 (br, 4H, 2 × NCH_2), 3.58 (br, 4H, 2 × CH_2OH), 3.73 (br, 2H, 2 × CHOH), 3.90 (s, 4H, 2 × $ArCH_2Ar$), 4.04-4.20 (br, CHOC(O)N & OH), 4.95 (br, $2H_n$, (2 × $CH{=}CH_2)_n$), 5.37 (br, $2H_n$, (cis $CH{=}CH)_n$), 5.41-5.48 (br, $2H_n$, (trans $CH{=}CH)_n$), 5.54-5.81 (br, H_n, $(CH_2{=}CH)_n$), 6.51 (4 × NH), 7.08-7.11 (AA'XX' system, 8H, 8 × ArH), 7.15-7.21 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} = 14.13 (CH_3), 19.73 (CH_3), 22.70 (CH_3), 24.94 (CH_3), 27.38 $(CH_2)_n$, 29.70 $(CH_2)_n$, 30.11 $(CH_2)_n$, 31.94 $(CH_2)_n$, 32.74 $(CH_2)_n$, 34.19 $(CH_2)_n$, 37.43 $(CH)_n$, 38.65 $(CH)_n$, 41.11 ($(CH_2)_n$ + CH_2), 43.64 ($ArCH_2Ar$), 47.87 ($ArCH_2Ar$), 118.96 (ArC), 128.3 (ArC), 129.42 cis$(CH{=}CH)_n$, 129.72 cis$(CH{=}CH)_n$ 130.51 trans$(CH{=}CH)_n$, 131.70 cis$(CH{=}CH)_n$, 136.51-136.69 (ArC), 142.67-143.14$(CH_2{=}CH)_n$, 153.68 (NHC(O)O), 157.11 (NHC(O)NH); GPC (THF) M_w = 11037, M_n = 6439, Đ = 1.7.

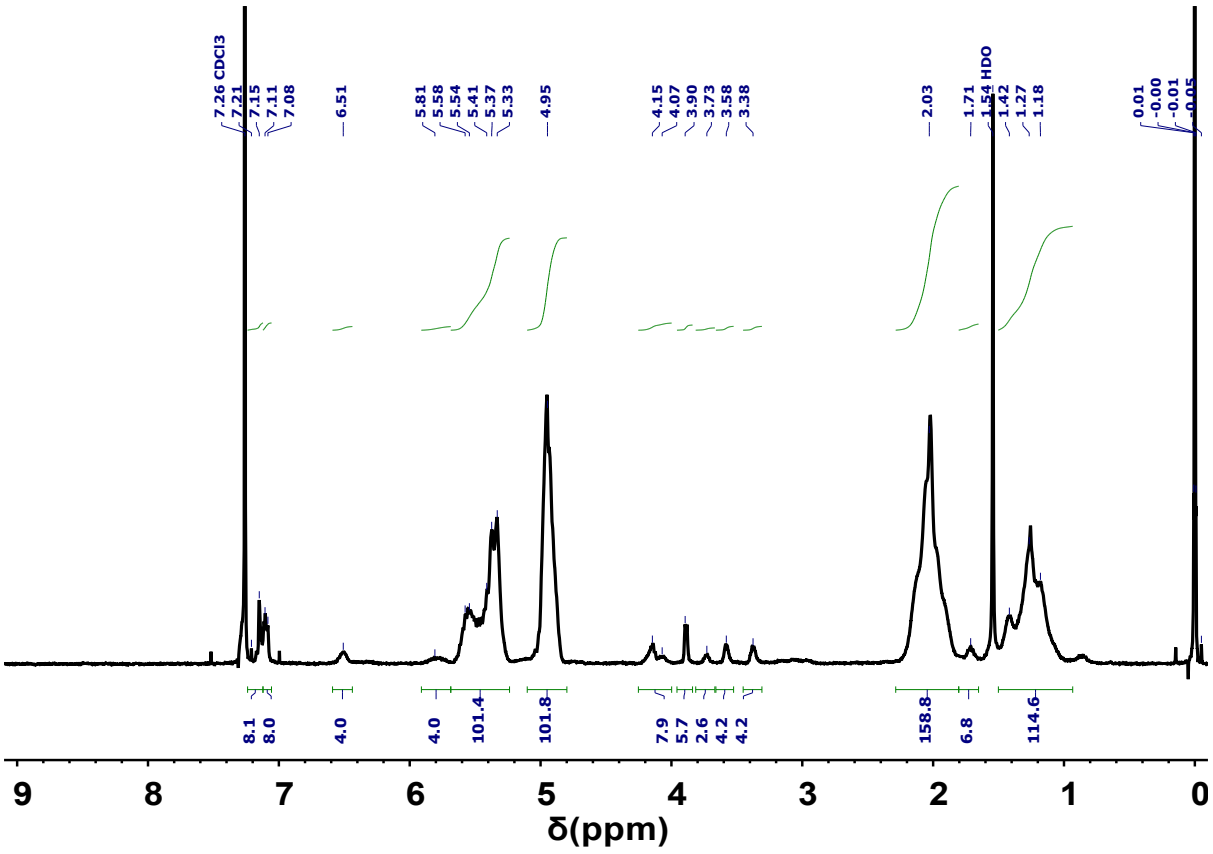


Figure S3: [1]H NMR spectra of SPU **2**.

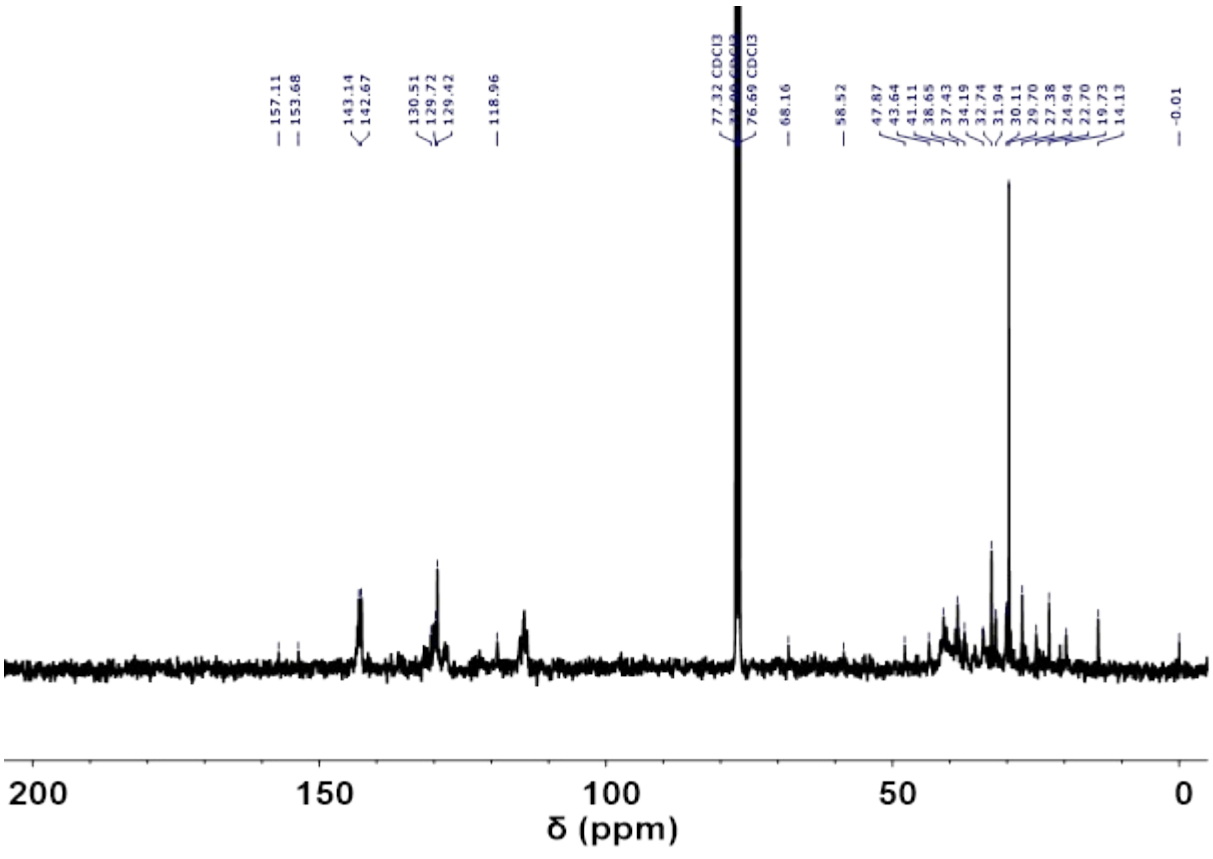
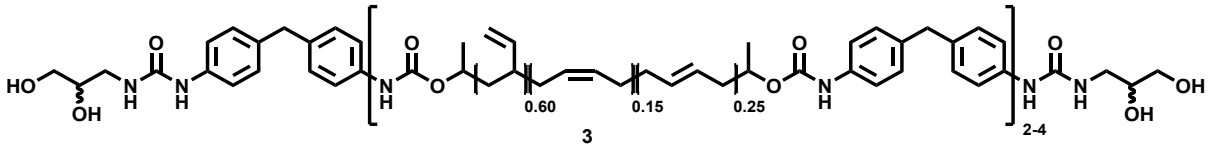


Figure S4: [13]C NMR spectra of SPU **2**.

Synthesis of ±-bis(4-(4-(3-(2,3-dihydroxypropyl)ureido) benzyl) phenylcarbamate) terminated poly(butadiene) 3



3

Supramolecular polyurethane **3** was synthesised via the general procedure using the direct addition approach outlined in the experimental section and 3000 g mol^{-1} hydroxy terminated poly(butadiene) as a white solid elastomer (3.30 g, 90.4 %). IR (Thin film, KBr) ν_{max}/cm^{-1} 3323, 3072, 2970, 2915, 2843, 1737, 1709, 1703, 1637, 1597, 1566, 1522, 1431, 1414; ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} = 1.07 6-1.54 (br, $2H_n$, $(CH_2)_n$), 2.02 (br m, $9H_n$, (4 × cis$(CH{=}CHCH_2)_n$ + 4 × trans $(CH{=}CHCH_2)_n$ + $(CH{=}CHCH)_n$), 3.21 (br, 4H, 2 × NCH_2), 3.43 (br, 4H, 2 × CH_2OH), 3.63 (br, 2H, 2 × CHOH), 3.77 (br, 2H, 2 × CHOH) , 3.88 (s, 4H, 2 × $ArCH_2Ar$), 4.03-4.18 (br, CHOC(O)N & OH), 4.92 (br, $2H_n$, (2 × $CH{=}CH_2)_n$), 5.43 (br, $2H_n$, (cis $CH{=}CH)_n$), 5.55 (br, $2H_n$, (trans $CH{=}CH)_n$), 5.81 (br, H_n, $(CH_2{=}CH)_n$), 6.53-6.71 (4 × NH), 7.00-7.10 (AA'XX' system, 8H, 8 × ArH), 7.14-7.29 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} = 24.95 (CH_3), 27.38 $(CH_2)_n$, 27.53 $(CH_2)_n$, 28.83 $(CH_2)_n$, 30.16 $(CH_2)_n$, 31.96 $(CH_2)_n$, 32.73 $(CH_2)_n$, 34.09 $(CH_2)_n$, 35.67 $(CH_2)_n$, 37.43 $(CH_2)_n$, 38.18 $(CH)_n$, 38.65 $(CH)_n$, 39.07-41.66 ($(CH_2)_n$ + CH_2), 43.56 ($ArCH_2Ar$), 63.58 (CH_2), 71.54 (CHO), 111.84 $(CH_2{=}CH)_n$, 113.78-114.98 $(CH_2{=}CH)_n$, 119.13 (ArC), 127.63 (ArC), 128.08 (ArC), 129.39 cis$(CH{=}CH)_n$, 130.06 trans$(CH{=}CH)_n$, 130.56 trans$(CH{=}CH)_n$, 131.19 cis$(CH{=}CH)_n$, 131.70 cis$(CH{=}CH)_n$, 135.95-136.23 (ArC), 142.66-143.40 $(CH_2{=}CH)_n$, 153.64 (NHC(O)O), 157.55 (NHC(O)NH); GPC (THF) M_w = 11634, M_n = 6679, Đ = 1.7.

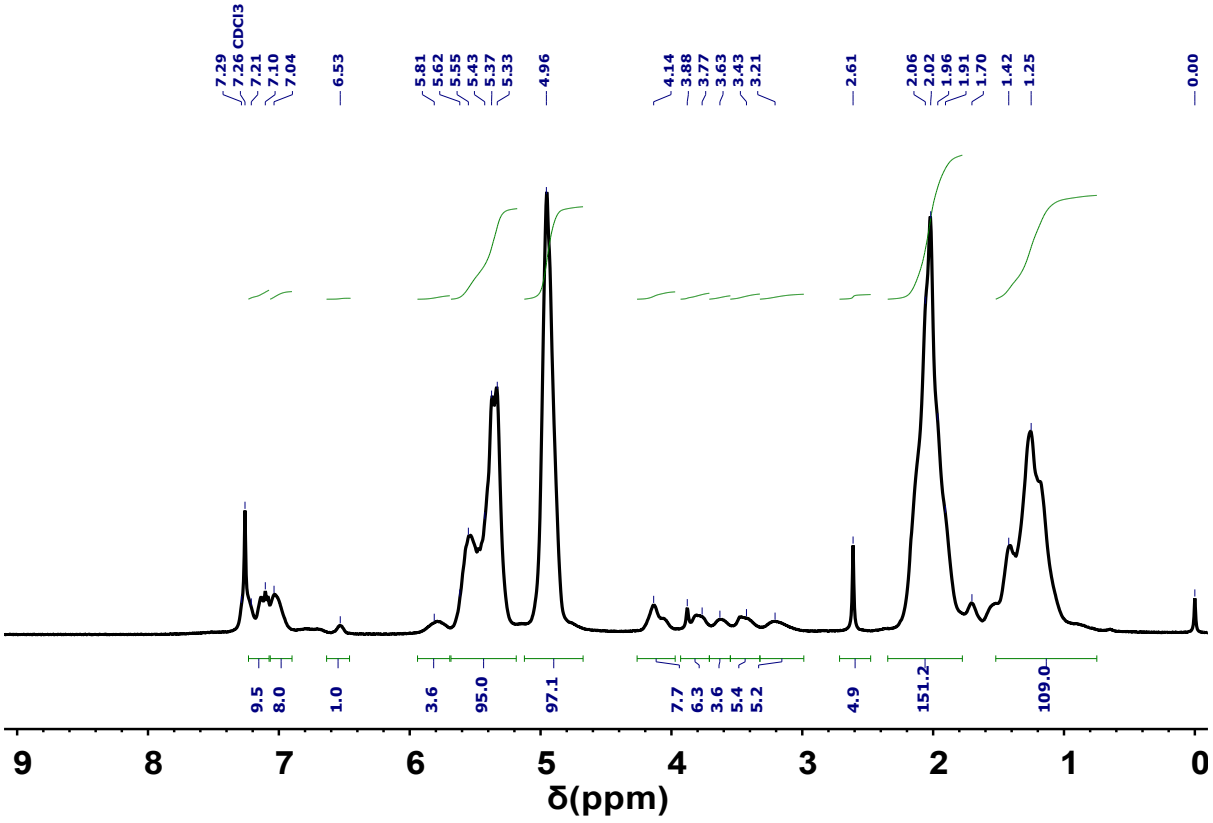


Figure S5: ^{1}H NMR spectra of SPU **3**.

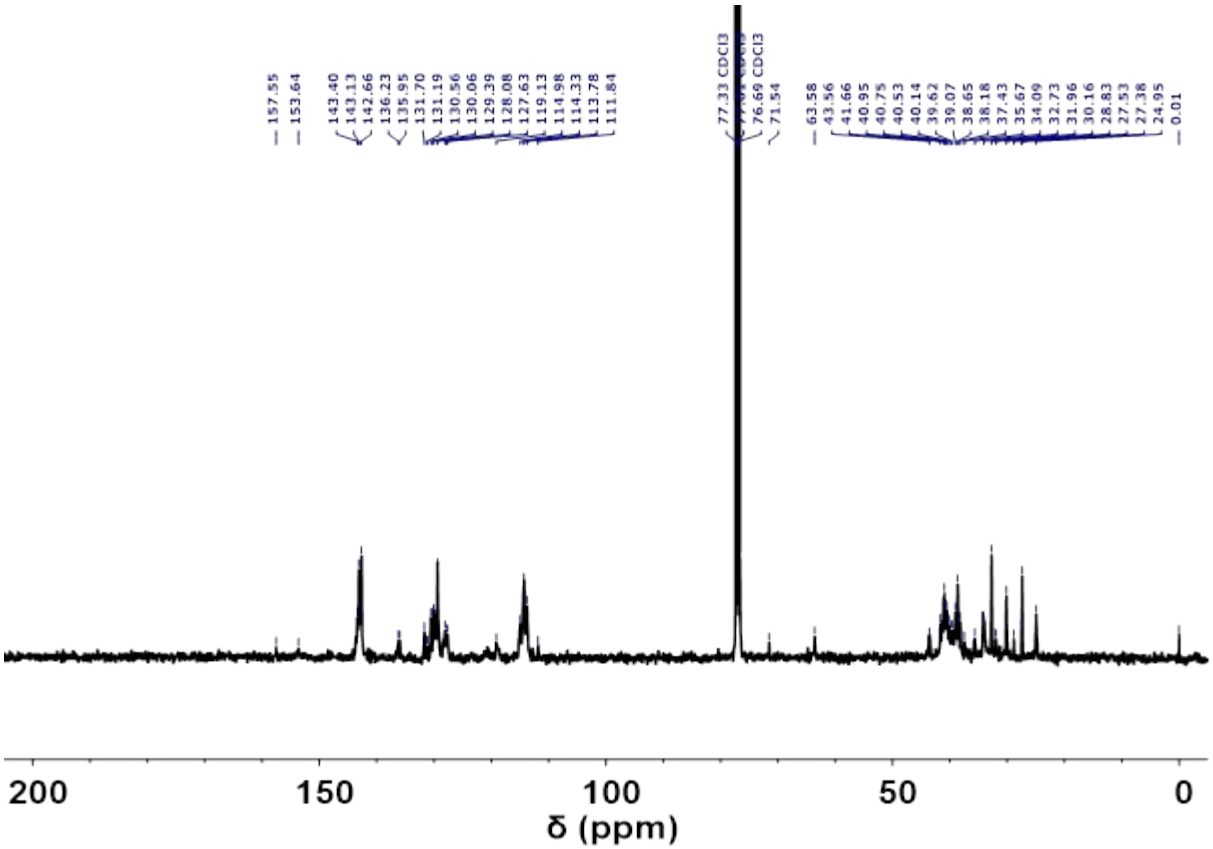
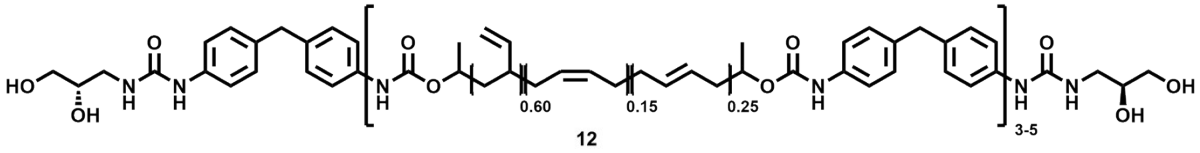


Figure S6: ^{13}C NMR spectra of SPU **3**.

Synthesis of *S*-bis(4-(4-(3-(2,3-dihydroxypropyl)ureido)benzyl) phenylcarbamate) terminated poly(butadiene) (5000) 12



12

Supramolecular polyurethane **12** was synthesised via the general procedure using the direct addition approach outlined in the experimental section and 5000 g mol^{-1} hydroxy terminated poly(butadiene) as a white solid elastomer (5.34 g, 86.1 %). IR (Thin film, KBr) ν_{max}/cm^{-1} 3320, 3072, 2970, 2915, 1731, 1710, 1704, 1632, 1596, 1551, 1517, 1432, 1414; ^{1}H NMR (400 MHz, $CDCl_3$)) δ_{ppm} = 1.12-1.50 (br, 2H$_n$, $(CH_2)_n$), 2.02 (br m, 9H$_n$, (4 × cis$(CH{=}CHCH_2)_n$ + 4 × trans $(CH{=}CHCH_2)_n$ + $(CH{=}CHCH)_n$),, 3.33 (br, 4H, 2 × NCH_2), 3.54 (br, 4H, 2 × CH_2OH), 3.69 (br, 2H, 2 × CHOH) , 3.88 (s, 4H, 2 × $ArCH_2Ar$), 4.96 (br, 2H$_n$, (2 × $CH{=}CH_2)_n$), 5.37 (br, 2H$_n$, (cis $CH{=}CH)_n$), 5.58 (br, 2H$_n$, (trans $CH{=}CH)_n$), 5.74-5.90 (br, H$_n$, $(CH_2{=}CH)_n$), 6.48 (4 × NH), 7.08-7.15 (AA'XX' system, 8H, 8 × ArH), 7.08-7.28 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (100 MHz, $CDCl_3$)) δ_{ppm} = 24.98 (CH_3), 27.40 $(CH_2)_n$, 27.55 $(CH_2)_n$, 30.18 $(CH_2)_n$, 31.98 $(CH_2)_n$, 32.74 $(CH_2)_n$, 32.78 $(CH_2)_n$, 34.26 $(CH_2)_n$, 35.74 $(CH_2)_n$, 37.46 $(CH_2)_n$, 38.20 $(CH)_n$, 38.67 $(CH)_n$, 39.08-41.67 ($(CH_2)_n$ + CH_2), 43.51 ($ArCH_2Ar$), 71.61 (CHO), 113.83-114.95 $(CH_2{=}CH)_n$, 118.90 (ArC), 128.24 (ArC), 129.43 cis$(CH{=}CH)_n$, 129.78 cis$(CH{=}CH)_n$, 130.01 trans$(CH{=}CH)_n$, 130.58 trans$(CH{=}CH)_n$, 131.28 cis$(CH{=}CH)_n$, 131.74 cis$(CH{=}CH)_n$, 142.69-143.17 $(CH_2{=}CH)_n$ 157.65 (NHC(O)O), 161.97 (NHC(O)NH); GPC (THF) M_w = 33299, M_n =15222, Đ = 2.2.

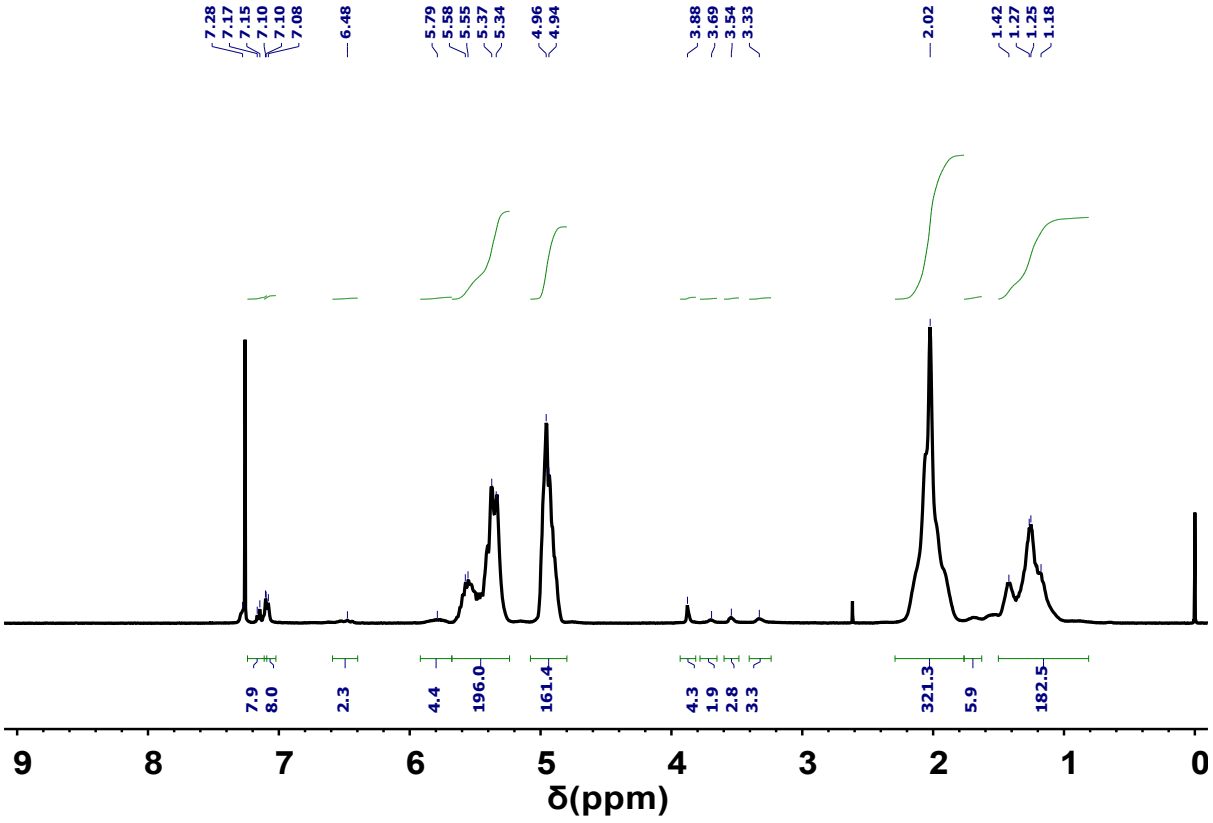


Figure S7: ^{1}H NMR spectra of SPU **12**.

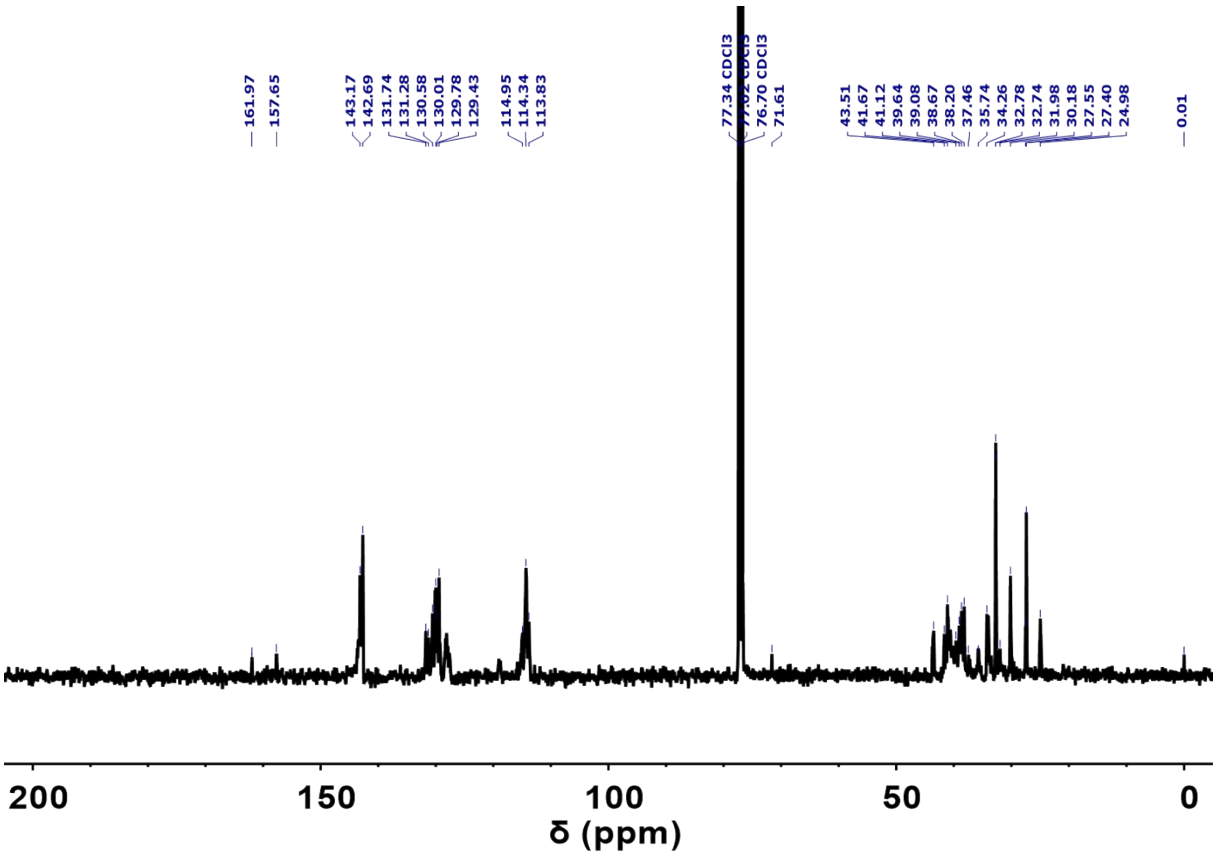


Figure S8: ^{13}C NMR spectra of SPU **12**.

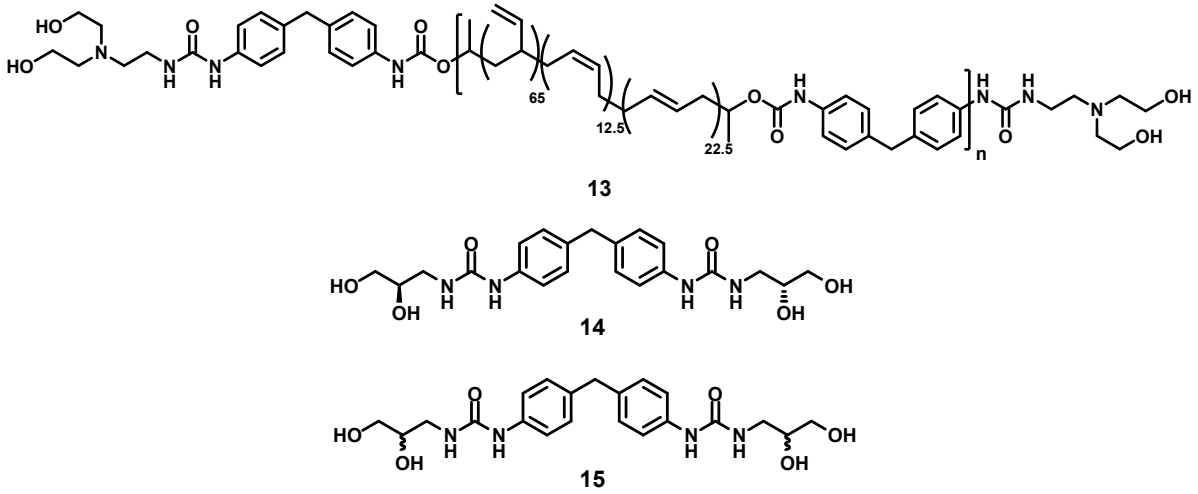


Figure S9: Structure of SPU **13** and model compounds **14** and **15**.

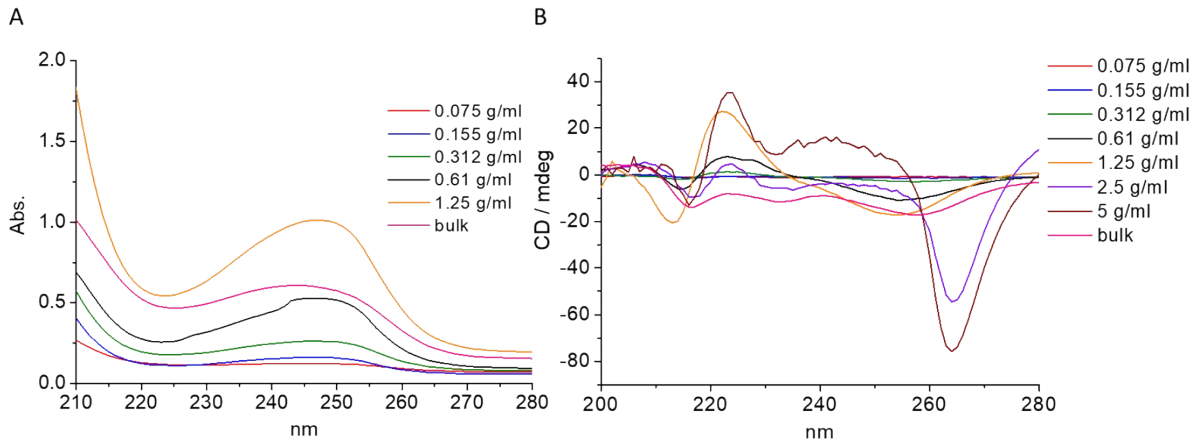


Figure S10 Solution UV-visible (A) and CD spectra (B) of SPU **1** (*S*-end group) as a function of concentration (solvent used: dichloromethane).

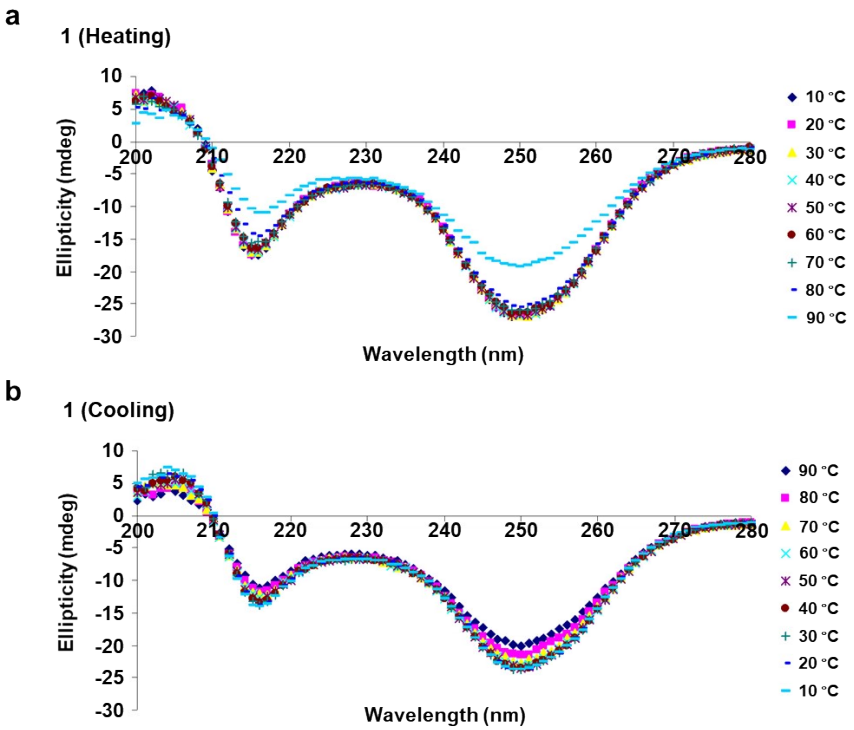


Figure S11: Variable temperature CD spectra (a) heating ramp and b) cooling ramp of the chiral supramolecular derivative **1-S**.

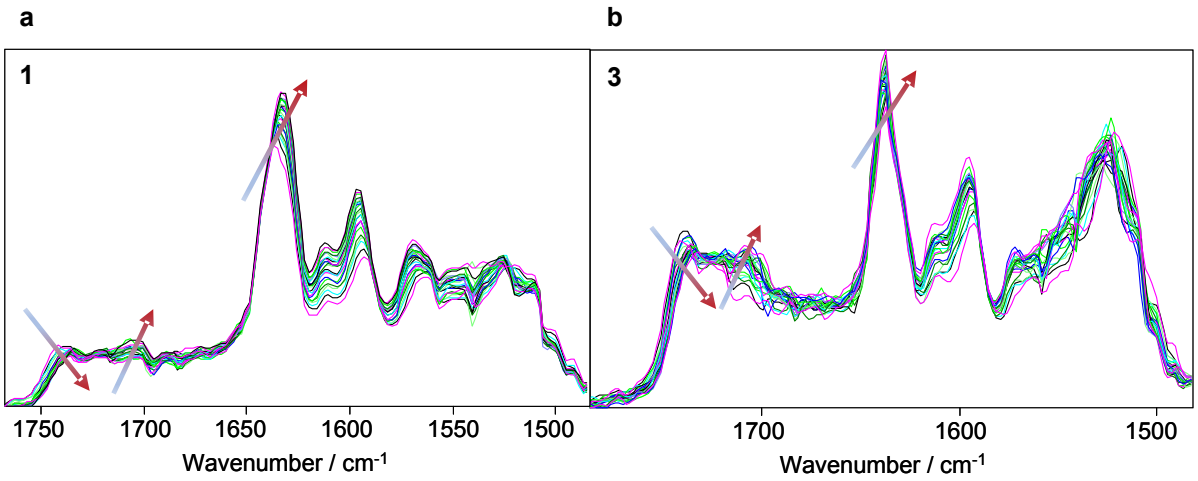


Figure S12: a) VT-FT-IR spectroscopic analysis upon cooling (150 °C-25 °C) of SPUs a) **1** and b) **3** both Urethane and Urea moieties spectral region. Trend arrows demonstrate the change in adsorpance profiles with respect to temperature from low (blue arrow terminus) to high (red arrow terminus) temperature.

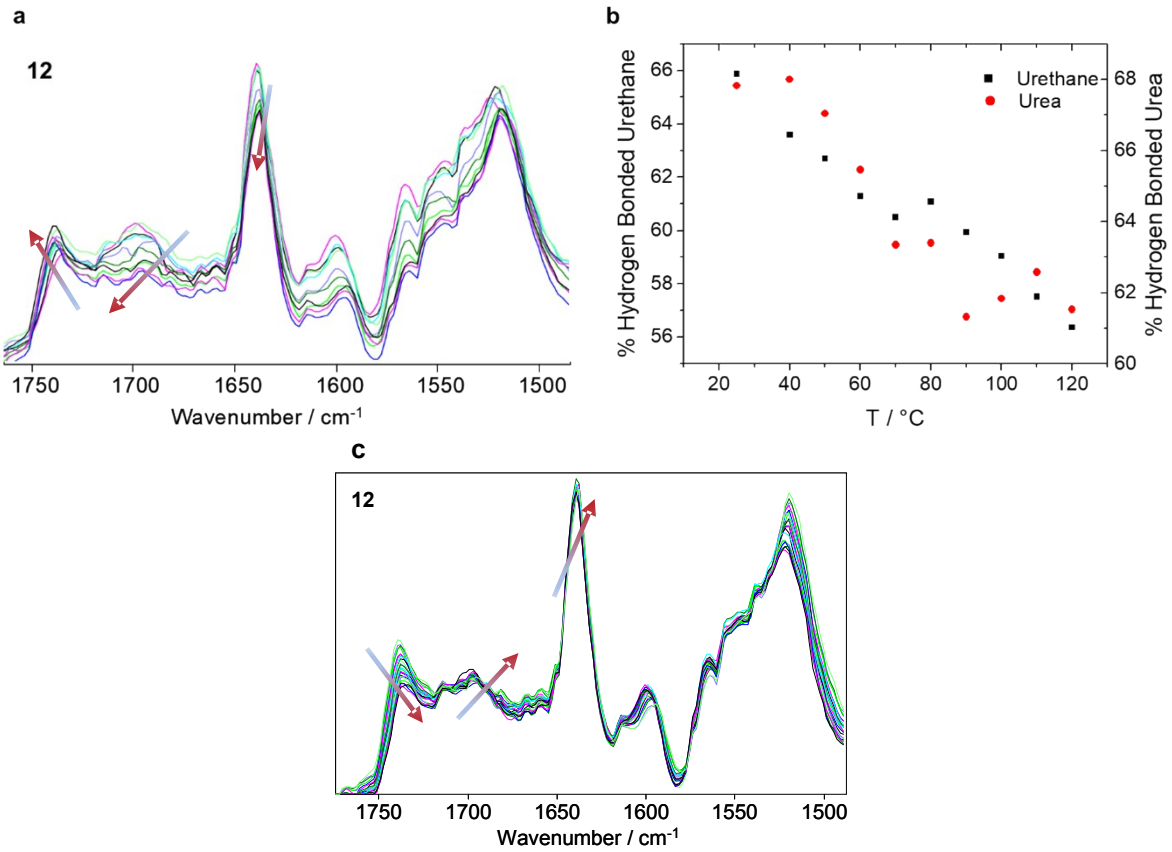


Figure S13: a) VT-FT-IR spectroscopic analysis (25 °C-150 °C) of SPU **12** b) Hydrogen bonding extent of both Urethane and Urea moieties in **12** and c) VT-FT-IR spectroscopic analysis upon cooling (150 °C-25 °C). Trend arrows demonstrate the change in adsorpance profiles with respect to temperature from low (blue arrow terminus) to high (red arrow terminus) temperature.

Quantitive analysis of the hydrogen bonding content of these SPUs has been determined using methods reported by Ning *et al.*[1] and Hermida-Merino *et al.*[2] employing **Equation 1**:

$$\%\ Hydrogen\ bonded\ urea\ or\ urethane\ = \frac{Area\ of\ hydrogen\ bonded\ urea\ of\ urethane\ carbonyl}{Total\ carbonyl\ area} \quad Equation\ 1$$

Where: total carbonyl area = area of free urethane/urea + hydrogen bonded urethane/urea

The polysegmented chain architecture with amorphous domains enables different arrangements either in an intra- or inter-molecular fashion withing the supramolecular network. Likewise, the main contribution of the hydrogen bonding to the vibration mode of the carbonyl region will be the N-H···C=O interaction but the presence of the OH of the alcohol will promote competitive interactions of the N-H···OH residues and the less intense OH···C=O couple.[3] The degree of hydrogen bonding in the SPUs has been calculated from the areas of the the characteristics vibration bands: 1730-1740 cm^{-1} free urethane carbonyl, 1703-1710 cm^{-1} hydrogen bonded urethane, 1690-1700 cm^{-1} free urea

carbonyl, 1660-1670 cm^{-1} hydrogen bonded urea carbonyl (disordered interaction), and 1630-1645 cm^{-1} hydrogen bonded urea carbonyl (ordered interaction).[1,2]

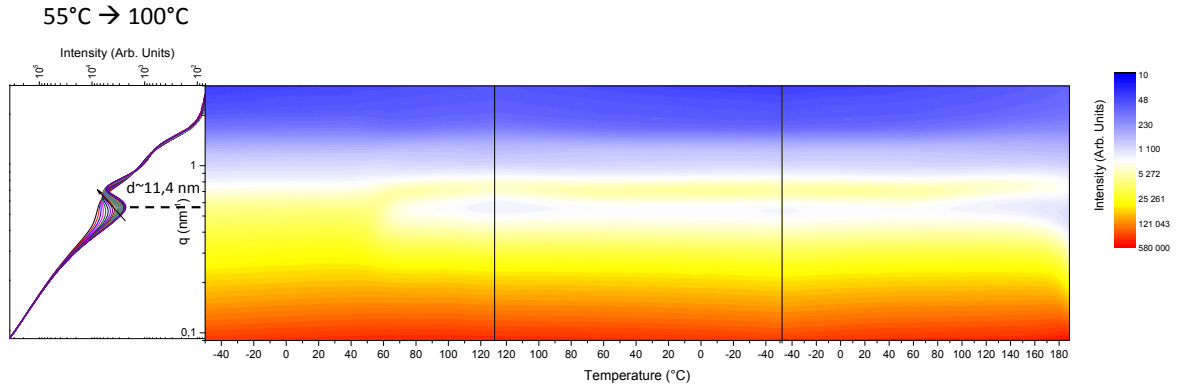


Figure S14: VT-SAXS profiles for supramolecular polyurethane **12**.

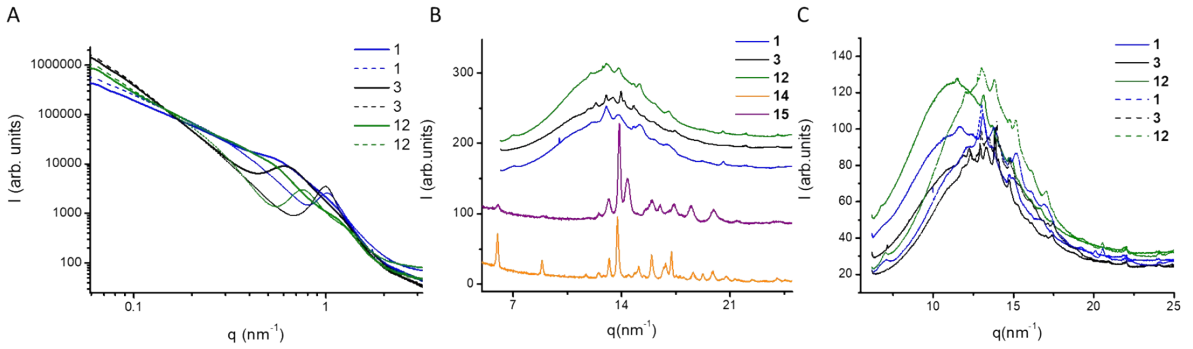


Figure S15: Comparison of 1) SAXS profiles of the SPUs derivatives (**1**,**3** and **12**) and WAXS profiles for SPUs derivative and the model compounds at B) room temperature and C) 180 °C.

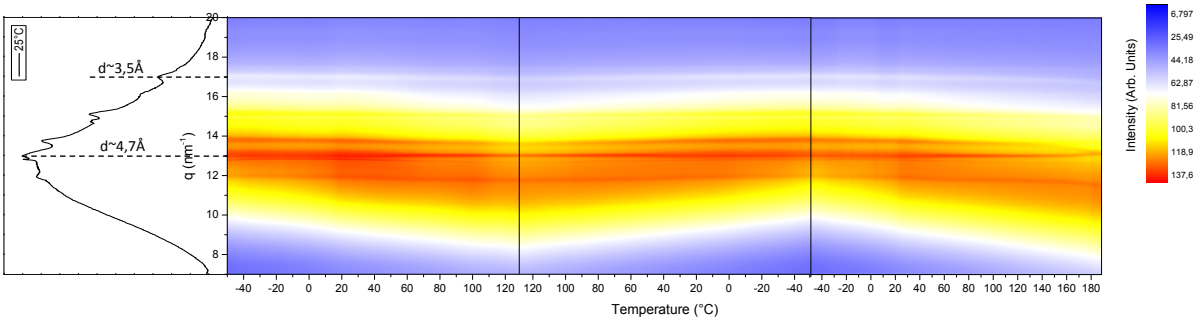


Figure S16: VT-WAXS profiles for supramolecular polyurethane **12**.

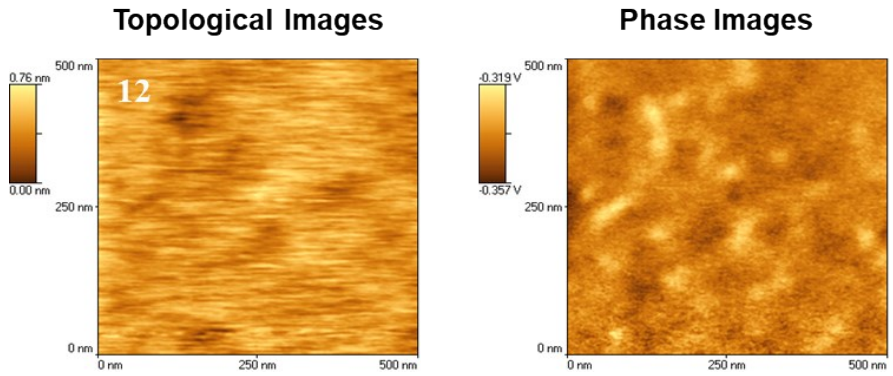


Figure S17: AFM Images of SPU **12**.

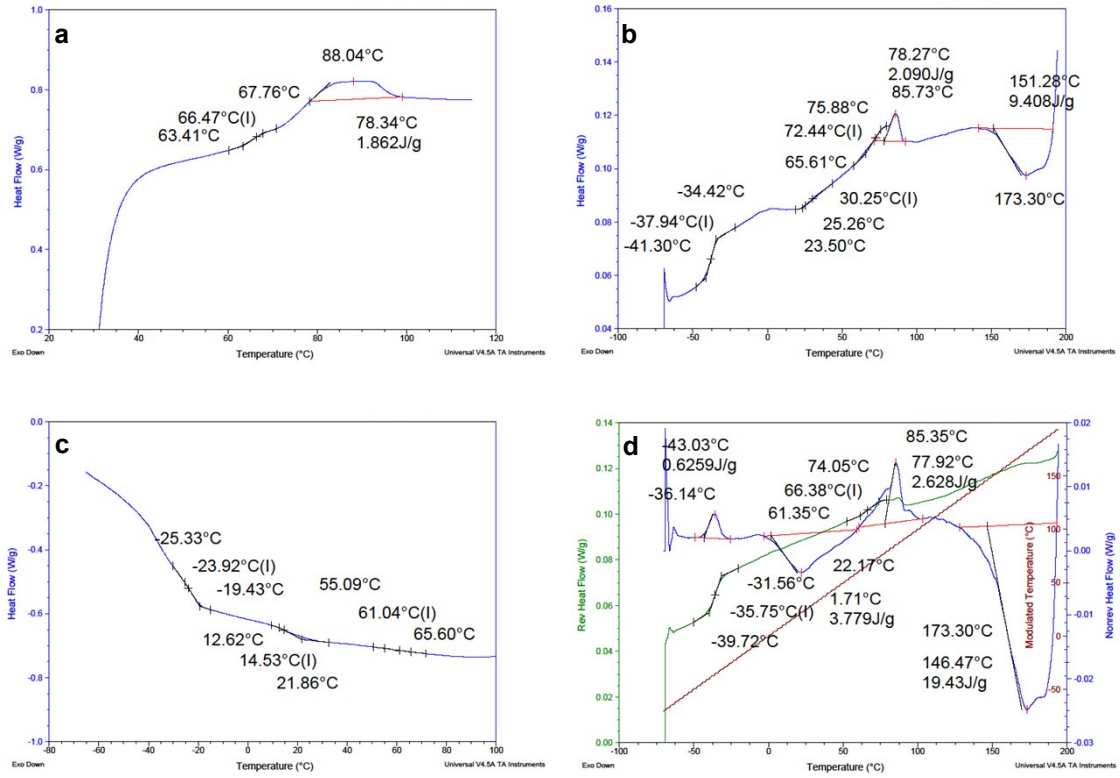


Figure S18: DSC thermograms of SPU **1** a) first heating, b) first cooling, c) second heating, d) second cooling.

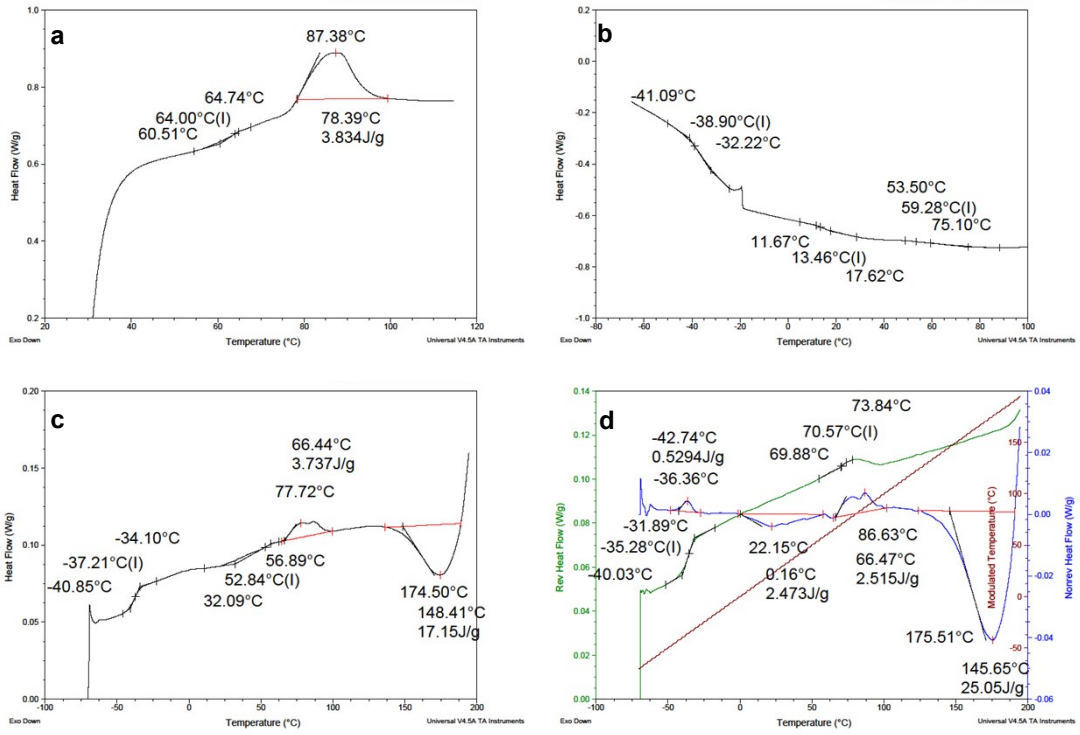


Figure S19: DSC thermograms of SPU **3** a) first heating, b) first cooling, c) second heating, d) second cooling heating.

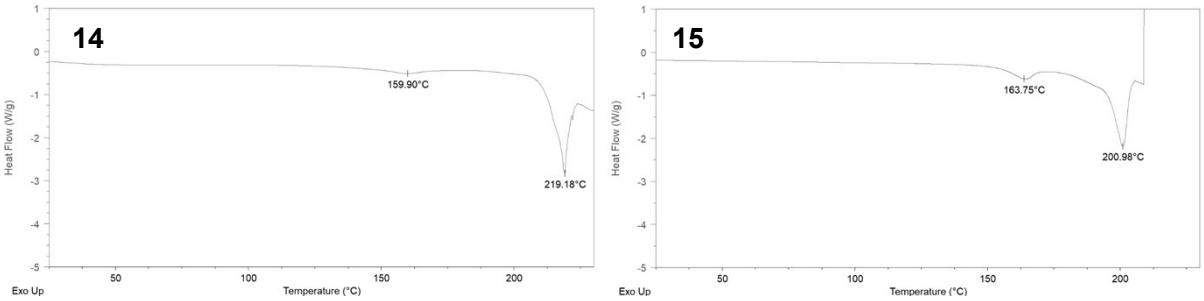


Figure S20: DSC thermograms of model compounds **14** and **15**.

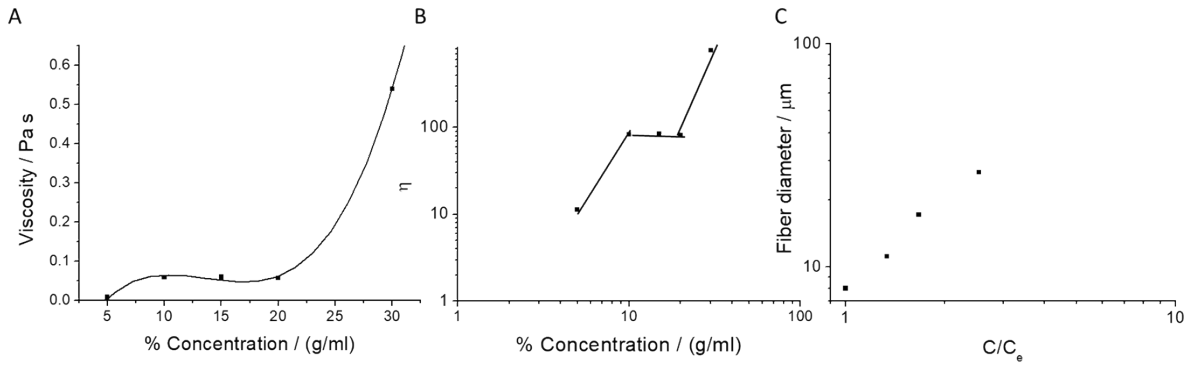


Figure S21: A) and B) Viscosity analysis of SPU **1** in dichloromethane; C) Fibre diameter against C/C_e for SPU **1**.

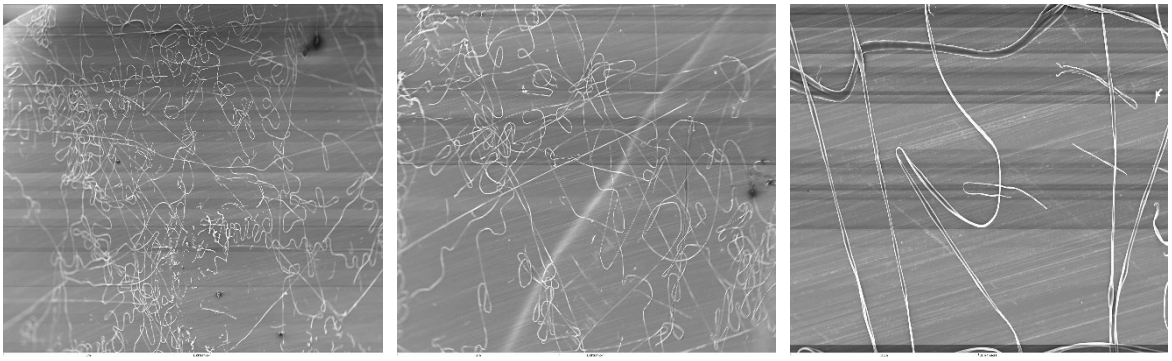


Figure S22: SEM image of the morphology of electrospun SPU **1**. Planar Electrode; Working Distance 25 cms, Working Voltage 12 kV, Temperature room-box 28.9 °C, Syringe 31.2 °C Relative Humidity 34 %, Mean Feature Regular fibres 18.5 µm., Polymer Concentration 20 % in dichloromethane. Motor Voltage 3.8 V, Needle Size 22G × ½ .

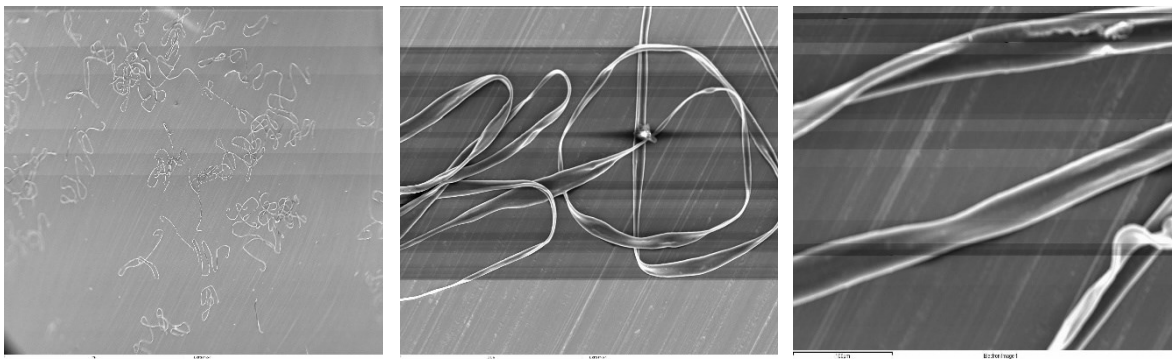


Figure S23: SEM image of morphology of electrospun SPU **1**. Planar Electrode; Working Distance 25 cms, Working Voltage – 12 kV, Temperature room-box 21.6 °C, Syringe 20.6 °C Relative Humidity 39.0 %, Mean Feature Wavy fibres 18.4-40.2 µm., Polymer Concentration 20 % in dichloromethane. Motor Voltage 3.8 V, Needle Size 22G × ½ .

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