Supplementary Material (ESI) for Polymer Chemistry

Supporting information

Reversible thermo-responsive microphase separated supramolecular polyurethanes

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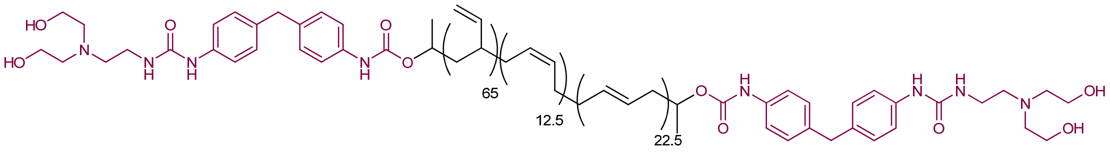
Synthesis and characterisation of polybutadiene derivatives 1, 3, 5 and 7

Synthesis of 4-((4'- 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl) ureidobenzyl)-phenyl-amino-carbonyl terminated poly(butadiene) 17

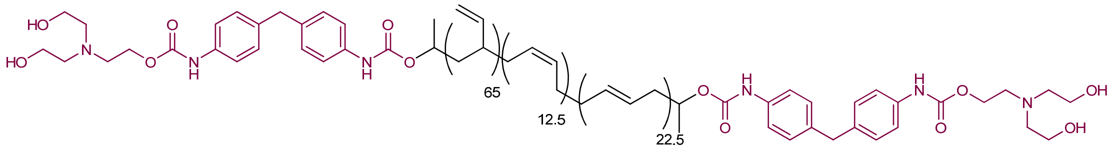


1

This analogue has been synthesised via the high dilution procedure described for 4,4'-methylene*bis*(phenyl-carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl ester) **1** (see section 2.2). 4-((4'- 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl) ureidobenzyl)-phenyl-amino-carbonyl terminated poly(butadiene) diol **17** was produced as a elastomeric translucent solid in a 89.1% yield (7.09 g) starting from poly(butadiene) diol end capped with 4,4'-methylenebis(phenylisocyanate) (7.04 g, 2.8 mmol) and *N,N*- *bis*-(2-hydroxyethyl-2H-)-ethylene diamine (0.876 g, 5.91 mmol).

IR ($CDCl_3$, KBr) ν_{max}/cm^{-1} 3330, 3072, 2969, 2916, 2834, 1714, 1639, 1597, 1522, 1448, 1415.^{1}H NMR (250 MHz, $CDCl_3$) δ 1.24-1.43 (br, 2H_n, $(CH_2)_n$), 2.02 (br m, 9H_n, (4 × *cis*$(CH{=}CHCH_2)_n$ + 4 × *trans* $(CH{=}CHCH_2)_n$ + $(CH{=}CHCH\ )_n$), 2.50 (br, 12H, (4 × NCH_2) + (2 × CH_2N)), 3.19-3.27 (br, 4H, 2 × CH_2N), 3.42-3.50 (br m, 8H, 4 × OCH_2), 3.62-3.71 (br, 4H, (2 × OCH_2), 3.82-3.87 (m, 4H, 2 × $ArCH_2Ar$), 4.96 (br, 2H_n, (2 × $CH{=}CH_2)_n$), 5.34 (br, 2H_n, (*cis* $CH{=}\ CH)_n$), 5.46-5.55 (br, 2H_n, (*trans* $CH{=}\ CH)_n$), 5.67-5.89 (br, H_n, $(CH_2{=}CH)_n$), 6.55-6.70 (4 × N*H*), 7.04-7.10 (AA'XX' system, 8H, 8 × ArH), 7.19-7.26 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.0 (CH_3), 27.4-27.6 $(CH_2)_n$, 30.2 $(CH_2)_n$, 32.0 $(CH_2)_n$, 37.5 $(CH)_n$, 38.7 (CH_3), 43.7 ($ArCH_2Ar$), 51.3 (CH_2), 56.6 (CH_2), 59.6 (OCH_2), 71.6 (CH_2), 114.3-115.0 $(CH_2{=}CH)_n$, 118.8 (Ar*C*), 127.7 *cis*$(CH{=}\ CH)_n$, 129.4 *trans*$(CH{=}\ CH)_n$, 131.3-131.7 *cis*$(CH{=}\ CH)_n$, 136.2-137.2 (Ar*C*), 142.7-144.2 $(CH_2{=}CH)_n$, 156.9 ($C{=}O$).

Synthesis of 4-((4'- carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(ethylene-*co*-butylene) diol 14



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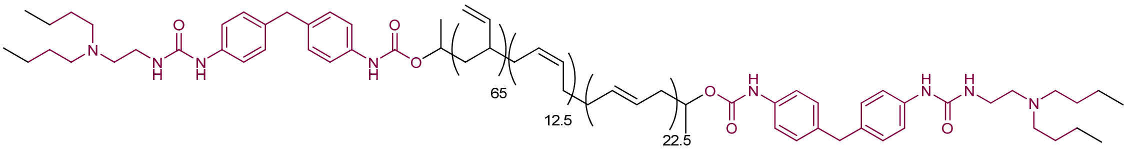
This material was produced using a high dilute procedure described for 4,4'-methylene*bis*(phenyl-carbamic acid 2-[bis-(2-hydroxyethyl)-amino]-ethyl ester) **21** (see section 2.2). The 4-((4'-Carbamic acid 2-[*bis*-(2-hydroxyethyl)-amino]-ethyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(polybutadiene) diol **14** was produced as a translucent elastomeric solid in 84.9% yield (10.1 g), starting from poly(butadiene) diol end capped with 4,4'-methylenebis(phenylisocyanate) (10.67 g, 4.10 mmol) and triethanolamine (1.224 g, 8.2 mmol).

IR ($CDCl_3$, KBr) ν_{max}/cm^{-1}; 3434, 3337, 3072, 2917, 2845, 1731, 1706, 1638, 1597, 1522, 1414. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.22-1.48 (br, 2H$_n$, (C*H*$_2$)$_n$), 2.02 (br m, 9H$_n$, (4 × *cis*(CH= CHC*H*$_2$)$_n$ + 4 × *trans* (CH=CHC*H*$_2$)$_n$ + (CH=CHC*H*)$_n$), 2.69-2.73 (t, 8H, C*H*$_2$N, *J*=5), 2.79-2.83 (t, 4H, 4 × NC*H*$_2$, *J* = 5.0), 3.58-3.63 (t, 8H, 4 × C*H*$_2$, *J* = 7.5), 3.81-3.87 (m, 4H, 2 × ArC*H*$_2$Ar), 4.09-4.11 (t, 4H, (2 × OC*H*$_2$), 4.21-4.26 (m 4H, (2 × C*H*$_2$O), 4.96 (br, 2H$_n$, (2 × CH=C*H*$_2$)$_n$), 5.33-5.36 (br, 2H$_n$, (*cis* C*H*= C*H*)$_n$), 5.45-5.56 (br, 2H$_n$, (*trans* C*H*= C*H*)$_n$), 5.72-5.84 (br, H$_n$, (CH$_2$=C*H*)$_n$) 6.56 (4 × N*H*), 7.07-7.10 (AA'XX' system, 8H, 8 × ArH), 7.26-7.39 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 24.95(*C*H$_3$), 27.38 (*C*H$_2$)$_n$, 30.13 (*C*H$_2$)$_n$, 31.96 (*C*H$_2$)$_n$, 38.19 (*C*H)$_n$, 40.52 (*C*H$_3$), 43.48 (Ar*C*H$_2$Ar), 54.17 (*C*H$_2$), 56.85 (*C*H$_2$), 59.66 (O*C*H$_2$), 113.83-115.01(C*H*$_2$=CH)$_n$, 118.85 (Ar*C*), 127.63 *cis*(C*H*= C*H*)$_n$, 130.11 *trans*(C*H*= C*H*)$_n$, 131.68 *cis*(C*H*= C*H*)$_n$, 135.99-136.21 (Ar*C*), 142.67-143.65 (C*H*$_2$= **C***H*)$_n$, 154 (*C*=O).

Synthesis of 4-((4’- 2-[*bis*butyl-amino]-ethyl) ureidobenzyl)-phenyl-amino-carbonyl terminated poly(butadiene) 18



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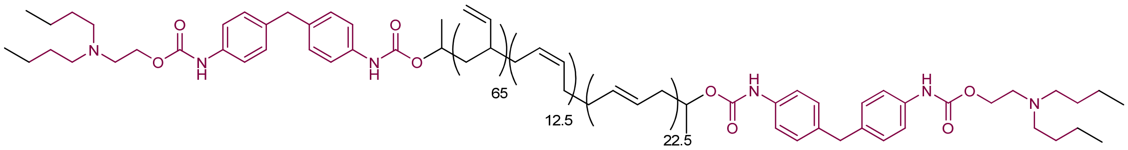
The synthesis has been carried using the direct addition approach used to synthesise 4,4’-methylene*bis*(phenyl-carbamic acid 2-[*N,N di*butyl)-amino]-ethyl ester) **2** (see section 2.2). 4-((4’-2-[*bis*butyl-amino]-ethyl) ureidobenzyl)-phenyl-amino-carbonyl terminated poly(butadiene) diol **18** was produced as a yellow viscous sticky rubbery solid in 84.8% yield (7.77 g) from poly(butadiene) diol end capped with 4,4’-methylenebis(phenylisocyanate) (8.05 g, 3.22 mmol) and *N,N’-di*butylethane-1,2-diamine (1.11 g, 6.44 mmol) .

IR ($CDCl_3$, KBr) ν_{max}/cm^{-1}; 3317, 3072, 2957, 2916, 2845, 1703, 1639, 1599, 1539, 1415. ^{1}H NMR (250MHz, $CDCl_3$) δ 0.87-0.90 (m, 12H, 4 × CH_3), 1.21-1.38 (br, $2H_n$, $(CH_2)_n$), 1.41-1.44 (br m, $16H_n$, (8 × CH_2), 2.02 (br m, $9H_n$, (4 × *cis*$(CH{=}CHCH_2)_n$ + 4 × *trans* $(CH{=}CHCH_2)_n$ + $(CH{=}CHCH\ )_n$), 2.60-2.64 (br, 8H, 4 × CH_2N), 2.68-2.72 (t, 4H, 2 × NCH_2, J = 5.0), 3.29-3.32 (br, 4H, 2 × CH_2N), 3.88-3.86 (br, 4H, 2 × $ArCH_2Ar$), 4.06-4.16 (m, 4H, (2 × OCH_2), 4.96 (br, $2H_n$, (2 × CH= $CH_2)_n$), 5.33-5.36 (br, $2H_n$, (*cis* CH= $CH)_n$), 5.46-5.59 (br, $2H_n$, (*trans* CH= $CH)_n$), 5.67-5.83 (br, H_n, $(CH_2{=}CH)_n$) 6.58-6.64 (4 × NH), 7.04-7.10 (AA’XX’ system, 8H, 8 × ArH), 7.22-7.26 (AA’XX’ system, 8H, 8 × ArH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.9 (CH_3), 20.2 (CH_2), 25 (CH_3), 27.4 $(CH_2)_n$, 30.2 $(CH_2)_n$, 32.8 $(CH_2)_n$, 37.5 $(CH)_n$, 39.7 (CH_2), 41.7 (CH_3), 43.5 ($ArCH_2Ar$), 53.9 (CH_2), 63.6 (OCH), 113.8-115.1 $(CH_2{=}CH)_n$, 118.9-120.7 (ArC), 127.7 *cis*$(CH{=}CH)_n$, 129.7 *trans*$(CH{=}CH)_n$, 131.7 *cis*$(CH{=}CH)_n$, 136.1-137.1 (ArC), 141.5-143.7 $(CH_2{=}CH)_n$, 157.3 (C=O).

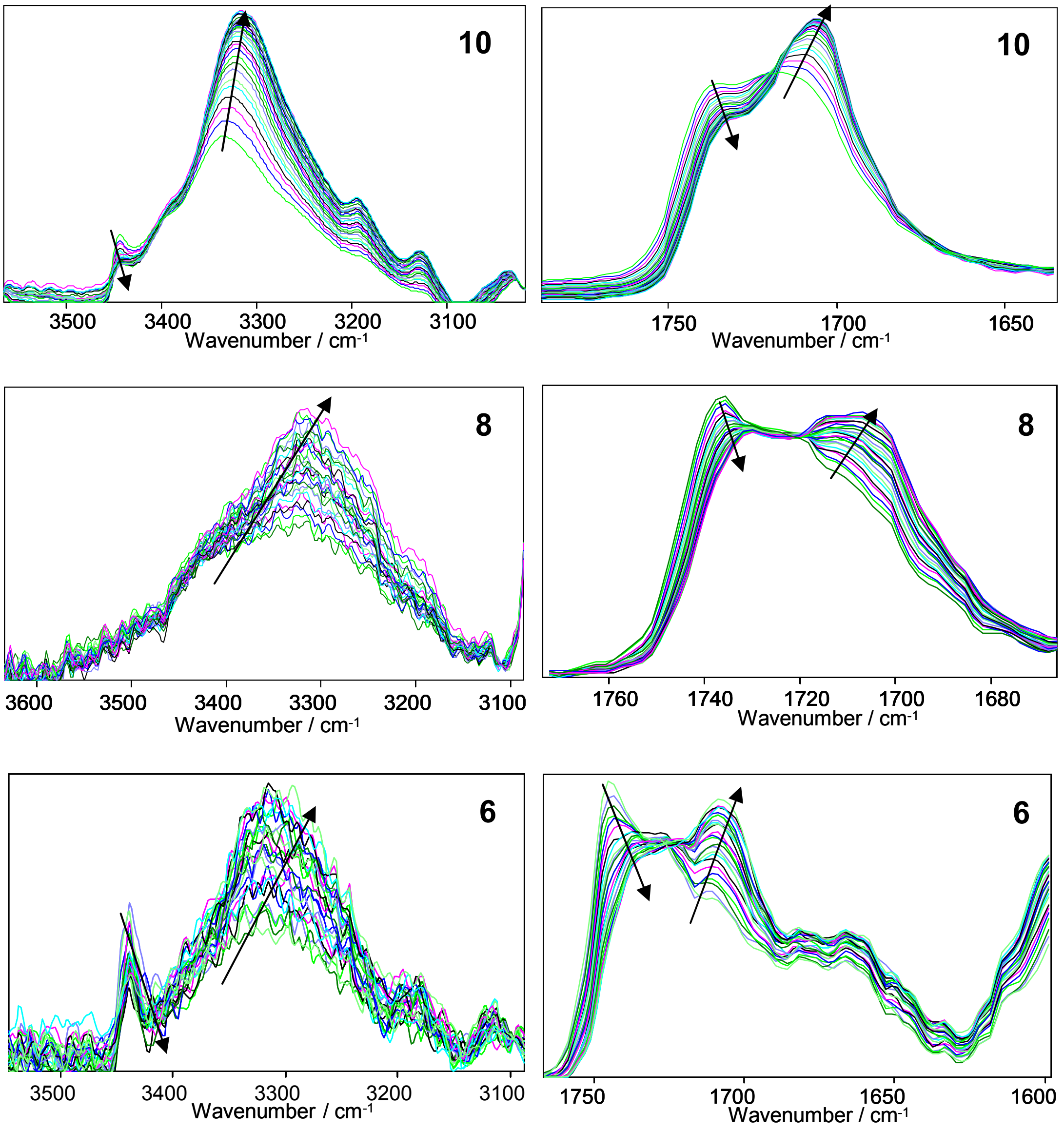
Synthesis of 4-((4'- carbamic acid 2-[*bis*butyl-amino]-ethyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(butadiene) diol 15



7

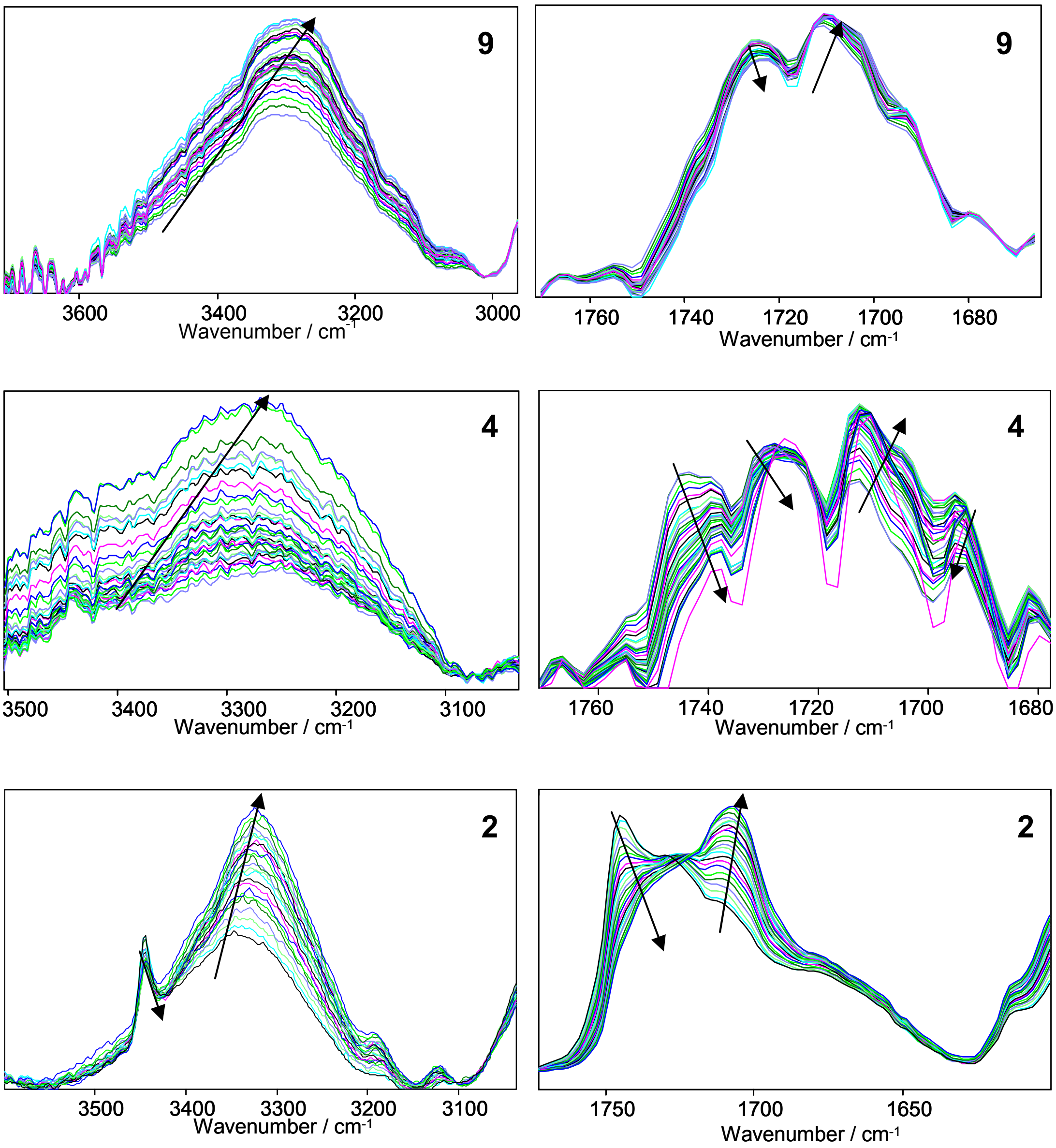
This analogue has been synthesised via the direct addition approach used to produce 4,4'-methylene*bis*(phenyl-carbamic acid 2-[*N,N di*butyl)-amino]-ethyl ester) **2** (see section 2.2). 4-((4'-Carbamic acid 2-[*bis*butyl-amino]-ethyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(butadiene) diol **15** was produced as a yellow viscous sticky solid in 84.8% yield (7.77 g) from poly(butadiene) diol end capped with 4,4'-methylenebis(phenylisocyanate) (8.05 g, 3.22 mmol) and 2-(*di*butylamino)ethanol (1.11 g, 6.44 mmol).

IR ($CDCl_3$, KBr) ν_{max}/cm^{-1}; 3400, 3322, 3072, 2969, 2915, 2843, 1707, 1639, 1599, 1533, 1436, 1415. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.93-0.96 (m, 12H, 4 × CH_3), 1.22-1.43 (br, $2H_n$, $(C\mathit{H}_2)_n$), 1.44-1.48 (br m, $8H_n$, (4 × $C\mathit{H}_2$), 2.02 (br m, $9H_n$, (4 × *cis*$(CH{=}CHC\mathit{H}_2)_n$ + 4 × *trans* $(CH{=}CHC\mathit{H}_2)_n$ + $(CH{=}CHC\mathit{H}\ )_n$), 2.44-2.50 (t, 8H, $C\mathit{H}_2N$, *J*=7.5), 2.69-2.74 (t, 4H, 2 × $NC\mathit{H}_2$, *J* = 5.0), 3.88 (s, 4H, 2 × $ArC\mathit{H}_2Ar$), 4.06-4.11 (m, 4H, (2 × $OC\mathit{H}_2$), 4.17-4.22 (m 4H, (2 × $C\mathit{H}_2O$), 4.96 (br, $2H_n$, (2 × $CH{=}C\mathit{H}_2)_n$), 5.33-5.36 (br, $2H_n$, (*cis* $C\mathit{H}{=}\ C\mathit{H})_n$), 5.46-5.56 (br, $2H_n$, (*trans* $C\mathit{H}{=}C\mathit{H})_n$), 5.77-5.81 (br, H_n, $(CH_2{=}C\mathit{H})_n$) 6.56-6.67 (4 × $N\mathit{H}$), 7.07-7.11 (AA'XX' system, 8H, 8 × ArH), 7.22-7.29 (AA'XX' system, 8H, 8 × ArH); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.12 ($\mathit{C}H_3$), 20.67 ($\mathit{C}H_2$) 24.99 ($\mathit{C}H_3$), 27.56 $(\mathit{C}H_2)_n$, 31.41 $(\mathit{C}H_2)_n$, 32.77 $(\mathit{C}H_2)_n$, 38.25 $(\mathit{C}H)_n$, 40.16 ($\mathit{C}H_3$), 43.48 ($Ar\mathit{C}H_2Ar$), 52.66 ($\mathit{C}H_2$), 54.45 ($\mathit{C}H_2$), 63.30 ($\mathit{C}H_2$), 67.99 ($O\mathit{C}H$), 113.83-114.94 $(\mathit{CH}_2{=}CH)_n$, 118.93 (Ar*C*), 127.66 *cis*$(C\mathit{H}{=}\ C\mathit{H})_n$, 130.03 *trans*$(C\mathit{H}{=}\ C\mathit{H})_n$, 131.76 *cis*$(C\mathit{H}{=}C\mathit{H})_n$, 135.99-136.31 (Ar*C*), 142.70-143.43 $(CH_2{=}\mathit{CH})_n$, 153.67 (*C*=O).



a) **b)**

Figure S1 FT–IR spectra on cooling (120 – 25 °C) the butyl terminated *bis*urethane system **10, 8** and **6** a) NH stretching region, b) Urethane stretching region.



a) **b)**

Figure S2 FT–IR spectra on cooling (120 – 25 °C) the butyl terminated *bis*urethane system **9, 4** and **2** a) NH stretching region, b) Urethane stretching region.

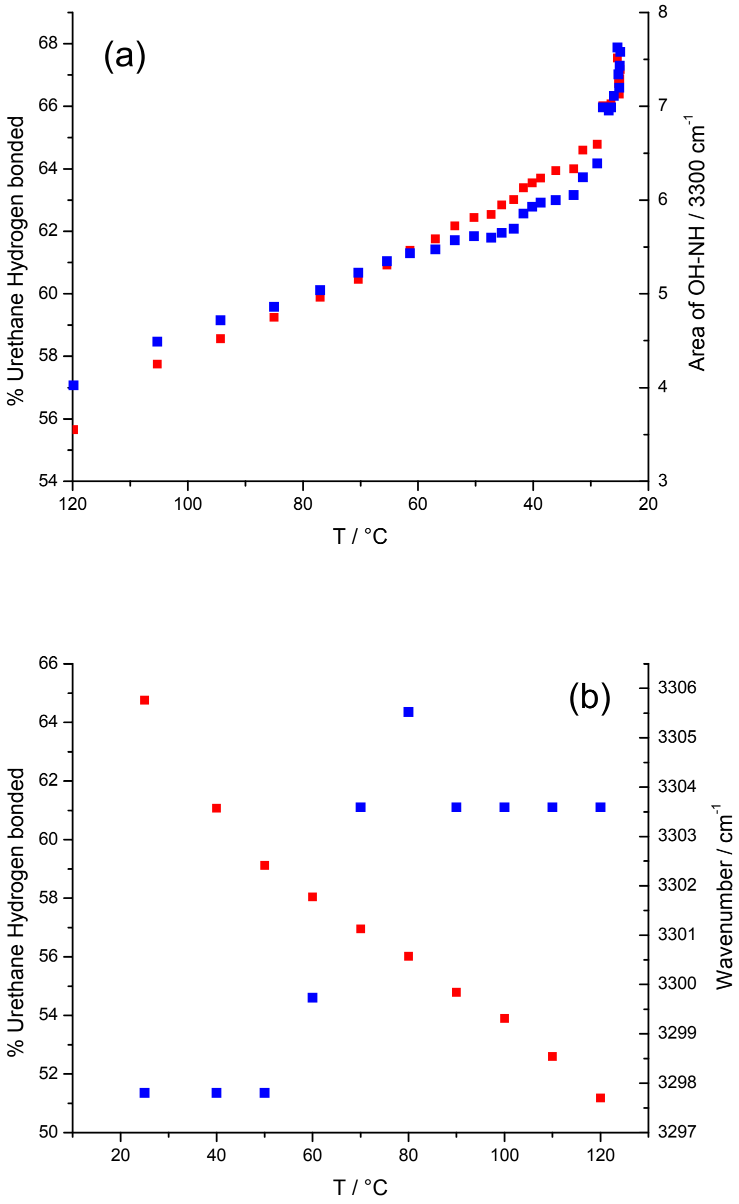


Figure S3 Summary of the extent of hydrogen bonding versus temperature a) Variation of the hydrogen bonding on the urethane region and the area of the NH/OH region b) Variation of the NH absorption bands. Red symbols denote the extent of hydrogen bonding, blue symbols denote the position of the maximum absorbance band of the NH vibration.