

## Supporting Information

### Enhancement of Microphase Ordering and Mechanical Properties of Supramolecular Hydrogen-Bonded Polyurethane Networks

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## Experimental

### Materials

The reagents used were commercially available from either Acros Chimica, Aldrich Chemical Company or Alfa Aesar and were used without further purification. The dry solvents involved were purchased and used as supplied or distilled with appropriate dehydration agents, i.e. tetrahydrofuran (THF) which was distilled from benzophenone and sodium. All other reagents such as polybutadiene Krasol LBH2000 [ $M_n$  1730 g mol<sup>-1</sup> and  $M_w$  2020 g mol<sup>-1</sup> ( $\bar{D}$  = 1.17); concentration of hydroxyl groups = 1.021 meq g<sup>-1</sup>;<sup>S1</sup> and isomer content; (1,2- = 60 wt%, 1,4-cis = 15 wt%, and 1,4-trans = 25 wt%), and 4,4'-methylenebis(phenylisocyanate) were supplied by Henkel Adhesive Technologies, Slough, UK. Thin-layer chromatography (TLC) was performed on aluminium sheets coated with Merck silicagel 60 F254. Column chromatography was performed using either SI60 sorbent silica (40-63  $\mu$ m) supplied from VWR international or Brockmann 1, standard grade, neutral activated aluminium oxide (*ca.* 150 mesh) supplied from Aldrich Chemical Company.

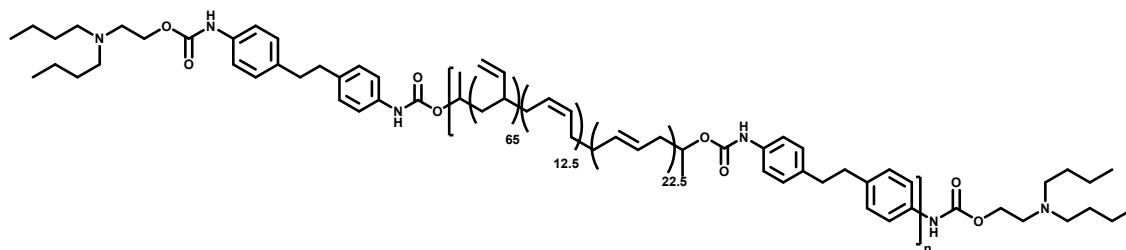
### Instrumentation

<sup>1</sup>H Nuclear Magnetic Resonance spectroscopy (<sup>1</sup>H-NMR) was conducted on either a Bruker DPX250 (250 MHz) or a Bruker AMX400 (400 MHz) spectrometer using the deuterated solvent as the lock. In the same manner, <sup>13</sup>C Nuclear Magnetic Resonance spectroscopy (<sup>13</sup>C-NMR) was performed on a Bruker DPX250 (62.5 MHz) or a Bruker AMX400 (100 MHz) spectrometers. FT Infrared spectroscopy was performed using a Perkin Elmer 1420-X spectrometer with the samples analysed as either neat films or in solution between two potassium bromide or sodium chloride disks. A Bruker MicroToF LC-MS instrument employing ionisation via electrospray was utilised to obtain mass spectrometric data and samples were injected by direct insertion via a syringe pump. An Electrothermal digital melting point instrument or a TA Instruments DSC 2920 differential scanning calorimeter were used to determine the melting point of the SPUs. The average molecular weight of the polymers generated was determined via Gel Permeation Chromatography (GPC) using a Polymer Laboratories PL-GPC 220 high temperature

chromatograph fitted with PL Mixed Gel columns at 40 °C. The samples were dissolved in analytical grade chloroform (5mg mL<sup>-1</sup>), and analysed against PL Easy-Cal Polystyrene as the calibrants. Samples for AFM analysis were prepared by spin-coating onto a silicon wafer from a solution of the respective compound (1% w/v) in THF. AFM micrographs were collected using a Veeco Explorer fitted with a tube-type 2 µm scanner and silicon cantilever tips (spring constant 1-5 N m<sup>-1</sup>; Veeco). For all measurements, the set-point amplitude (free oscillating amplitude of the cantilever divided by the actual oscillating amplitude) was maintained between 60 and 100 kHz in a tapping mode. Polymer crystallization (SAXS/WAXS) experiments were conducted on Dutch-Belgian Beamline (DUBBLE) BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France).<sup>S2</sup> The samples were introduced in pans DSC 600 heating stage from Linkam that were previously pierced in order to produce X-ray windows. The windows are made of mica and the capsules were sealed avoiding sample loss. The distance to the SAXS detector was *ca.* 5 m using a wavelength of 0.145 nm. A-2D multiwire detector was employed with a resolution of 512 × 515 pixels and a pixel size of 260 µm<sup>2</sup>. Standard corrections for sample absorption and background subtraction were performed. WAXS images were recorded using a CCD-based X-ray digital camera (Photonic science) with a pixel size of 44 µm<sup>2</sup>. Thin films of the polyurethanes were produced for mechanical testing via a solution casting procedure. All polyurethanes were dissolved in THF and the solution was poured into flat PTFE moulds. This was subsequently placed in a vacuum oven at 70 °C with a pressure of approximately 0.6 to 0.8 bar for a duration of 24 hours. Polyurethane films of uniform thickness between 200 and 500 µm were obtained at the end of this procedure without residual solvent. Rheological analysis was performed on circular samples (25 mm diameter) that were obtained from moulded films using a steel punch cutter. Rheometry was performed using a TA instruments AR2000 rheometer. The frequency sweeps were performed between 0.1 and 100 rad/s at a strain amplitude of 0.1 % for each selected temperature, each time the temperature was held for 5 minutes before data were gathered. Temperature sweeps were performed at a single frequency of 10 Hz with a strain amplitude of 0.1 %. Initially, the samples were placed on the rheometer, heated to 70 °C and held for one hour. Then, the temperature was decreased to -60 °C at a rate of 3 °C per minute whilst data were collected. The sample was again heated to 70 °C at 3 °C per minute. Three cycles of tests were measured, and the results show that the repeating heating does not change the properties significantly

## Synthesis

*Synthesis of 4-((4'- carbamic acid 2-[bisbutyl-amino]-ethyl ester) phenethyl)-phenyl-amino-carbonyl terminated poly(butadiene) diol 1*



To a stirred solution of the prepolymer **7** (2.59 g, 1.02 mmol) generated<sup>S3</sup> from the polybutadiene diol **5** with 4,4'-dibenzyl diisocyanate (DBDI) **6** in dry THF (50 mL) under a nitrogen atmosphere was added 2-(dibutylamino)ethanol **8** (0.35 g 2.05 mmol) to furnish the desired polymer **1** as a yellow elastomeric material (2.35 g, 79.7%). IR (CDCl<sub>3</sub>, KBr)  $\nu_{\max}/\text{cm}^{-1}$  3314, 3071, 2912, 2840, 1731, 1705, 1641, 1598, 1541, 1452, 1415.. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 0.88-0.94 (t, 12H, 4  $\times$  CH<sub>3</sub>,  $J = 7.5$ ), 1.23-1.43 (br, 2H<sub>n</sub>, (CH<sub>2</sub>)<sub>n</sub>), 1.25-1.31 (m, 8H, 4  $\times$  CH<sub>2</sub>), 1.41-1.45 (m, 8H, 4  $\times$  CH<sub>2</sub>,  $J = 5$ ) 2.02 (br m, 9H<sub>n</sub>, (4  $\times$  cis(CH=CHCH<sub>2</sub>)<sub>n</sub> + 4  $\times$  trans(CH=CHCH<sub>2</sub>)<sub>n</sub> + (CH=CHCH) <sub>n</sub>), 2.42-2.48 (m, 8H, 4  $\times$  N CH<sub>2</sub>,  $J = 7.5$ ), 2.70-2.75 (t, 4H, 2  $\times$  CH<sub>2</sub>N,  $J = 6.2$ ), 2.83 (s, 8H, 2  $\times$  ArCH<sub>2</sub>CH<sub>2</sub>Ar), 4.18-4.21 (t, 4H, (2  $\times$  OCH<sub>2</sub>)  $J = 7.5$ ), 4.12-4.23 (m 4H, (2  $\times$  CHO), 4.96 (br, 2H<sub>n</sub>, (2  $\times$  CH=CH<sub>2</sub>)<sub>n</sub>), 5.33-5.35 (br, 2H<sub>n</sub>, (cis CH=CH)<sub>n</sub>), 5.46-5.56 (br, 2H<sub>n</sub>, (trans CH=CH)<sub>n</sub>), 5.77-5.81 (br, H<sub>n</sub>, (CH<sub>2</sub>=CH)<sub>n</sub>) 6.54-6.63 (4  $\times$  NH), 7.06-7.10 (AA'XX' system, 8H, 8  $\times$  ArH), 7.21-7.28 (AA'XX' system, 8H, 8  $\times$  ArH); <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 14.1 (CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 24.9 (CH<sub>3</sub>), 27.5 (CH<sub>2</sub>)<sub>n</sub>, 30.2 (CH<sub>2</sub>)<sub>n</sub>, 32.7 (CH<sub>2</sub>)<sub>n</sub>, 35.6 (ArCH<sub>2</sub>CH<sub>2</sub>Ar), 37.2 (CH)<sub>n</sub>, 38.2-41.7 ((CH<sub>2</sub>)<sub>n</sub> + CH<sub>2</sub>), 52.6 (CH<sub>2</sub>), 54.4 (CH<sub>2</sub>), 63.3 (OCH<sub>2</sub>), 113.8-115.0 (CH<sub>2</sub>=CH)<sub>n</sub>, 118.7 (ArC), 128.1 cis(CH=CH)<sub>n</sub>, 130.1 trans(CH=CH)<sub>n</sub>, 131.7 cis(CH=CH)<sub>n</sub>, 135.7-136.8 (ArC), 142.6-143.4 (CH<sub>2</sub>=CH)<sub>n</sub>, 153.6 (C=O); GPC (THF)  $M_w = 8900$ ,  $M_n = 5600$ ,  $D = 1.6$ .

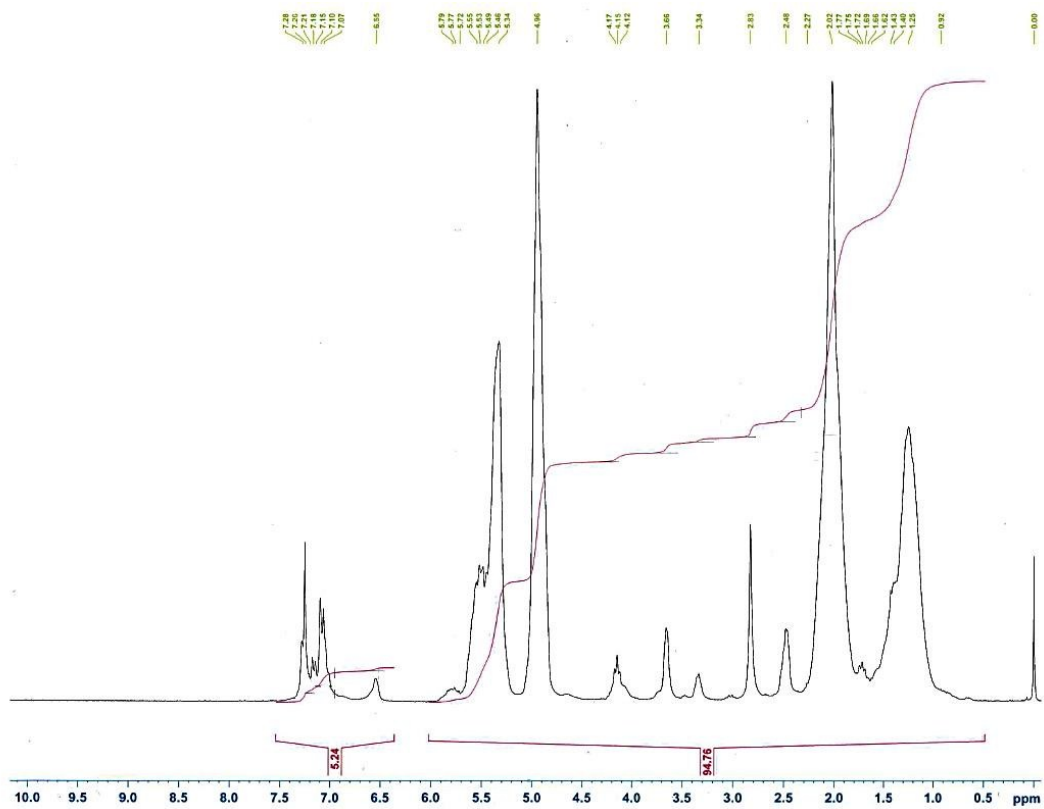
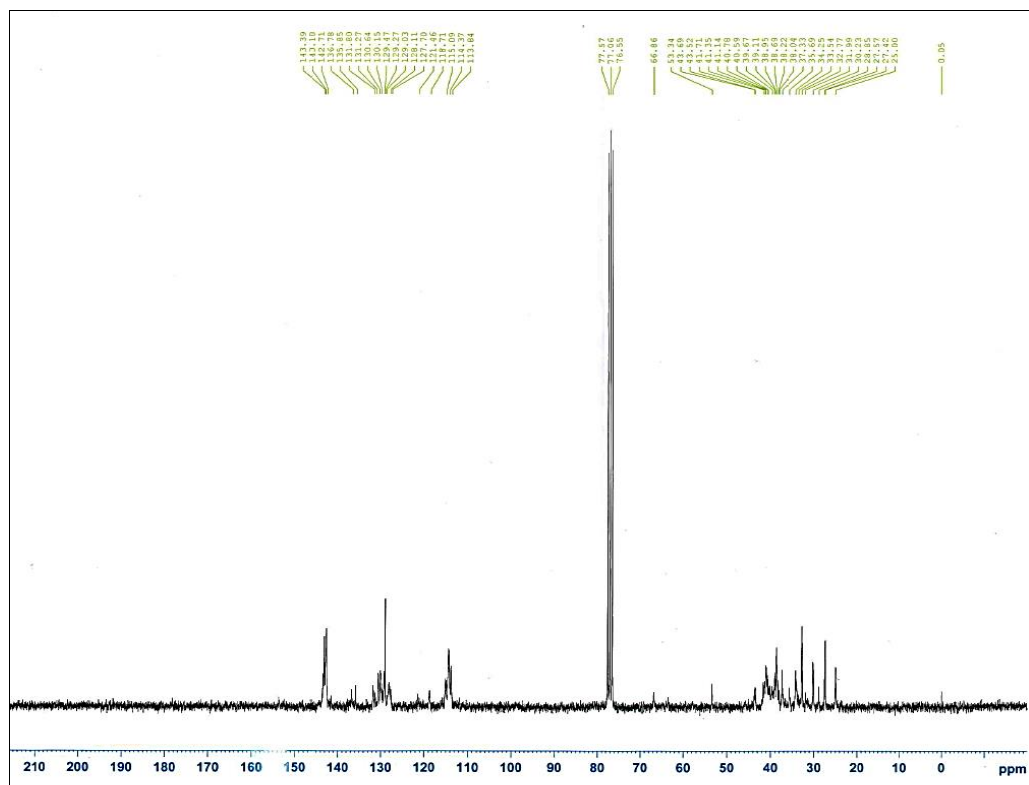
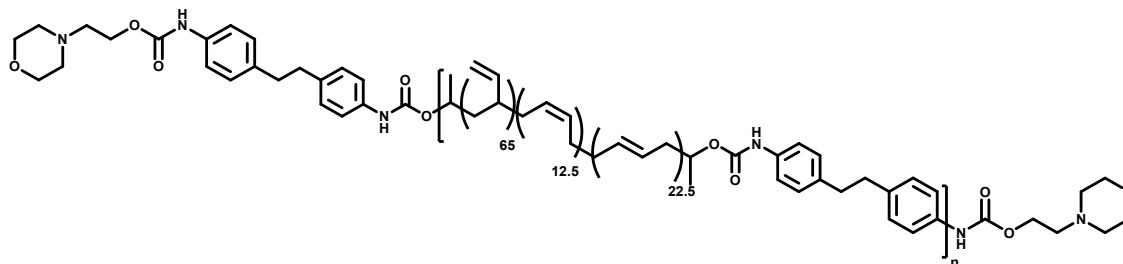


Figure S1:  $^1\text{H}$  NMR spectra of polymer **1** in  $\text{CDCl}_3$  at  $25\text{ }^\circ\text{C}$ .



**Figure S2:**  $^{13}\text{C}$  NMR spectra of polymer **1** in  $\text{CDCl}_3$  at 25 °C.  
*Synthesis of 4-((4'-carbamic acid 2-[bismorpholine]-ethyl ester) phenethyl)-phenyl-amino-carbonyl terminated poly(butadiene) diol **2***



To a stirred solution of the prepolymer **7** (2.59 g, 1.02 mmol) generated<sup>S3</sup> from the reaction of polybutadiene diol **5** with 4,4'-dibenzyl diisocyanate (DBDI) **6** in dry THF (50 mL) under a nitrogen atmosphere was added N-(2-hydroxyethyl)-morpholine **10** (0.27 g 2.05 mmol) to furnish the desired polymer **2** as a yellow elastomeric material (2.56 g, 89.5 %). IR ( $\text{CDCl}_3$ , KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3311, 3070, 2912, 2840, 1733, 1703, 1637, 1598, 1541, 1452, 1411.;  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 1.25-1.43 (br,  $2\text{H}_n$ ,  $(\text{CH}_2)_n$ ), 2.02 (br m,  $9\text{H}_n$ ,  $(4 \times \text{cis}(\text{CH}=\text{CHCH}_2)_n + 4 \times \text{trans}(\text{CH}=\text{CHCH}_2)_n + (\text{CH}=\text{CHCH})_n$ ), 2.51-2.54 (t,  $8\text{H}$ ,  $4 \times \text{NCH}_2$ ,  $J = 7.5$ ), 2.65-2.69 (t,  $4\text{H}$ ,  $2 \times \text{CH}_2\text{N}$ ,  $J = 5.0$ ), 2.84 (s,  $8\text{H}$ ,  $2 \times \text{ArCH}_2\text{CH}_2\text{Ar}$ ), 3.71-3.75 (t,  $8\text{H}$ ,  $4 \times \text{OCH}_2$ ,  $J = 5.0$ ), 4.07-4.17 (m,  $4\text{H}$ ,  $(2 \times \text{CHO})$ ), 4.27-4.31 (t,  $4\text{H}$ ,  $(2 \times \text{CH}_2\text{O}$ ,  $J = 5$ ), 4.96 (br,  $2\text{H}_n$ ,  $(2 \times \text{CH}=\text{CH}_2)_n$ ), 5.33-5.35 (br,  $2\text{H}_n$ ,  $(\text{cis CH}=\text{CH})_n$ ), 5.45-5.56 (br,  $2\text{H}_n$ ,  $(\text{trans CH}=\text{CH})_n$ ), 5.67-5.84 (br,  $\text{H}_n$ ,  $(\text{CH}_2=\text{CH})_n$ ) 6.57-6.71 ( $4 \times \text{NH}$ ), 7.06-7.09 (AA'XX' system,  $8\text{H}$ ,  $8 \times \text{ArH}$ ), 7.26-7.28 (AA'XX' system,  $8\text{H}$ ,  $8 \times \text{ArH}$ );  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 24.9 ( $\text{CH}_3$ ), 27.4 ( $(\text{CH}_2)_n$ ), 30.2 ( $(\text{CH}_2)_n$ ), 32.2 ( $(\text{CH}_2)_n$ ), 35.7 ( $\text{ArCH}_2\text{CH}_2\text{Ar}$ ), 38.2 ( $(\text{CH})_n$ ), 39.7 ( $\text{CH}_3$ ), 53.8 ( $\text{CH}_2\text{N}$ ), 57.5 ( $\text{NCH}_2$ ), 61.7( $\text{OCH}_2$ ), 66.8 ( $\text{CH}_2\text{O}$ ), 113.8-115.2 ( $(\text{CH}_2=\text{CH})_n$ ), 118.7 ( $\text{ArC}$ ), 127.7  $\text{cis}(\text{CH}=\text{CH})_n$ , 130.1  $\text{trans}(\text{CH}=\text{CH})_n$ , 131.7  $\text{cis}(\text{CH}=\text{CH})_n$ , 135.6-136.8 ( $\text{ArC}$ ), 142.6-143.1 ( $(\text{CH}_2=\text{CH})_n$ ), 153.4 ( $\text{C}=\text{O}$ ); GPC (THF)  $M_w = 12200$ ,  $M_n = 6500$ ,  $\text{Đ} = 1.9$ .

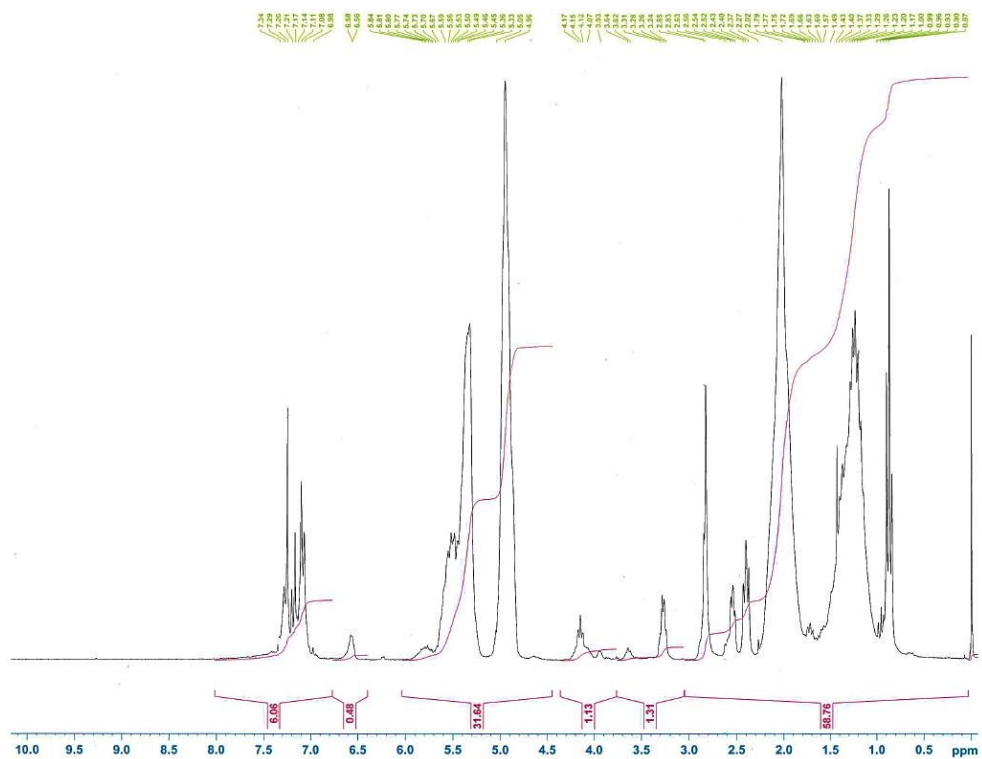


Figure S3:  $^1\text{H}$  NMR spectra of polymer **2** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

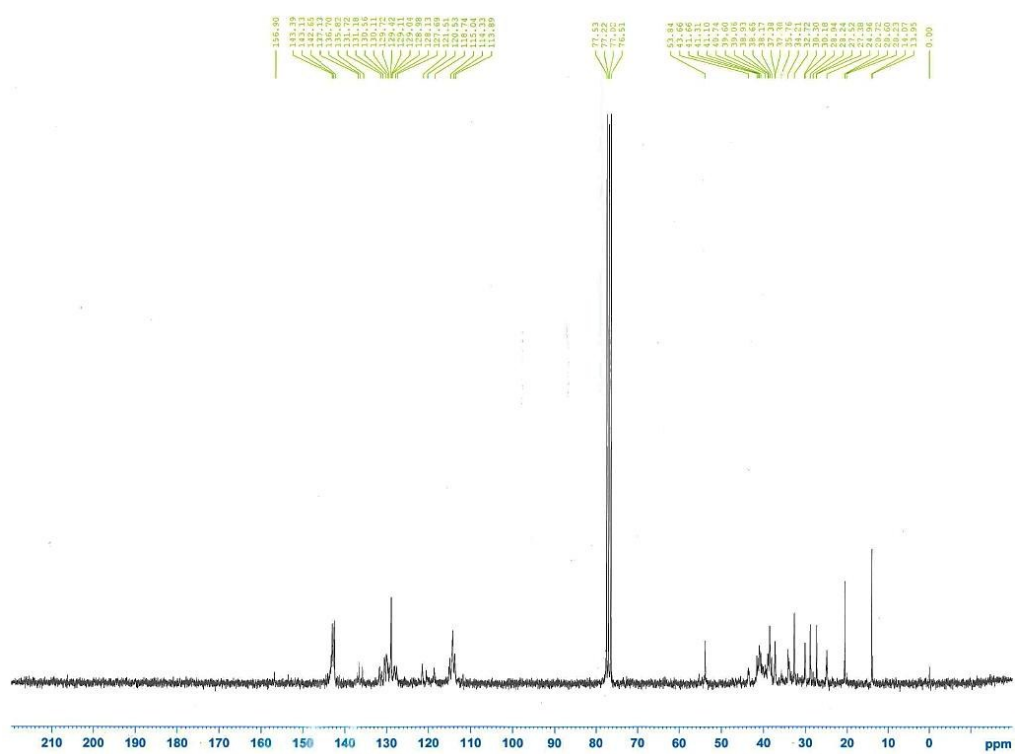
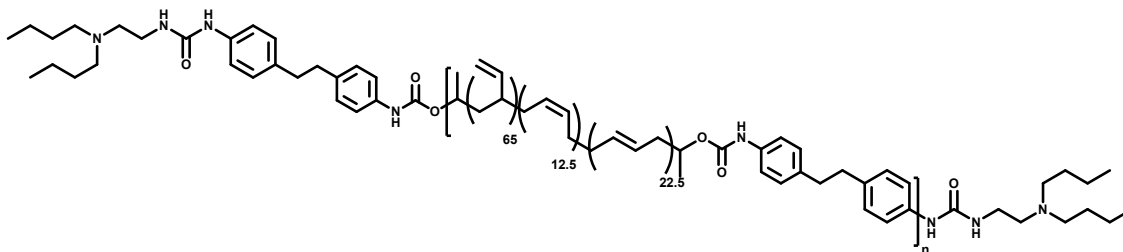


Figure S4:  $^{13}\text{C}$  NMR spectra of polymer **2** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

*Synthesis of 4-((4'-2-[bisbutyl-amino]-ethyl) ureidophenethyl)-phenyl-amino-carbonyl terminated poly(butadiene) 3*

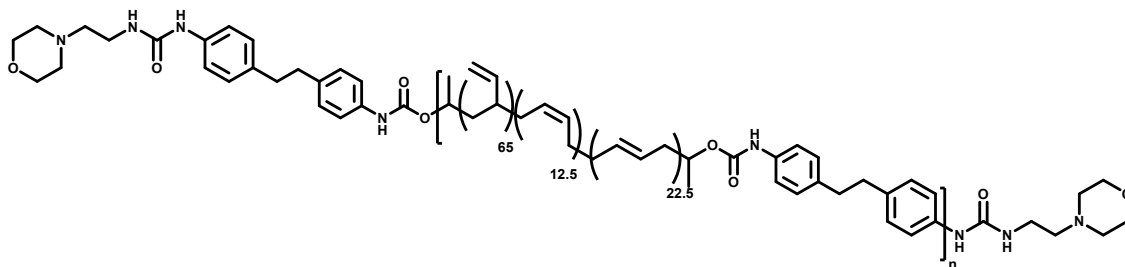


To a stirred solution of the prepolymer **7** (5.13 g, 2.03 mmol) generated<sup>S3</sup> from the polybutadiene diol **5** with 4,4'-dibenzyl diisocyanate (DBDI) **6** in dry THF (50 mL) under a nitrogen atmosphere was added N,N'-dibutylethane-1,2-diamine **9** (0.69 g 4.06 mmol) to furnish the desired polymer **3** as a yellow elastomeric material (5.83 g, 87.5 %). IR (CDCl<sub>3</sub>, KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3314, 3072, 2912, 2840, 1731, 1700, 1639, 1598, 1541, 1452, 1415. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 0.87-0.93 (t, 12H, 4  $\times$  CH<sub>3</sub>,  $J = 7.5$ ), 1.17-1.43 (br, 2H<sub>n</sub>, (CH<sub>2</sub>)<sub>n</sub>), 1.23-1.29 (m, 8H, 4  $\times$  CH<sub>2</sub>), 1.37-1.43 (m, 8H, 4  $\times$  CH<sub>2</sub>,  $J = 5$ ) 2.02 (br m, 9H<sub>n</sub>, (4  $\times$  cis(CH=CHCH<sub>2</sub>)<sub>n</sub> + 4  $\times$  trans (CH=CHCH<sub>2</sub>)<sub>n</sub> + (CH=CHCH<sub>2</sub>)<sub>n</sub>), 2.37-2.43 (t, 8H, 4  $\times$  NCH<sub>2</sub>,  $J = 7.5$ ), 2.52-2.56 (t, 4H, 2  $\times$  CH<sub>2</sub>N,  $J = 5$ ), 2.83 (s, 8H, 2  $\times$  ArCH<sub>2</sub>CH<sub>2</sub>Ar), 3.24-3.31(m, 4H, (2  $\times$  OCH<sub>2</sub>)), 4.12-4.17 (m 2H, (2  $\times$  CHO), 4.96 (br, 2H<sub>n</sub>, (2  $\times$  CH=CH<sub>2</sub>)<sub>n</sub>), 5.33-5.36 (br, 2H<sub>n</sub>, (cis CH=CH)<sub>n</sub>), 5.46-5.59 (br, 2H<sub>n</sub>, (trans CH=CH)<sub>n</sub>), 5.77-5.84 (br, H<sub>n</sub>, (CH<sub>2</sub>=CH)<sub>n</sub>) 6.56-6.58 (4  $\times$  NH), 7.08-7.11 (AA'XX' system, 8H, 8  $\times$  ArH), 7.21-7.29 (AA'XX' system, 8H, 8  $\times$  ArH); <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 13.9 (CH<sub>3</sub>), 20.6 (CH<sub>2</sub>), 24.9 (CH<sub>3</sub>), 27.5 (CH<sub>2</sub>)<sub>n</sub>, 30.2 (CH<sub>2</sub>)<sub>n</sub>, 32.7 (CH<sub>2</sub>)<sub>n</sub>, 35.8 (ArCH<sub>2</sub>CH<sub>2</sub>Ar), 37.4 (CH)<sub>n</sub>, 38.2-41.7 ((CH<sub>2</sub>)<sub>n</sub> + CH<sub>2</sub>), 53.8 (CH<sub>2</sub>), 113.9-115.0 (CH<sub>2</sub>=CH)<sub>n</sub>, 118.7-121.5 (ArC), 129.4 cis(CH=CH)<sub>n</sub>, 130.1 trans(CH=CH)<sub>n</sub>, 131.7 cis(CH=CH)<sub>n</sub>, 135.8-137.1 (ArC), 142.6-143.4 (CH<sub>2</sub>=CH)<sub>n</sub>, 156.9 (C=O); GPC (THF)  $M_w = 10800$   $M_n = 6200$ ,  $\text{Đ} = 1.7$ .





*Synthesis of 4-((4'-2-[bismorpholine]-ethyl) ureido phenethylbenzyl)-phenyl-amino-carbonyl terminated poly(butadiene) 4*



To a stirred solution of the prepolymer **7** (5.44 g, 2.15 mmol) generated<sup>S3</sup> from the polybutadiene diol **5** with 4,4'-dibenzyl diisocyanate (DBDI) **6** in dry THF (50 mL) under a nitrogen atmosphere was added N-(2-aminoethyl)-morpholine **11** (0.56 g 4.3 mmol) to furnish the desired polymer **4** as a yellow elastomeric material (4.8 g, 80.0 %). IR (CDCl<sub>3</sub>, KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3311, 3069, 2912, 2840, 1733, 1705, 1639, 1598, 1541, 1451, 1413.; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 1.25 (br, 2H<sub>n</sub>, (CH<sub>2</sub>)<sub>n</sub>), 2.02 (br m, 9H<sub>n</sub>, (4 × cis(CH=CHCH<sub>2</sub>)<sub>n</sub> + 4 × trans(CH=CHCH<sub>2</sub>)<sub>n</sub> + (CH=CHCH) <sub>n</sub>), 2.44-2.51 (m, 12H, 4 × NCH<sub>2</sub> + 2 × CH<sub>2</sub>N), 2.83 (s, 8H, 2 × ArCH<sub>2</sub>CH<sub>2</sub>Ar), 3.33-3.35 (m, 4H, 2 × HNCH<sub>2</sub>), 3.63-3.66 (m, 4H, (2 × CH<sub>2</sub>O), 4.12-4.17 (m 2H, (2 × CHO), 4.96 (br, 2H<sub>n</sub>, (2 × CH=CH<sub>2</sub>)<sub>n</sub>), 5.33 (br, 2H<sub>n</sub>, (cis CH=CH)<sub>n</sub>), 5.46-5.55 (br, 2H<sub>n</sub>, trans (CH=CH)<sub>n</sub>), 5.77 (br, H<sub>n</sub>, (CH<sub>2</sub>=CH)<sub>n</sub>), 6.64 (4 × NH), 7.06-7.09 (AA'XX' system, 8H, 8 × ArH), 7.17-7.28 (AA'XX' system, 8H, 8 × ArH); <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 25.0 (CH<sub>3</sub>), 27.4 (CH<sub>2</sub>)<sub>n</sub>, 30.2 (CH<sub>2</sub>)<sub>n</sub>, 32.8 (CH<sub>2</sub>)<sub>n</sub>, 35.7 (ArCH<sub>2</sub>CH<sub>2</sub>Ar), 38.2-41.7 ((CH<sub>2</sub>)<sub>n</sub> + CH<sub>2</sub>), 53.3 ((CH<sub>2</sub>N)+(NCH<sub>2</sub>)), 66.9 (CH<sub>2</sub>O), 113.8-115.1 (CH<sub>2</sub>=CH)<sub>n</sub>, 118.7-121.5 (ArC), 127.7 cis(CH=CH)<sub>n</sub>, 130.1 trans(CH=CH)<sub>n</sub>, 131.8 cis(CH=CH)<sub>n</sub>, 135.8-136.8 (ArC), 142.7-143.4 (CH<sub>2</sub>=CH)<sub>n</sub>; GPC (THF):  $M_w = 10800$ ,  $M_n = 6200$ ,  $D = 1.7$ .

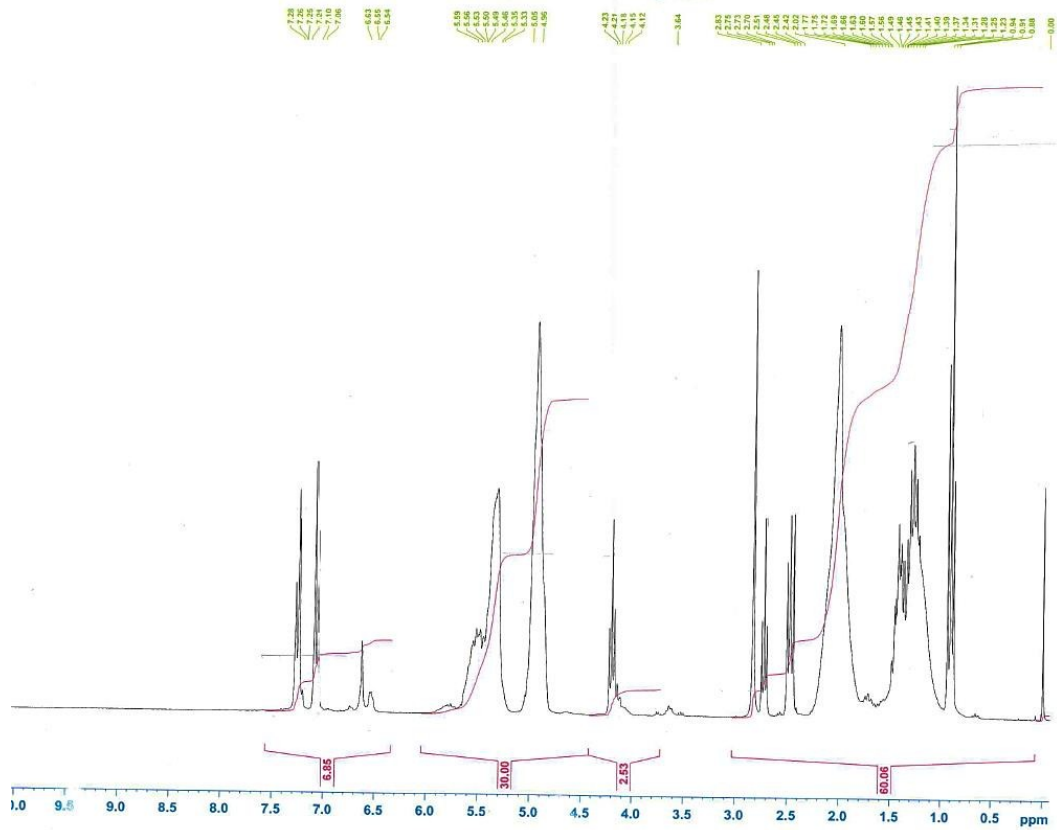


Figure S7:  $^1\text{H}$  NMR spectra of polymer **4** in  $\text{CDCl}_3$  at  $25\text{ }^\circ\text{C}$

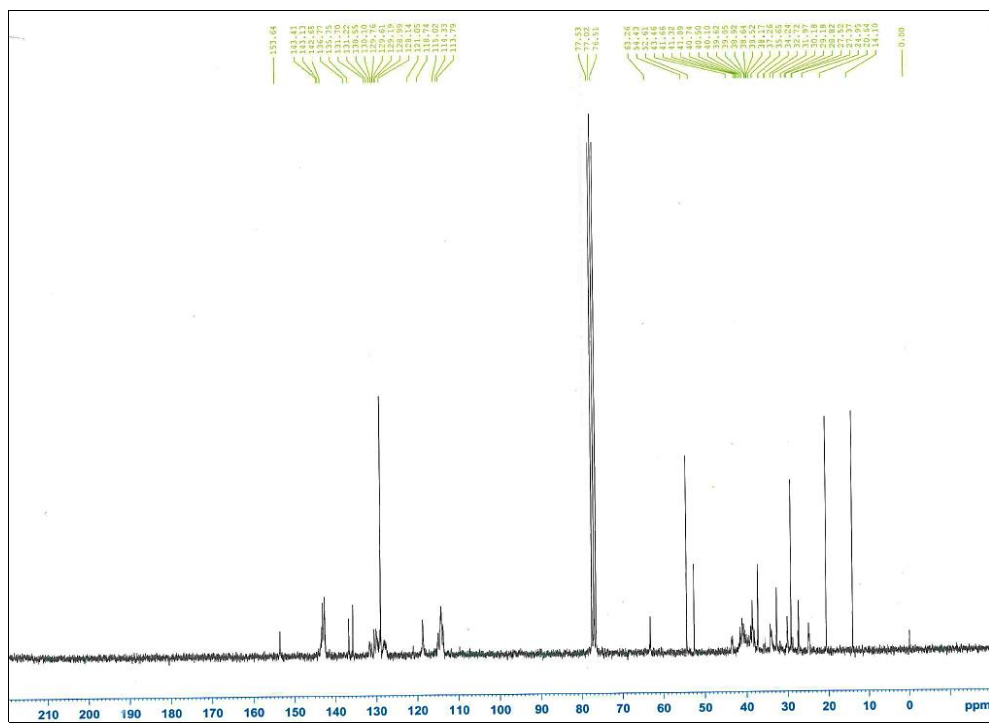
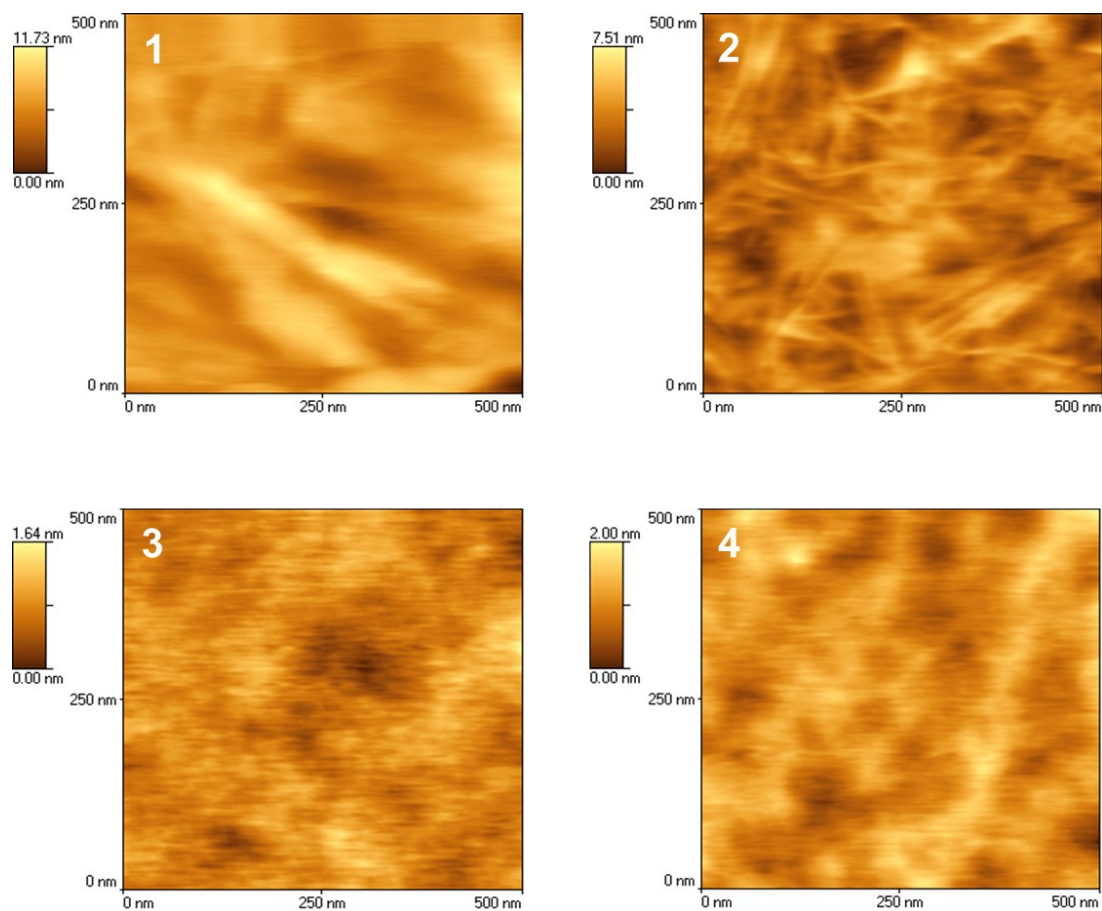


Figure S8:  $^{13}\text{C}$  NMR spectra of polymer **4** in  $\text{CDCl}_3$  at  $25\text{ }^\circ\text{C}$



**Figure S9:** Topological AFM micrographs of the SPUs 1-4.

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