

Thermally Responsive Elastomeric Supramolecular Polymers Featuring Flexible Aliphatic Hydrogen Bonding End-Groups

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Materials

Polyisobutylene diol (Oppanol DLTM) with $M_n=5050$ and $M_w/M_n = 1.56$ was supplied by BASF. The 4,4'-Methylene bis(phenylisocyanate) (MDI) terminated poly(isobutylene) diol was supplied by Henkel Adhesives, Slough, UK and prepared by reacting the polymeric diol with MDI at 110 °C under vacuum with an NCO/OH ratio of 2/1. Reagents were purchased from either Acros Chimica or the Aldrich Chemical Company and were used without further purification. Dry tetrahydrofuran (THF) was distilled from benzophenone and sodium.

Characterisation

¹H Nuclear magnetic resonance (¹H NMR) spectroscopy was performed on a Bruker AMX400 (400 MHz) spectrometer (using the deuterated solvent as lock). ¹³C Nuclear magnetic resonance (¹³C NMR) spectroscopy was performed on Bruker AMX400 (100 MHz) spectrometer. Infrared spectroscopy was performed using a Perkin Elmer 1720-X Spectrometer with the samples analysed as either neat films or in solution between two potassium bromide or sodium chloride disks. Gel Permeation Chromatography (GPC) was performed on a Polymer Laboratories PL-GPC 220 high temperature chromatograph using PL Mixed Gel columns at 40 °C, using samples dissolved in analytical grade chloroform (5 mg/mL), using PL Easy-Cal Polystyrene

calibrants. Glass transition points (T_g) were determined using a TA Instruments DSC 2920 differential scanning calorimeter. DSC was performed via two methods, either scanning from -50 °C to 105 °C (at a rate of 3 K/min modulated), or from 75 °C down to -50 °C (at a rate of 2 K/min non-modulated). All of the thermal analysis data were analysed using TA Instruments universal analysis software. DSC analysis involved software controlled smoothing (15°) of the derivative (differential) of complex C_p . Rheological measurements (temperature ramps of dynamic moduli) were performed on a TA Instruments AR2000 Rheometer at a constant frequency of 10 Hz. Frequency sweep measurements as a function of temperature were performed on a Rheometrics RSA II rheometer using a shear sandwich geometry and a strain 5%, which was checked to be within the linear viscoelastic regime.

Synthesis

*Synthesis of 4-((4'-carbamic acid 2-[bis-(2-hydroxyethyl)-amino]-ethyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(isobutylene) diol **8***

To a stirred solution of triethanolamine (0.26 g, 1.70 mmol) in dry THF (25 mL) under an argon atmosphere maintained under reflux, a solution of 4,4'-methylenebis(phenylisocyanate) terminated poly(isobutylene) diol (5.00 g, 0.90 mmol) in dry THF (75 mL) was added in a dropwise fashion over a period of approximately 90 minutes. This mixture was then heated and stirred for 1 hour and then allowed to cool to room temperature. The reaction was then poured into methanol (*ca.* 350 mL) that was cooled down to -78 °C. A white precipitate formed which was filtered off under vacuum. This material was dissolved in THF and reprecipitated from methanol a further two times and the residual solvent was removed under high vacuum to furnish the desired product **8** as a clear colourless elastomeric gel (4.74 g, 90 %). δ_H (400 MHz, $CDCl_3$) 1.11 (6H_n, s, 2 × CH₃), 1.41 (2H_n, s, CH₂), 2.72-2.76 (8H, m, 4 × NCH₂), 2.82-2.87 (4H, m, 2 × CH₂N), 3.60-3.64 (8H, m, 4 × CH₂OH), 3.88 (4H, s, 2 × ArCH₂Ar), 4.08-4.14 (4H, m, 2 × OCH₂), 4.24-4.28 (4H, m, CH₂O), 7.08-7.11 (8H, AA'XX' system, 8 × ArH), 7.26-7.30 (8H, AA'XX' system, 8 × ArH). δ_C (100 MHz, $CDCl_3$) 30.7-31.3 (CH₃)_n, 37.8-38.3 (C)_n, 41.4 (ArCH₂Ar), 55.6 (CH₂N), 56.9 (CH₂), 59.0-59.8 ((CH₂)_n + CH₂OH), 63.5 (OCH₂) 66.15 (OCH₂), 118.8 (ArC), 129.4 (ArC), 136.0 (ArC), 136.2

(ArC), 153.7 (C=O). ν_{\max} (CDCl₃, KBr)/cm⁻¹ 3689, 3436, 3155, 2955, 1793, 1713, 1600, 1522, 1472, 1413, 1389, 1366. GPC (Chloroform): M_w 16914, PDI 3.89.

Synthesis of 4-(((4'-carbamic acid 2-[bisbutyl-amino]-ethyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(isobutylene) diol **9**

To a stirred solution of 4,4'-methylenebis(phenylisocyanate) terminated poly(isobutylene) diol (5.00 g, 0.90 mmol) in THF (50 mL) maintained under reflux under an argon atmosphere was added 2-hydroxyethyl-*N,N*-bisbutylamine (0.35 mL, 1.70 mmol). The mixture was stirred under reflux for approximately four hours and then allowed to cool to room temperature. The mixture was then poured into methanol (*ca.* 350 mL) that was cooled down to -78 °C. An off white precipitate formed which was filtered off under vacuum. This material was purified by repeated precipitation from methanol maintained at -78 °C to afford the desired product **9** as a light brown coloured viscous oil (4.26 g, 80 %). δ_H (400 MHz, CDCl₃) 0.90-1.41 (8H_n + 28H, br m, ((CH₂ + (2 × CH₃))_n + ((8 × CH₂) + (4 × CH₃))), 2.45-2.51 (8H, m, 4 × NCH₂), 2.72-2.75 (4H, m, 2 × CH₂N), 3.88 (4H, s, 2 × ArCH₂Ar), 4.09-4.11 (4H, m, 2 × O CH₂), 4.18-4.23 (2H, m, CH₂O), 7.08-7.11 (8H, AA'XX' system, 8 × ArH), 7.26-7.29 (8H, AA'XX' system, 8 × ArH). δ_C (100 MHz, CDCl₃) 14.06 (CH₃), 20.6 (CH₂), 29.33 (CH₂), 31.22 (CH₃)_n, 37.82-38.51 (C)_n, 40.53 (ArCH₂Ar), 52.54 (CH₂), 54.31 (CH₂), 59.50 (CH₂)_n, 66.15 (CH₂), 125.40 (ArC), 129.4 (ArC), 136.00 (ArC), 136.20 (ArC), 153.70 (C=O). ν_{\max} (CDCl₃, KBr)/cm⁻¹ 2953, 2893, 1729, 1594, 1522, 1472, 1389, 1366, 1310, 1229, 1049. GPC (Chloroform): M_w 15997, PDI 2.48.

Synthesis of 4-((4'- carbamic acid methyl ester) benzyl)-phenyl-amino-carbonyl terminated poly(isobutylene) diol **10**

This analogue was produced via the procedure used to generate **9** using MDI terminated poly(isobutylene) diol (4.91 g, 0.72 mmol) and dry methanol (2 mL) and the product was purified by repeated precipitation from methanol at -78 °C to furnish **10** as an off white tacky gel (3.69 g, 88 %). δ_H (400 MHz, CDCl₃) 1.11 (6H_n, s, 2 × CH₃), 1.41 (2H_n, s, CH₂), 3.76 (6H, s, 2 × CH₃), 3.88 (4H, s, 2 × ArCH₂Ar), 4.24-4.28 (4H, m, CH₂O), 7.09-7.11 (8H, AA'XX' system, 8 × ArH), 7.27-7.29 (8H, AA'XX' system, 8 × ArH). δ_C (100 MHz, CDCl₃) 31.3 (CH₃)_n, 37.8-38.3(C)_n, 41.4 (ArCH₂Ar), 52.3 (CH₃), 59.1-59.7 (CH₂)_n,

118.9 (ArC), 129.4 (ArC), 135.9 (ArC), 136.2 (ArC), 154.1 (C=O). ν_{\max} (CDCl₃, KBr)/cm⁻¹ 2954, 2254, 1794, 1735, 1523, 1468, 1389, 1366, 1220, 1096, 911, 741. GPC (Chloroform): M_w 14276, PDI 1.61.

*Synthesis of 4-((4'- 2-[bis-(2-hydroxyethyl)-amino]-ethyl) ureidobenzyl)-phenyl-amino-carbonyl terminated poly(isobutylene) diol **11***

This compound was synthesised via the procedure used to generate **8** using 2-aminoethyl-*N,N*-bis(2-hydroxyethyl) amine (0.25 g, 1.70 mmol) and MDI terminated poly(isobutylene) diol (4.94 g, 0.85 mmol). The product **11** was purified via precipitation from methanol at -78 °C to afford a clear colourless elastomeric solid (4.02 g, 77 %). δ_H (400 MHz, CDCl₃) 1.11 (6H_n, s, 2 × CH₃), 1.41 (2H_n, s, CH₂), 2.78 (8H, m, 4 × NCH₂), 2.92 (4H, m, 2 × CH₂N), 3.56 (4H, m, 2 × NHCH₂), 3.60-3.64 (8H, m, 4 × CH₂OH), 3.88 (4H, s, 2 × ArCH₂Ar), 4.08-4.14 (4H, m, CH₂O), 4.21-4.27 (4H, br s, 4 × OH), 7.01-7.15 (8H, 2 × AA'XX' system, 2 × (4 × ArH)), 7.18-7.29 (8H, 2 × AA'XX' system, 2 × (4 × ArH)). δ_C (100 MHz, CDCl₃) 30.6-31.2 (CH₃)_n, 37.8-38.3 (NHCH₂) + (C)_n, 40.5 (ArCH₂Ar), 55.6 (CH₂N), 56.9 (CH₂), 59.0-59.7 ((CH₂)_n + CH₂OH), 66.1 (OCH₂), 118.8 (ArC), 125.4 (ArC), 129.4 (ArC), 136.0 (ArC), 136.2 (ArC), 153.7 (C=O), 157.8 (C=O). ν_{\max} (CDCl₃, KBr)/cm⁻¹ 3435, 2953, 2253, 1794, 1725, 1523, 1468, 1389, 1633, 1230, 1095, 912. GPC (Chloroform): M_w 12391, PDI 4.67.

*Synthesis of 4-((4'-2-[bisbutyl-amino]-ethyl) ureidobenzyl)-phenyl-amino-carbonyl terminated poly(isobutylene) diol **12***

This analogue was produced via the procedure used to afford **9** employing 2-aminoethyl-*N,N*-bisbutyl amine (0.43 g, 2.5 mmol) and MDI terminated poly(isobutylene) diol (7.15 g, 1.24 mmol). The polymer was purified via precipitation from methanol at -78 °C, which furnished the desired product **12** as a clear light yellow elastomeric solid (6.99 g, 92 %). δ_H (400MHz, CDCl₃) 1.11 (6H_n, s, 2 × CH₃), 1.41 (2H_n, s, CH₂), 2.38-2.44 (8H, m, 4 × NCH₂), 2.55-2.58 (4H, m, 2 × CH₂N), 3.26-3.28 (4H, m, 2 × NHCH₂), 3.89 (4H, s, 2 × ArCH₂), 4.08-4.14 (4H, m, CH₂O), 6.52 (2H, s, 2 × NH), 7.08-7.37 (16H, 4 × AA'XX' system, 4 × (4 × ArH)). δ_C (100 MHz, CDCl₃) 14.1 (CH₃), 20.6 (CH₂), 29.4 (CH₂), 30.8-32.2 (CH₃)_n, 37.8-38.3 (NHCH₂) + (C)_n, 40.6 (ArCH₂Ar), 53.9 (CH₂N), 55.6

(NCH₂), 59.5 (CH₂)_n, 118.8 (ArC), 122.9 (ArC), 129.4 (ArC), 129.5 (ArC), 136.0 (ArC), 136.2 (ArC), 153.7 (C=O), 156.7 (C=O). ν_{\max} (CDCl₃, KBr)/cm⁻¹ 2954, 2892, 2360, 2254, 1793, 1710, 1524, 1468, 1389, 1366, 1228, 1095, 909. GPC (Chloroform): M_w 14482, PDI 2.06.

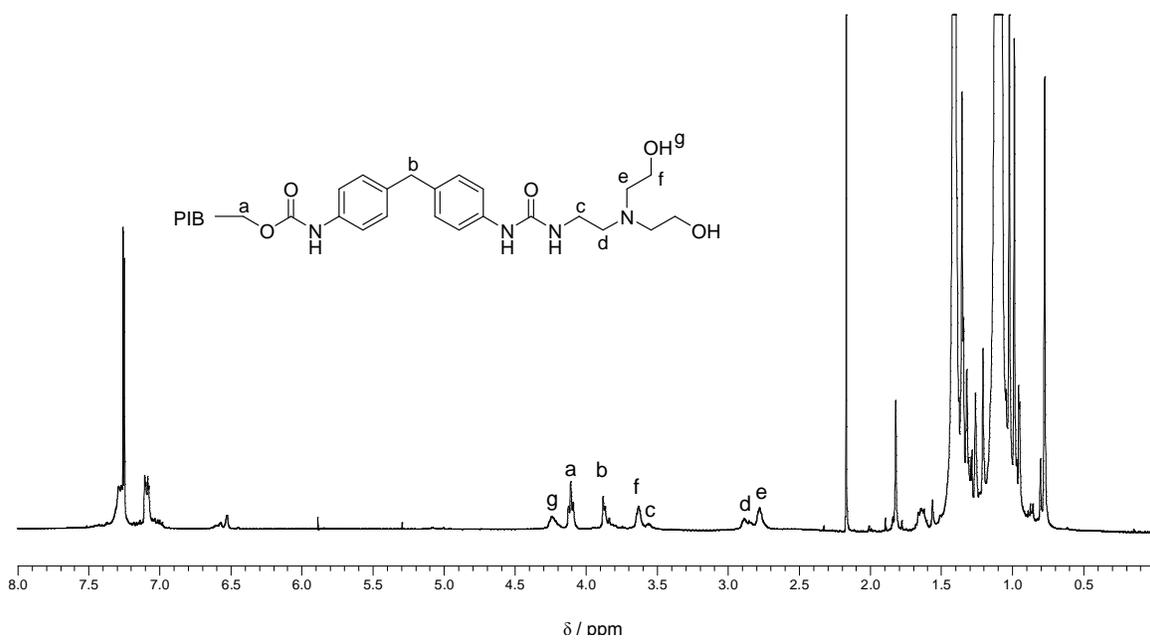


Figure S1 ¹H NMR spectrum (400 MHz, CDCl₃, 23 °C) of **11**