Electronic Supplementary Information for

Diversity in cyclic carbonates: Synthesis of triazole-functional monomers using click chemistry

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Experimental Details

Materials

2-(Bromomethyl)-2-methyltrimethylene carbonate (BMTC, **1a**) and 2-(bromomethyl)-2-ethyltrimethylene carbonate (BETC, **1b**) were synthesised as described elsewhere.[1] 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU) was synthesised according to a literature procedure.[2] Chloroform-*d* was purchased from Larodan Fine Chemicals and stored over 4 Å molecular sieves and solid K_2CO_3. DMSO-d_6 was purchased from Larodan Fine Chemicals and stored over 3 Å molecular sieves. All other chemicals, including dry solvents (Acros Organics), were obtained from commercial sources and used as received.

Instrumentation

^{1}H NMR spectra were recorded at 25 °C on a JEOL Eclipse+ 400 MHz or a Bruker Avance DRX 400 MHz NMR spectrometer using the solvent signal as an internal standard. *J* values are given in Hz. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer. Thermal properties were measured using differential scanning calorimetry on a TA Instruments DSC Q1000. Melting points were obtained as the onset of the melting endotherm at a heating rate of 0.5 °C/min and the purity (mol%) was estimated using purity analysis in Universal Analysis 2000 version 4.7A (TA Instruments). GPC analysis was performed on a Verotech PL-GPC 50 equipped with a refractive index detector and two PolarGel-M organic GPC columns. Samples were injected using a PL-AS RT autosampler and chloroform was used as the eluent at a flow rate of 1 ml/min. Flow rate fluctuations were corrected by an internal standard and the system was calibrated against narrow polystyrene standards.

2-(Azidomethyl)-2-methyltrimethylene carbonate (2a)

9.4 g (45 mmol) of 2-bromomethyl-2-methyltrimethylene carbonate and 3.5 g (54 mmol, 1.2 eq.) of NaN_3 were stirred in 50 ml of DMF at 80 °C for 4 h. The reaction mixture was partitioned between 150 ml of deionised water and 150 ml of EtOAc. The organic phase was separated and extracted with 150 ml of saturated $NaHCO_3$, dried with $MgSO_4$ and the solvent was evaporated. The crude product was recrystallised from THF/diethyl ether to yield pure 2-(azidomethyl)-2-methyltrimethylene carbonate (4.20 g, 55%) as colourless flakes, mp 81.0 °C (99.3% purity). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (3 H, s, $–CH_3$), 3.48 (2 H, s, $–CH_2–N_3$), 4.12 (2 H, BB' of AA'BB', $–CH_2–O$), 4.24 (2 H, AA' of AA'BB', $–CH_2–O$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.58 ($–CH_3$), 32.9 (>C<), 54.1 ($–CH_2–N_3$), 73.8 ($–CH_2–O$), 147.7 (O–C(=O)–O). Found: C, 42.0; H, 5.3; N, 24.3. $C_6H_9N_3O_3$ requires C, 42.1; H, 5.3; N, 24.55%.

2-(Azidomethyl)-2-ethyltrimethylene carbonate (2b)

10.0 g (45 mmol) of 2-bromomethyl-2-ethyltrimethylene carbonate and 3.5 g (54 mmol, 1.2 eq.) of NaN_3 were stirred in 50 ml of DMF at 80 °C for 4 h. The reaction mixture was partitioned between 150 ml of deionised water and 150 ml of EtOAc. The organic phase was separated and extracted with 150 ml of saturated $NaHCO_3$, dried with $MgSO_4$ and the solvent was evaporated. The crude product was recrystallised from diethyl ether to yield pure 2-(azidomethyl)-2-ethyltrimethylene carbonate (5.86 g, 71%) as colourless needles, mp 37.0 °C (99.8% purity). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (3 H, t, J = 7.7, $–CH_3$), 1.51 (2 H, q, J = 7.7, $–CH_2–$), 3.51 (2 H, s, $–CH_2–N_3$), 4.15 (2 H, BB' of AA'BB', $–CH_2–O$), 4.24 (2 H, AA' of AA'BB', $–CH_2–O$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.3 ($–CH_3$), 23.6 ($–CH_2–$), 35.3 (>C<), 51.1 ($–CH_2–N_3$), 72.8 ($–CH_2–O$), 148.0 (O–C(=O)–O). Found: C, 45.2; H, 6.05; N, 22.3. $C_7H_{11}N_3O_3$ requires C, 45.4; H, 6.0; N, 22.7%.

2-((4-Phenyl-1H-1,2,3-triazol-1-yl)methyl)-2-ethyltrimethylene carbonate (3b)

To 0.59 g (3.2 mmol) of 2-ethyl-2-(azidomethyl)trimethylene carbonate and 67 mg (0.35 mmol) of CuI in 5 ml of dry DMF was added 0.38 ml (3.5 mmol) of phenylacetylene and 0.05 ml (0.35 mmol) of triethylamine under Ar. The reaction was allowed to proceed overnight at r.t. The reaction mixture was diluted with 15 ml of ethyl acetate and filtered through a pad of Celite that was washed with another 20 ml of ethyl acetatae. The filtrate was extracted with 40 ml of 1 M HCl and 40 ml of saturated $NaHCO_3$. The organic phase was dried with $MgSO_4$ and filtered through a pad of silica to remove traces of copper. The solvent was evaporated and the crude product was recrystallised from THF/diethyl ether to give pure **3b** (0.52 g, 57%) as a colourless solid, mp 110.9 °C (99.2% purity). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (3H, t, J = 7.7, $–CH_3$), 1.52 (2 H, q, J = 7.7, $–CH_2–$), 4.19 (2 H, BB' of AA'BB', $–CH_2–O$), 4.29 (2 H, AA' of AA'BB', $–CH_2–O$), 4.56 (2 H, s, $–CH_2–N$), 7.36 (1 H, m, ArH), 7.44 (2 H, m, ArH), 7.83 (1 H, s, =CH–N), 7.84 (2 H, m, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.2 ($–CH_3$), 23.4 ($–CH_2–$), 36.2 (>C<), 49.1 ($–CH_2–N$), 72.8 ($–CH_2–O$), 121.4 (=CH–N), 125.9 (ArC), 128.7 (ArC), 129.1

(ArC), 130.0 (ArC), 147.6 (O–C(=O)–O), 148.2 (=C<). Found: C, 62.7; H, 6.0; N, 14.65. $C_{15}H_{17}N_3O_3$ requires C, 62.7; H, 6.0; N, 14.6%.

General procedure for the synthesis of triazole-functional trimethylene carbonates

To 3.2 mmol of 2-(azidomethyl)-2-alkyltrimethylene carbonate and 67 mg (0.35 mmol) of CuI in 5 ml of dry DMF was added 3.8 mmol (1.2 eq.) of alkyne and 0.05 ml (0.35 mmol) of triethylamine under Ar. The reaction was allowed to proceed at r.t. until the azide-functional starting material had been fully consumed as determined by FT-IR. The reaction mixture was diluted with 25 ml of ethyl acetate. The resulting suspension was filtered through a pad of silica. The filtrate was concentrated using rotational evaporation and the product was crystallised from a mixture of THF and diethyl ether.

2-((4-Phenyl-1H-1,2,3-triazol-1-yl)methyl)-2-methyltrimethylene carbonate (3a)

Yield: 0.73 g (84%) as colourless crystals, mp 157.4 °C (98.0% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.95 (3 H, s, –CH_3), 4.29 (4 H, AA'BB', –CH_2–O), 4.56 (2 H, s, –CH_2–N), 7.34 (1 H, m, ArH), 7.46 (2 H, m, ArH), 7.88 (2 H, m, ArH), 8.59 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 16.5 (–CH_3), 32.3 (>C<), 51.7 (–CH_2–N), 73.3 (–CH_2–O), 123.1 (=CH–N), 125.3 (ArC), 127.9 (ArC), 128.9 (ArC), 130.5 (ArC), 146.2 (=C<), 147.2 (O–C(=O)–O). Found: C, 61.2; H, 5.5; N, 15.3. $C_{14}H_{15}N_3O_3$ requires C, 61.5; H, 5.5; N, 15.4%.

2-((4-Cyclopropyl-1H-1,2,3-triazol-1-yl)methyl)-2-methyltrimethylene carbonate (4a)

Yield: 0.59 g (77%) as a slightly beige solid, mp 77.8 °C (97.7% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83–0.87 (2 H, m, –CH_2–), 0.95–0.99 (2 H, m, –CH_2–), 1.10 (3 H, s, –CH_3), 1.95 (1 H, dddd, J = 5.1, 8.4, >CH–), 4.16 (2 H, BB' of AA'BB', –CH_2–O), 4.20 (2 H, AA' of AA'BB', –CH_2–O), 4.40 (2 H, s, –CH_2–N), 7.29 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.7 (–CH<), 8.0 (–CH_2–), 17.6 (–CH_3), 33.4 (>C<), 52.1 (–CH_2–N), 73.9 (–CH_2–O), 121.6 (=CH–N), 147.4 (O–C(=O)–O), 150.7 (=C<). Found: C, 55.3; H, 6.4; N, 17.6. $C_{11}H_{15}N_3O_3$ requires C, 55.7; H, 6.4; N, 17.7%.

2-((4-Cyclopropyl-1H-1,2,3-triazol-1-yl)methyl)-2-ethyltrimethylene carbonate (4b)

Yield: 0.55 g (69%) as slightly beige crystals, mp 100.9 °C (98.4% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81–0.85 (2 H, m, –CH_2–), 0.92–0.97 (2 H, m, –CH_2–), 1.01 (3 H, t, J = 7.7, –CH_3), 1.45 (2 H, q, J = 7.7, –CH_2–), 1.92 (1 H, dddd, J = 5.1, 8.4, >CH–), 4.13 (2 H, BB' of AA'BB', –CH_2–O), 4.24 (2 H, AA' of AA'BB', –CH_2–O), 4.41 (2 H, s, –CH_2–N), 7.29 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.7 (–CH<), 7.2 (–CH_3), 8.0 (–CH_2–), 23.4 (–CH_2–), 36.0 (>C<), 48.9 (–CH_2–N), 72.8 (–CH_2–O), 121.6 (=CH–N), 147.7 (O–C(=O)–O), 150.6 (=C<). Found: C, 57.1; H, 6.7; N, 16.4. $C_{12}H_{17}N_3O_3$ requires C, 57.4; H, 6.8; N, 16.7%.

2-((4-Isopropyl-1H-1,2,3-triazol-1-yl)methyl)-2-methyltrimethylene carbonate (5a)

Yield: 0.55 g (72%) as a colourless solid, mp 121.0 °C (98.5% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (3 H, s, –CH_3), 1.30 (6 H, d, J = 7.0, –CH_3), 3.09 (1 H, m, J = 7.0, >CH–), 4.16–4.23 (4 H, AA'BB', –CH_2–O), 4.43 (2 H, s, –CH_2–N), 7.31 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6 (–CH_3), 22.6 (–CH_3), 25.9 (–CH<), 33.4 (>C<), 52.1 (–CH_2–N), 73.9 (–CH_2–O), 121.3 (=CH–N), 147.4 (O–C(=O)–O), 155.0 (=C<). Found: C, 54.5; H, 7.0; N, 17.3. $C_{11}H_{17}N_3O_3$ requires C, 55.2; H, 7.2; N, 17.6%.

2-((4-Isopropyl-1H-1,2,3-triazol-1-yl)methyl)-2-ethyltrimethylene carbonate (5b)

Yield: 0.57 g (70%) as greenish crystals, mp 114.5 °C (98.4% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (3 H, t, J = 7.7, –CH_3), 1.30 (6 H, d, J = 7.0, –CH_3), 1.48 (2 H, q, J = 7.7, –CH_2–), 3.08 (1 H, m, J = 7.0, >CH–), 4.14 (2 H, BB' of AA'BB', –CH_2–O), 4.25 (2 H, AA' of AA'BB', –CH_2–O), 4.44 (2 H, s, –CH_2–N), 7.30 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.2 (–CH_3), 22.6 (–CH_3), 23.4 (–CH_2–), 25.9 (–CH<), 36.0 (>C<), 48.9 (–CH_2–N), 72.8 (–CH_2–O), 121.2 (=CH–N), 147.7 (O–C(=O)–O), 155.0 (=C<). Found: C, 56.6; H, 7.4; N, 16.5. $C_{12}H_{19}N_3O_3$ requires C, 56.9; H, 7.6; N, 16.6%.

2-((4-(Prop-1-en-2-yl)-1H-1,2,3-triazol-1-yl)methyl)-2-methyltrimethylene carbonate (6a)

Yield: 0.58 g (77%) as a peach-coloured solid, mp 109.5 °C (98.2% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (3 H, s, –CH_3), 2.12 (3 H, unresolved m, –CH_3), 4.17–4.24 (4 H, AA'BB', –CH_2–O), 4.47 (2 H, s, –CH_2–N), 5.13 (1 H, unresolved m, =CH–H), 5.73 (1 H, unresolved m, =CH–H), 7.57 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5 (–CH_3), 20.7 (–CH_3), 33.4 (>C<), 52.1 (–CH_2–N), 73.8 (–CH_2–O), 113.4 (=CH_2), 121.5 (=CH–N), 133.1 (=C<), 147.4 (O–C(=O)–O), 149.1 (=C<). Found: C, 55.4; H, 6.5; N, 17.55. $C_{11}H_{15}N_3O_3$ requires C, 55.7; H, 6.4; N, 17.7%.

2-((4-(Prop-1-en-2-yl)-1H-1,2,3-triazol-1-yl)methyl)-2-ethyltrimethylene carbonate (6b)

Yield: 0.56 g (71%) as fine, slightly beige needles, mp 125.0 °C (98.7% purity, from THF/diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (3 H, t, J = 7.7, –CH_3), 1.48 (2 H, q, J = 7.7, –CH_2–), 2.12 (3 H, unresolved m, –CH_3), 4.15 (2 H, BB' of AA'BB', –CH_2–O), 4.27 (2 H, AA' of AA'BB', –CH_2–O), 4.49 (2 H, s, –CH_2–N), 5.13 (1 H, unresolved m, =CH–H), 5.73 (1 H, unresolved m, =CH–H), 7.55 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.2 (–CH_3), 20.7 (–CH_3), 23.4 (–CH_2–), 36.1 (>C<), 48.9 (–CH_2–N), 72.8 (–CH_2–O), 113.4 (=CH_2), 121.4 (=CH–N), 133.2 (=C<), 147.7 (O–C(=O)–O), 149.1 (=C<). Found: C, 57.25; H, 6.85; N, 16.6. $C_{12}H_{17}N_3O_3$ requires C, 57.4; H, 6.8; N, 16.7%.

2-((4-(2-Hydroxypropan-2-yl)-1H-1,2,3-triazol-1-yl)methyl)-2-methyltrimethylene carbonate (7a)

Yield: 0.43 g (52%) as a colourless solid, mp 130.6 °C (99.4% purity, from THF). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.89 (3 H, s, –CH_3), 1.46 (6 H, s, –CH_3), 4.22 (4 H, s, –CH_2–O), 4.47 (2 H, s, –CH_2–N), 5.11 (1 H, s, –OH), 7.85 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 16.5 (–CH_3), 30.6 (–CH_3), 32.3 (>C<), 51.2 (–CH_2–N), 67.0 (–$C(CH_3)_2$–OH), 73.3 (–CH_2–O), 122.4 (=CH–N), 147.2 (O–C(=O)–O), 155.7 (=C<). Found: C, 51.7; H, 6.7; N, 16.4. $C_{11}H_{17}N_3O_4$ requires C, 51.8; H, 6.7; N, 16.5%.

2-((4-(2-Hydroxypropan-2-yl)-1H-1,2,3-triazol-1-yl)methyl)-2-ethyltrimethylene carbonate (7b)

Yield: 0.59 g (69%) as a colourless solid, mp 145.5 °C (98.6% purity). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.88 (3 H, t, J = 7.7, –CH_3), 1.27 (2 H, q, J = 7.7, –CH_2–), 1.46 (6 H, s, –CH_3), 4.22 (2 H, BB' of AA'BB', –CH_2–O), 4.29 (2 H, AA' of AA'BB', –CH_2–O), 4.48 (2 H, s, –CH_2–N), 5.11 (1 H, s, –OH), 7.84 (1 H, s, =CH–N). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 6.8 (–CH_3), 22.3 (–CH_2–), 30.6 (–CH_3), 34.9 (>C<), 48.6 (–CH_2–N), 67.0 (–$C(CH_3)_2$–OH), 72.1 (–CH_2–O), 122.3 (=CH–N), 147.4 (O–C(=O)–O), 155.8 (=C<). Found: C, 53.4; H, 7.1; N, 15.6. $C_{12}H_{19}N_3O_4$ requires C, 53.5; H, 7.1; N, 15.6%.

Ring-opening polymerisation of 3b

In a glove box under Ar, 0.29 g (1.0 mmol) of **3b** and 19 mg (0.05 mmol) of TU were charged in an oven-dried round-bottom flask. The flask was sealed and transferred out and the contents were dissolved in 1 ml of dry DCM. 2 µl (0.02 mmol, for DP = 50) of benzyl alcohol was added as an initiator and 7 µl (0.05 mmol) of DBU was added to start polymerisation. After 3 h at r.t., 7 µl (0.12 mmol) of acetic acid was added to quench the reaction. The polymer was precipitated in cold methanol and dried *in vacuo*. Yield: 0.21g (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (m, –CH_3, poly), 1.45 (m, –CH_2–, poly), 4.09 (s, –CH_2–O, poly), 4.40 (s, –CH_2–N, poly), 5.16 (2 H, s, –CH_2–Ph, α-end), 7.23–7.27 (m, ArH, poly), 7.31–7.34 (m, ArH, poly), 7.80–7.82 (m, ArH, poly), 7.94 (m, =CH–N, poly). GPC ($CHCl_3$): M_n 5600, PDI 1.13.

Ring-opening polymerisation of 4b

In a glove box under Ar, 0.25 g (1.0 mmol) of **4b** and 19 mg (0.05 mmol) of TU were charged in an oven-dried round-bottom flask. The flask was sealed and transferred out and the contents were dissolved in 1 ml of dry DCM. 2 µl (0.02 mmol, for DP = 50) of benzyl alcohol was added as an initiator and 7 µl (0.05 mmol) of DBU was added to start polymerisation. After 6 h at r.t., 7 µl (0.12 mmol) of acetic acid was added to quench the reaction. The polymer was precipitated in diethyl ether and dried *in vacuo*. Yield: 0.12 g (47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (m, –CH_2–, poly), 0.93 (m, –CH_2–, poly), 0.97 (m, –CH_3, poly), 1.47 (m, –CH_2–, poly), 1.94 (m, >CH–, poly), 4.07 (s, –CH_2–O, poly), 4.39 (s, –CH_2–N, poly), 5.17 (2 H, s, –CH_2–Ph, α-end), 7.39 (s, =CH–N, poly). GPC ($CHCl_3$): M_n 2300, PDI 1.16.

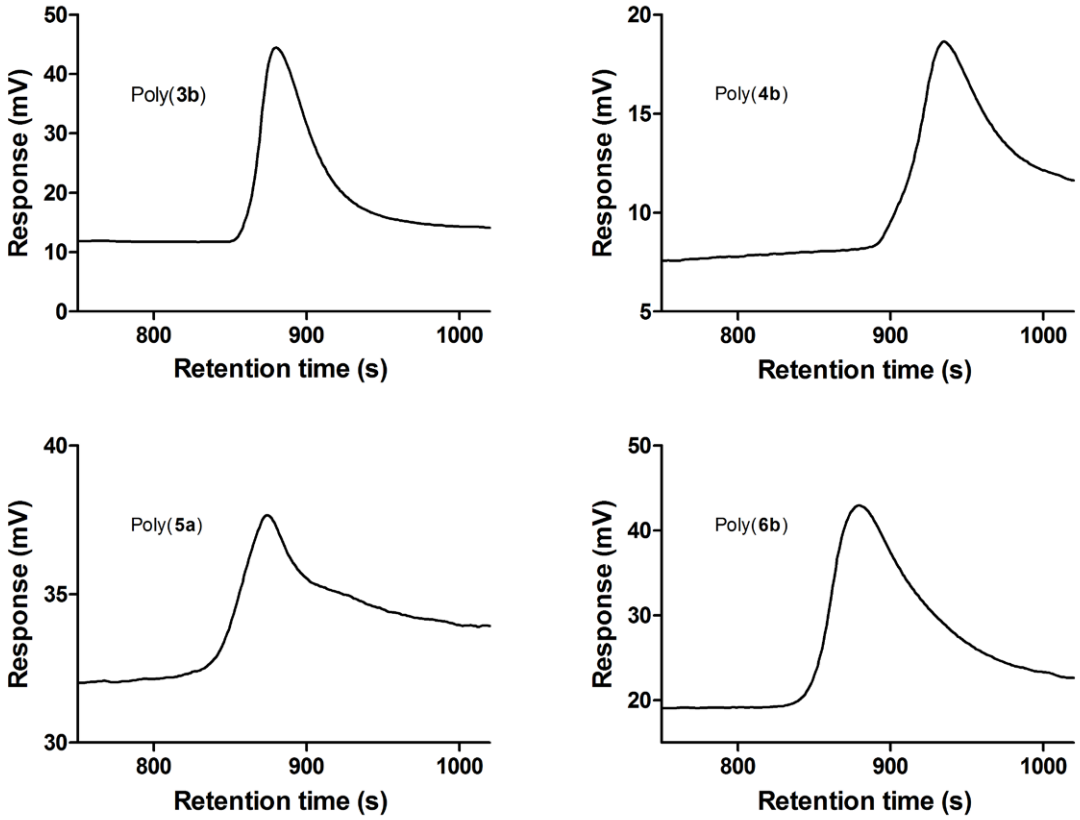
Ring-opening polymerisation of 5a

In a glove box under Ar, 0.24 g (1.0 mmol) of **5a** and 19 mg (0.05 mmol) of TU were charged in an oven-dried round-bottom flask. The flask was sealed and transferred out and the contents were dissolved in 1 ml of dry DCM. 2 µl (0.02 mmol, for DP = 50) of benzyl alcohol was added as an initiator and 7 µl (0.05 mmol) of DBU was added to start polymerisation. After 5 h at r.t., 7 µl (0.12 mmol) of acetic acid was added to quench the reaction. The polymer was precipitated in diethyl ether and dried *in vacuo*. Yield: 0.13 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (s, –CH_3, poly), 1.29 (m, –CH_3, poly), 3.07 (m, >CH–, poly), 4.09 (s, –CH_2–O, poly), 4.42 (s, –CH_2–N, poly), 5.17 (2 H, s, –CH_2–Ph, α-end), 7.39 (s, =CH–N, poly). GPC ($CHCl_3$): M_n 5400, PDI 1.25.

Ring-opening polymerisation of 6b

In a glove box under Ar, 0.25 g (1.0 mmol) of **6b** and 19 mg (0.05 mmol) of TU were charged in an oven-dried round-bottom flask. The flask was sealed and transferred out and the contents were dissolved in 1 ml of dry DCM. 2 µl (0.02 mmol, for DP = 50) of benzyl alcohol was added as an initiator and 7 µl (0.05 mmol) of DBU was added to start polymerisation. After 5 h at r.t., 7 µl (0.12 mmol) of acetic acid was added to quench the reaction. The polymer was precipitated in diethyl ether and dried *in vacuo*. Yield: 0.15 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (m, –CH_3, poly), 1.48 (m, –CH_2–, poly), 2.10 (s, –CH_3, poly), 4.10 (s, –CH_2–O, poly), 4.44 (s, –CH_2–N, poly), 5.07 (s, =CH–H, poly), 5.17 (2 H, s, –CH_2–Ph, α-end), 5.69 (s, =CH–H, poly), 7.64 (m, =CH–N, poly). GPC ($CHCl_3$): M_n 5000, PDI 1.24.

GPC Traces



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