

Mechanically-Linked Polycarbonate

Charles-André Fustin^{1§}, Christian Bailly^{1}, Guy J. Clarkson², Philippe De Groote³, Trent H. Galow⁴, David A. Leigh^{4*}, Duncan Robertson⁵, Alexandra M. Z. Slawin⁶ and Jenny K. Y. Wong⁴*

¹ Unité de Physique et de Chimie des Hauts Polymères, Université catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium.

² Centre for Supramolecular and Macromolecular Chemistry, Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom.

³ UCB Chemicals, Research and Technology, Analytical Department, Anderlechtstraat 33, B-1620 Drogenboos, Belgium

⁴ School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, United Kingdom.

⁵ ICI, The Wilton Centre, Wilton, Cleveland TS10 4RF, United Kingdom.

⁶ Department of Chemistry, University of St Andrews, St Andrews KY16 9ST, United Kingdom.

[§] Present address: Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

* To whom correspondence may be addressed: bailly@poly.ucl.ac.be (fax +32-10-451593) or David.Leigh@ed.ac.uk (fax +44-131-6679085)

Synthesis

All the solvents used were commercial HPLC grade. All other chemicals were purchased from Aldrich or Acros and used as received.

Polycarbonate oligomers. Bisphenol A (10g, 0.0439mole) and diphenyl carbonate (9.86g, 0.0461mole) were introduced into a glass reactor previously treated with HCl 3N for 12 hours. Tetrabutyl ammonium hydroxide (55 μ l of a 0.4M solution in water, i.e. 5×10^{-4} mole / mole of bisphenol) and sodium hydroxide (78 μ l of a 5.65×10^{-4} M solution in water, i.e. 10^{-6} mole / mole of bisphenol) were then added as catalysts. Polymerization was carried out using the following temperature program: i) 210°C at 260 mbar for 35 min; ii) 210°C at 130 mbar for 35 min; iii) 240°C at 20 mbar for 40 min; iv) 270°C at 2 mbar for 30 min; v) 300°C at 0.8 mbar for 30 min. Heating was performed using a salt bath enabling temperature control within 2°C. The mixture was stirred with a stainless steel agitator previously treated with phosphoric acid 50% for 12 hours. Stirring speed was set to 30 rpm. Polycarbonate oligomers were extracted from the reactor by dissolving them in dichloromethane. Solvent was then evaporated under vacuum.

[2]*Catenane 1.* 5-Allyloxyisophthalic acid **2** (43.3g, 195mmol) and hydroxybenzotriazole (55.3g, 409mmol, 2.1 equiv.) were dissolved in dry THF (400ml) and the solution cooled in ice. Dicyclohexylcarbodiimide (84.5g, 409mmoles, 2.1 equiv.) was added in four portions over 20 minutes and the mixture stirred overnight. The solid was removed by filtration and the filtrate added dropwise to a stirred, ice cooled solution of 4-aminobenzylamine (50g, 409mmol, 2.1 equiv.) in dry THF (100ml) over 60 minutes. After the addition, the mixture was stirred overnight. The solvent was removed under reduced pressure and the oil taken up in ethyl acetate (500ml) and washed with sodium hydroxide solution (1N, 3 \times 100ml). The ethyl acetate was dried over magnesium sulphate, filtered and the solvent removed under reduced pressure and the

resulting thick oil crystallized from ethanol/water. Filtration afforded the bisaniline as a colorless powder (65.5g, 78%) m.p. 147-148°C. m/z 430 (M)⁺, $C_{25}H_{26}O_3N_4$ requires C, 69.75; H, 6.09 and N, 13.02%. Found C, 69.6; H, 6.1 and N, 12.9%. ¹H NMR; (400MHz, d_6 -DMSO) δ 8.90 (2H, t, $J=5.8$ Hz, NH), 7.98 (1H, t, $J=1.4$ Hz, ArH), 7.58 (2H, d, $J=1.4$ Hz, ArH), 7.00 (4H, d, $J=8.4$ Hz, ArH), 6.53 (4H, d, $J=8.4$ Hz, ArH), 6.08 (1H, m, vinyl H), 5.43 (1H, dd, $J=17.2$ and 1.6 Hz, vinyl H), 5.35 (1H, dd, $J=10.5$ and 1.6Hz, vinyl H), 4.97 (4H, br s, NH₂), 4.68 (2H, br d, $J=5.2$ Hz, allylic CH₂) and 4.68 (4H, d, $J=5.8$ Hz, benzylic CH₂). ¹³C NMR; (75MHz, d_6 -DMSO): δ 165.5, 158.4, 147.9, 136.5, 133.7, 128.7, 126.7, 119.2, 117.9, 116.3, 114.0, 68.9 and 42.9.

A 3 litre round bottomed flask was charged with the bisaniline prepared above (1.5g, 3.5mmol), a large stirring bar and dry acetonitrile (40ml). The mixture was heated and swirled till the bisaniline dissolved. Dry dichloromethane (1.5 litres) and triethylamine (1.1ml, 0.8g, 7.9mmol) were added. A 250ml pressure equilibrated dropping funnel and a drying tube were attached and charged with dry dichloromethane (150ml) and sebacoyl chloride (0.75ml, 0.84g, 3.5mmol) and the mixture added to the rapidly stirred solution over about 15 minutes. After 5 minutes, the solution becomes cloudy and stirring was continued for 12 hours. The reaction mixture was filtered and the solids washed with chloroform (2 x 10 ml). The filtrate was washed with aqueous hydrochloric acid (1N, 200ml) and saturated sodium bicarbonate solution (200ml), dried over magnesium sulphate, filtered and the solvent removed under reduced pressure. The solvent was removed to about 10ml and this was transferred to a small conical flask. The reaction flask was rinsed with an additional 5-10ml of dichloromethane and this was also added to the conical flask. The flask was stoppered and allowed to stand for 24 hours. Catenane **3** was separated by filtration as a colorless solid (0.46g, 22%). m.p. 252-255°C m/z 1193 ($M+H$)⁺, $C_{70}H_{80}O_{10}N_8$ requires C, 70.45; H, 6.76 and N, 9.39%. Found C, 70.4; H, 6.9 and N, 9.3%. ¹H NMR;

(400MHz, d_6 -DMSO) δ 9.71(4H, br s, NH), 8.36(4H, br s, NH), 7.74 (2H, s, ArH), 7.46 (4H, br s, ArH), 7.33 (8H, d, $J=7.9$ Hz, ArH), 6.93 (8H, d, $J=7.9$ Hz, ArH), 6.05 (2H, m, vinyl H), 5.40 (2H, br d, $J=17$ Hz, vinyl H), 5.29 (2H, br d, $J=10.5$ Hz, vinyl H), 4.52 (4H, vbr s, allylic CH_2), 4.09 (8H, vbr s, $ArCH_2N$), 2.15 (8H, br s, $COCH_2$), 1.32 (8H, br s, $COCH_2CH_2$) and 0.83 (16H, br s, CH_2). ^{13}C NMR; (75MHz, d_6 -DMSO): δ 171.7, 166.2, 158.3, 138.5, 136.6, 133.6, 132.9, 128.5, 119.1, 118.1, 117.8, 116.6, 68.7, 43.4, 36.4, 29.5, 28.3 and 25.6. FT-IR (KBr) 3300, 2930, 1647, 1607, 1540, 1518, 1415, 1310 and 1255cm^{-1} . The original solids from the reaction mixture were placed in a cellulose thimble and subjected to constant extraction with a mixture of chloroform/methanol (1:1) for 12 hours. The solids from evaporation of the solvent were dissolved in dimethylformamide and stored at 4 °C for several days. The precipitate was filtered and washed with a little cold dimethylformamide, then diethyl ether and dried to give macrocycle **4** (0.55g, 26%). m.p.311-314°C (decomp.), m/z 597 ($M+H$)⁺, $C_{35}H_{40}O_5N_4$ requires C, 70.45; H, 6.76 and N, 9.39%. Found C, 70.2; H, 7.0 and N, 9.3%. 1H NMR; (400MHz, d_6 -DMSO) δ 9.80 (2H, br s, NH), 9.18 (2H, brt, $J=5.5$ Hz, NH), 7.70 (1H, br s, ArH), 7.52 (4H, d, $J=8.4$ Hz, ArH), 7.49 (2H, br s, ArH), 7.24 (4H, d, $J=8.4$ Hz, ArH), 6.08 (1H, ddt, $J=17.3, 10.5, 5.1$ Hz, vinyl H), 5.45 (1H, br d, $J=17.3$ Hz, vinyl H), 5.30 (1H, br d, $J=10.5$ Hz, vinyl H), 4.70 (2H, br d, $J=5.1$ Hz, allylic CH_2), 4.38 (4H, br d, $J=5.5$ Hz, benzylic CH_2), 2.29 (4H, br t, $J=6.3$ Hz, $COCH_2$), 1.57 (4H, br m, $COCH_2CH_2$) and 1.24 (8H, br s, CH_2). ^{13}C NMR; (75MHz, d_6 -DMSO): δ 175.3, 169.9, 162.2, 142.4, 140.5, 137.7, 137.5, 132.6, 123.1, 122.1, 121.7, 120.2, 72.6, 46.9 40.0, 33.2, 32.2 and 29.3. FT-IR (KBr) 3300, 2930, 1665, 1608, 1540, 1518, 1415, 1333, 1311 and 1270cm^{-1}

Catenane **3** (1.5g, 1.26mmoles) was dissolved in the minimum amount (~3ml) of hot DMSO and allowed to cool. The solution was placed under an argon atmosphere and dry THF (10ml) was added. The reaction mixture was stirred and sodium hydride (0.16g, 6.3mmoles, 5 equiv.,

60% dispersion in oil) was added carefully. Once effervescence had ceased, methyl iodide (0.9g, 0.4ml, 6.3mmoles) was added. The reaction was stirred and heated at 40°C for 5 hours. A similar quantity of sodium hydride and methyl iodide was added every 5 hours and stirring and heating continued until TLC (CH₂Cl₂/MeOH(10%)) showed only one spot (in general another two additions were required). The reaction was then allowed to cool and very carefully quenched by the addition of water (20ml) and ammonia solution (20ml, 33% solution). The reaction mixture was extracted with dichloromethane (3×20ml) and the combined organic extracts washed with 1N sodium hydroxide solution (2×10ml). The organic layer was dried (MgSO₄) and evaporated at reduced pressure to give a foam. This was dissolved in the minimum of dichloromethane and precipitated into an excess of rapidly stirred diethyl ether. The colorless precipitate was filtered and washed with a little diethyl ether and the solid dried to give the octa-*N*-methyl [2]catenane (1.5g, 91%), m/z 1304 (M)⁺, C₇₈H₉₆O₁₀N₈ requires C, 71.75; H, 7.41 and N, 8.58%. Found C, 71.5; H, 7.2 and N, 8.4%. ¹H NMR; (400MHz, D₂C₂Cl₄ at 130°C) δ 7.32 (8H, d, J=8.3Hz, ArH), 7.05 (4H, d, J=1.3Hz ArH), 7.02 (8H, d, J=8.3Hz, ArH), 6.88 (2H, br s, ArH), 6.07 (8H, ddt, J=17.3, 10.6, 5.2Hz, vinyl H), 5.44 (2H, br d, J=17.3Hz, vinyl H), 5.33 (2H, br d, J=10.6Hz, vinyl H), 4.63 (4H, br d, J=5.2Hz, allylic CH₂), 4.61 (8H, s, ArCH₂N), 3.17 (12H, br s, NMe), 2.97 (12H, br s, NMe), 1.85 (8H, t, J=7.6Hz, COCH₂), 1.26 (8H, p, J=7.6Hz, COCH₂CH₂), 0.82 (8H, br s, CH₂) and 0.66 (8H, br s, CH₂). FT-IR (KBr) 2925, 1640 and 1395cm⁻¹.

To a solution of the catenane (1g, 0.82 mmoles) in ethanol (20ml) was added triethylamine (1ml), formic acid (0.5ml), triphenylphosphine (20mg) and palladium acetate (10mg). The mixture was stirred at room temperature for two days until TLC (EtOAc/MeOH(10%)) showed complete consumption of the starting material with no allyl groups remaining (stain with KMnO₄

solution). The reaction mixture was evaporated to a small volume and partitioned between dichloromethane (20ml) and water (20ml). The aqueous layer was extracted twice more with dichloromethane (2×20ml) and the combined organic layer washed with 2N sodium bicarbonate solution (2×10ml). The organic extracts were dried (MgSO₄) and evaporated at reduced pressure to give a foam. This was taken up in the minimum of dichloromethane and precipitated into a large excess of rapidly stirred diethyl ether. The solid was filtered and dried to give the octa-*N*-methyl bisphenol catenane **1** (0.8g, 80%) m/z 1225 (M+H)⁺, C₇₂H₈₈O₁₀N₈ requires C, 70.56; H, 7.24 and N, 9.14%. Found C, 70.9; H, 7.2 and N, 8.9%. δ ¹H NMR; (400MHz, C₂D₂Cl₄ at 130 °C) δ 7.31 (8H, d, J=8.2Hz, ArH), 7.03 (8H, d, J=8.2Hz, ArH), 7.00 (4H, br s, ArH), 6.95 (2H, br s, ArH), 4.57 (8H, s, ArCH₂N), 3.23 (12H, s, NMe), 2.97 (12H, s, NMe), 1.82 (8H, br t, J=7.4Hz, COCH₂), 1.21 (8H, br m, COCH₂CH₂), 0.60 (8H, br s, CH₂) and 0.53 (8H, br s, CH₂).

FT-IR (KBr) 3420, 2925 and 1640cm⁻¹.

Copolymers. Copolymerization was performed on batches of 300mg. Polycarbonate oligomers and catenane **1** (10, 20 or 30% w/w) or macrocycle **2** (10% w/w) or 4,4'-(9-fluorenylidene)diphenol **6** (10 % w/w) were dissolved in 5 ml of dichloromethane. Solvent was evaporated under vacuum while stirring the solution and the resulting powder was dried under vacuum for 12 hours at 50°C. The blend was crystallized under acetone vapors for 4 hours then vacuum dried for 12 hours at 50°C. The blend was ground to obtain a finely divided powder. Solid state polymerization was performed under vacuum (6×10⁻² mbar) applying the following temperature program i) room temperature for 20 min; ii) 190°C for 1h; iii) 200°C for 2h30; iv) 210°C for 19h; v) 215°C for 5h.

Model Compound 5. [2]Catenane **1** (73.4 mg; 6×10^{-5} mole) and triethylamine (12.2mg; 1.21×10^{-4} mole) were dissolved in 2 ml of dry dichloromethane. Phenyl chloroformate (19.7mg; 1.26×10^{-4} mole) was added to 2 ml of dry dichloromethane under argon atmosphere. The solution of catenane and triethylamine was added to the solution of phenyl chloroformate under vigorous stirring and argon atmosphere. The reaction medium was stirred for 17 hours at room temperature. The obtained solution was then washed twice with HCl 0.1N and rinsed twice with water. The organic phase was dried with magnesium sulphate then condensed under vacuum to yield **5** as a pale yellow powder (73mg, 83%).

X-Ray crystallography

Catenane **1**. $C_{78}H_{96}N_8O_{10}$, $M=1305.63$, crystal size $0.40 \times 0.14 \times 0.06$ mm, monoclinic, $P2(1)/n$, $a=16.3629(6)$, $b=25.1227(9)$, $c=16.8767(6)$ Å, $\beta=91.036(2)^\circ$, $V=6936.5(4)$ Å³, $Z=4$, $\rho_{\text{calcd}}=1.250$ Mg m⁻³; Mo K α radiation (graphite monochromator, $\lambda=0.71073$ Å), $\mu=0.083$ mm⁻¹, $T=150(2)$ K. 34541 data (16899 unique, $R_{\text{int}}=0.0382$, $1.84 < \theta < 29.47^\circ$), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semi-empirically for absorption and incident beam decay (transmission 0.96-1.00). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give $wR=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}=0.3983$, conventional $R=0.1461$ for F values of

16899 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S=2.662$ for 485 parameters. Residual electron density extremes were 1.393 and -1.429 \AA^{-3} .

Bis-O-allyl-protected catenane 1: $C_{78}H_{100}N_8O_{11}$, $M=1325.66$, crystal size 0.35×0.2×0.18 mm, triclinic, P-1, $a=16.0178(3)$, $b=23.1950(6)$, $c=23.2949(5)$ \AA , $\alpha=71.3310(10)$, $\beta=83.9370(10)$, $\gamma=79.5650(10)^\circ$, $V=8053.3(3)$ \AA^3 , $Z=4$, $\rho_{\text{calcd}}=1.093$ Mg m^{-3} ; Mo K α radiation (graphite monochromator, $\lambda=0.71073$ \AA), $\mu=0.073$ mm^{-1} , $T=293(2)$ K. 37390 data (22686 unique, $R_{\text{int}}=0.0965$, $1.54 < \theta < 23.33^\circ$), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semi-empirically for absorption and incident beam decay (transmission 0.32-1.00). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give $wR=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}=0.5043$, conventional $R=0.1680$ for F values of 22686 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S=1.588$ for 1446 parameters. Residual electron density extremes were 1.363 and -0.478 \AA^{-3} .

Catenane 3: $C_{70}H_{85}N_8O_{12.50}$, $M=1238.49$, crystal size 0.18×0.18×0.18 mm, monoclinic, C 2/c, $a=27.154(7)$, $b=12.48(5)$, $c=41.59(1)$ \AA , $\beta=95.94(2)^\circ$, $V=14013.9(5)$ \AA^3 , $Z=8$, $\rho_{\text{calcd}}=1.174$ Mg m^{-3} ; Cu K α radiation (graphite monochromator, $\lambda=1.5418$ \AA), $\mu=0.66$ mm^{-1} , $T=293(2)$ K. 11247 data (4606 unique, $R_{\text{int}}=0.09533$, $3.20 < \theta < 60.22^\circ$), were collected on MSC/AFC Diffractometer Control. The structure was solved by direct methods and refined by full-matrix least-squares on

F^2 values of all data (teXsan (MSC, 1992-1997)) to give $wR=\{\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}=0.0887$, conventional $R=0.0936$ for F values of 4606 reflections with $F_O^2>2\sigma(F_O^2)$, $S=2.620$ for 821 parameters. Residual electron density extremes were 0.90 and -0.21 Å⁻³.

Bishydroxy catenane 3. C_{70.5}H₉₀N₈O_{14.50}, $M=1281.51$, crystal size 0.15×0.11×0.08 mm, triclinic, P1, $a=12.70810(10)$, $b=16.9611(2)$, $c=17.2671(2)$ Å, $\alpha=84.8760(10)$, $\beta=68.5300(10)$, $\gamma=87.9360(10)^\circ$, $V=3449.69(6)$ Å³, $Z=2$, $\rho_{\text{calcd}}=1.234$ Mg m⁻³; Mo K α radiation (graphite monochromator, $\lambda=0.68740$ Å), $\mu=0.087$ mm⁻¹, $T=293(2)$ K. 26175 data (14366 unique, $R_{\text{int}}=0.1224$, $1.17<\theta<27.13^\circ$), were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semi-empirically for absorption and incident beam decay (transmission 0.61-1.00). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments, Madison WI, USA, 1994, version 5) to give $wR=\{\Sigma[w(F_O^2-F_C^2)^2]/\Sigma[w(F_O^2)^2]\}^{1/2}=0.3197$, conventional $R=0.1055$ for F values of 14366 reflections with $F_O^2>2\sigma(F_O^2)$, $S=1.299$ for 859 parameters. Residual electron density extremes were 0.828 and -0.432 Å⁻³.

Macrocycle 4. C₃₅H₄₂N₄O₆, $M=614.74$, crystal size 0.23×0.15×0.03 mm, monoclinic, P21/n, $a=11.37(1)$, $b=12.39(1)$, $c=23.492(7)$ Å, $\beta=93.70(5)^\circ$, $V=3303(4)$ Å³, $Z=4$, $\rho_{\text{calcd}}=1.236$ Mg m⁻³; Cu K α radiation (graphite monochromator, $\lambda=1.5418$ Å), $\mu=0.69$ mm⁻¹, $T=293(2)$ K. 5466 data

(1978 unique, $R_{\text{int}}=0.34645$, $3.57<\theta<60.12^\circ$), were collected on MSC/AFC Diffractometer Control. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (teXsan (MSC, 1992-1997)) to give $wR=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}=0.0624$, conventional $R=0.1068$ for F values of 1978 reflections with $F_o^2>2\sigma(F_o^2)$, $S=2.988$ for 407 parameters. Residual electron density extremes were 0.29 and -0.31 \AA^{-3} .