Dithioacetalisation of PEEK: a general technique for the solubilisation and characterisation of crystalline aromatic polyketones

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ELECTRONIC SUPPLEMENTARY INFORMATION

A. Starting materials

B. Instrumental techniques

C. Representative synthetic procedures and characterisation data for polymers and macrocycles

A. Starting materials

The cyclic dimer and trimer of PEEK were isolated by column chromatography from a mixture of cyclic oligomers prepared by cyclo-condensation of hydroquinone and 4,4'difluorobenzophenone under *pseudo*-high dilution conditions.[8,9] Boron trifluoride diethyl etherate, trifluoroacetic acid (TFA), dimethylsulfoxide (DMSO), 1,2-ethanedithiol and 1,3-propanedithiol were supplied by Aldrich. Dichloromethane, chloroform and methanol were bought from Fisher, and 2-iodo-methylpropane from Acros. Samples of PEK (**2**) and PEKEKK (**3**) were obtained from ICI plc and BASF GmbH respectively. All chemicals and polymers were used as received from the suppliers.

B. Instrumental techniques

Proton and ^{13}C NMR spectra were obtained on Bruker DPX250 spectrometer at 250 and 62.8 MHz respectively. Resonances were recorded in δ (ppm) and referenced to residual solvent resonances or to tetramethylsilane.

MALDI-TOF MS spectra were obtained on an SAI-LT3 LaserTof spectrometer in reflexion mode, with an accelerating potential of 20 keV. Typically, 40µL of a solution of the compound in dichloromethane (1 mg mL^{-1}) was added to 20 µL of a solution of the matrix (1,8,9-trihydroxyanthracene, "dithranol", 30 mg mL^{-1}) and 20 µL of a solution of the cationising agent in tetrahydrofuran (10 mg mL^{-1}). The mixture was mixed and deposited on a sample plate and left to dry before analysis.

Infra-red spectra were obtained as films from evaporated chloroform solutions on KBr plates, and were recorded on a Perkin-Elmer FT 1700 instrument.

Differential scanning calorimetry was carried out on a Mettler DSC20 system under nitrogen flow (60 mL min^{-1}) at a heating rate of 10 or 20 °C min^{-1}. The temperature was calibrated by the melting peak and endotherm of a sample containing known weights of indium, zinc and lead. Glass transition temperatures are recorded as the mid-points and melting temperatures are quoted as the peaks of the endotherms.

Inherent viscosities (η_{inh}) were determined at 25 °C from 0.1 wt % filtered solutions of polymer using a Schott AVS 470 auto-viscometer and a Schott CT52 thermostatted water bath. Dithioacetal polymers were dissolved in chloroform and characterised using a Schott-Geräte Ubbelohde capillary No. 53103. Inherent viscosities were calculated from the following equation:

$$\eta_{inh} = \frac{\ln(t_2/t_1)}{c}$$

where t_1 is the flow time of the solvent in seconds, t_2 is the flow time of the polymer solution in seconds and c is the polymer concentration in g dL^{-1}.

High temperature GPC of PEEK was carried out by RAPRA Technology on a Polymer Laboratories GPC120 instrument fitted with a PL GPC-AS MT heated autosampler in 50:50 (w/w) 1,2,4-trichlorobenzene:phenol with anti-oxidant. Analyses were done at 115

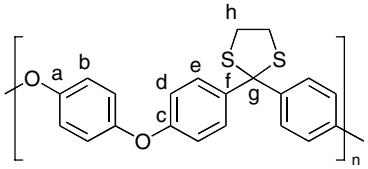
°C at 0.8 mL min^{-1} with two mixed bed-B columns, 30 cm, 10μm, and a refractive index detector calibrated with polystyrene standards.

Gel-permeation chromatography in chloroform was carried out at 35 °C on a Polymer Laboratories GPC220 instrument with two 10 μm mixed-B PL columns (300 x 7.5 mm). The refractive index detector was calibrated with ten polystyrene standards (Polymer Laboratories Easycal PS2). The light scattering analyses were carried out with a PD2000 LS detector. The detector constants and the interdetector delay were calibrated with a single PMMA standard (M_p = 100,000) of known concentration. The incremental refractive indexes (*d*n/*d*c) of the samples were calculated from their concentrations and from the detector constant previously determined. The LS response at 15° was used only for molecular weights greater than 10,000 Da.

Single crystal X-ray data were measured on an Oxford Diffraction X-Calibur CCD diffractometer using Mo-Kα radiation at 150K. Full details of the structure solution and refinement for compound **10** is given in the associated CIF file.

C. Representative synthetic procedures and characterisation data

Synthesis of poly(ether-ether-1,3-dithiolane) **4**

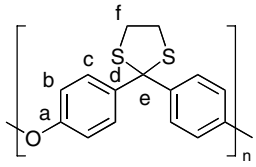


4

To a stirred solution of PEEK (1.153 g) in dichloromethane (20 mL) and trifluoroacetic acid (5 mL) was added 1,2-ethanedithiol (0.752 g, 7.99 mmol) followed by boron trifluoride diethyl etherate (0.571 g, 4.02 mmol) under an atmosphere of nitrogen. After 18 h at room temperature the deep red solution was diluted with dichloromethane (50 mL) and poured into cold methanol (100 mL). Poly(ether ether 1,3-dithiolane) **4** (1.456 g, 100% yield) was recovered upon filtration as a white fine powder, ν_{max}/cm^{-1} 3039 (C-H), 2926 (C-H), 1603 (C-C), 1490 (C-C), 1224 (C-O-C), 1192 (C-H); δ_H (250 MHz, $CDCl_3$) 3.40 (4 H, s, H_h), 6.88 (4 H, AA'XX', H_d), 6.99 (4 H, s, H_b), 7.53 (4 H, AA'XX', H_e); δC (62.5 MHz, $CDCl_3$) 40.6 (C_h), 76.5 (C_g), 117.6 (C_d), 121.2 (C_b), 130.2 (C_e), 139.3 (C_f), 152.8

(C_c), 157.4 (C_a); η_{inh} ($CHCl_3$) = 0.35 ; GPC (RI) : M_n = 19,900, M_w = 52,400; GPC (LS) M_n = 15,800, M_w = 47,900.

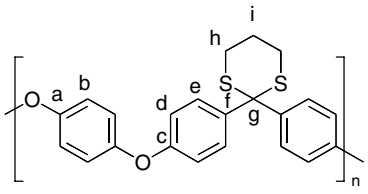
Preparation of poly(ether-1,3-dithiolane) **5**



5

To a stirred suspension of PEK (0.392 g) in dichloromethane (25 mL) and trifluoroacetic acid (2 mL) was added 1,2-ethanedithiol (0.393 g, 4.17 mmol) followed by boron trifluoride diethyl etherate (0.280 g, 1.97 mmol) under an atmosphere of nitrogen. After three days at room temperature the deep red solution was poured into methanol (100 mL). Poly(ether-1,3-dithiolane) **5** (0.532 g, 98% yield) was recovered upon filtration and washing with methanol as a white powder, ν_{max}/cm^{-1} 2929 (C-H), 1603 (C-C), 1492 (C-C), 1225 (C-O-C), 1193 (C-H); δ_H (250 MHz, $CDCl_3$) 3.39 (4 H, s, H_f), 6.85 (4 H, AA'XX', H_b), 7.55 (4 H, AA'XX', H_e); δC (62.5 MHz, $CDCl_3$) 40.7 (C_e), 76.5 (C_f), 118.5 (C_b), 130.2 (C_c), 139.7 (C_d), 156.4 (C_a); η_{inh} ($CHCl_3$) = 0.31; GPC (RI) : M_n = 28,200, M_w = 62,900; GPC (LS) M_n = 18,900, M_w = 61,700.

Preparation of poly(ether-ether-1,3-dithiane) **7**

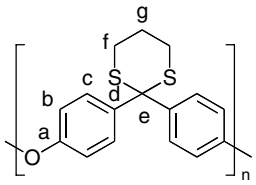


7

To a stirred solution of PEEK (0.576 g) in dichloromethane (20 mL) and trifluoroacetic acid (2 mL) was added 1,3-propanedithiol (0.431 g, 3.98 mmol) followed by boron trifluoride diethyl etherate (0.291 g, 2.05 mmol) under an atmosphere of nitrogen. After five days at room temperature the dark red solution was poured into methanol (100 mL). Poly(ether-ether-1,3-dithiane) **7** (0.705 g, 93% yield) was recovered upon filtration as a white powder, ν_{max}/cm^{-1} 3039 (C-H), 2907 (C-H), 1602 (C-C), 1490 (C-C), 1225 (C-O-C), 1192 (C-H); δ_H (250 MHz, $CDCl_3$) 1.99 (2H, br, H_i), 2.76 (4 H, br, H_h), 6.91 (4 H, AA'XX', H_d), 7.02 (4 H, s, H_b), 7.59 (4 H, AA'XX', H_e); δC (62.5 MHz, $CDCl_3$) 24.8 (C_i), 29.9 (C_h), 62.2 (C_g), 117.9 (C_d), 121.4 (C_b), 131.3 (C_e), 137.3 (C_f), 152.8 (C_c), 157.6 (C_a);

η_{inh} ($CHCl_3$) = 0.39; GPC (RI) : M_n = 22,000, M_w = 73,800; GPC (LS) M_n = 19,200, M_w = 76,900.

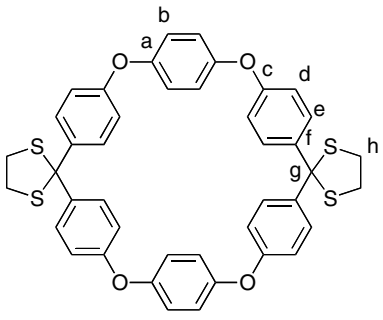
Preparation of poly(ether 1,3-dithiane) **8**



8

To a stirred solution of PEK (0.392 g) in dichloromethane (20 mL) and trifluoroacetic acid (2 mL) was added 1,3-propanedithiol (0.431 g, 3.98 mmol) followed by boron trifluoride diethyl etherate (0.291 g, 2.05 mmol) under an atmosphere of nitrogen. After three days at room temperature the deep red solution was poured into methanol (100 mL). Poly(ether 1,3-dithiane) **8** (0.558 g, 97% yield) was recovered upon filtration. The white powder was dried at 60 °C in a vacuum oven, ν_{max}/cm^{-1} 3039 (C-H), 2907 (C-H), 1602 (C-C), 1490 (C-C), 1225 (C-O-C), 1192 (C-H); δ_H (250 MHz, $CDCl_3$) 2.00 (2H, br, H_i), 2.55 (4 H, br, H_h), 6.97 (4 H, AA'XX', H_b), 7.65 (4 H, AA'XX', H_c); δC (62.5 MHz, $CDCl_3$) 24.8 (C_g), 29.9 (C_f), 62.3 (C_e), 119.0 (C_b), 131.3 (C_c), 137.9 (C_d), 156.6 (C_a); η_{inh} ($CHCl_3$) = 0.37; GPC (RI) : M_n = 22,700, M_w = 89,700; GPC (LS) M_n = 24,400, M_w = 100,000.

Tricyclic bis(1,3-dithiolane) **10**

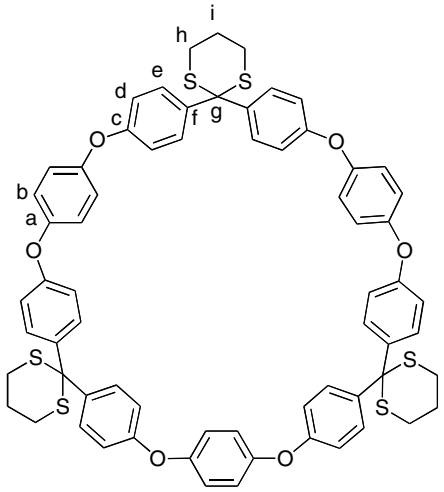


10

To a stirred solution of PEEK cyclic dimer (0.144 g, 0.25 mmol) in dichloromethane (20 mL) and trifluoroacetic acid (2 mL) was added 1,2-ethanedithiol (0.472 g, 5.01 mmol) followed by boron trifluoride diethyl etherate (0.071 g, 0.50 mmol) under an atmosphere of nitrogen. After 16 h at room temperature the deep red solution poured into cold methanol (100 mL). The tricyclic compound **10** (0.178 g, 98% yield) was recovered upon filtration as a white powder, ν_{max}/cm^{-1} 3039 (C-H), 2924 (C-H), 1604 (C-C), 1498 (C-C), 1229 (C-

O-C); δ_H (250 MHz, $CDCl_3$) 3.45 (8 H, s, H_h), 6.85 (12 H, m, H_d, H_b), 7.51 (8 H, AA'XX'. H_e); δC (62.5 MHz, $CDCl_3$) 40.3 (C_h), 76.7 (C_g), 118.6 (C_d), 119.8 (C_b), 130.2 (C_e), 139.3 (C_f), 154.4 (C_c), 156.8 (C_a); m/z (MALDI-ToF) = 729.1 $[M+H]^+$, calc. = 729.1256. Anal. calc. for $C_{42}H_{32}O_4S_4$: C, 69.20; H, 4.42; S, 17.59. Found: C, 68.51; H, 4.40; S 17.22%. Single crystals suitable for X-Ray analysis were grown by vapour diffusion of methanol into a dichloromethane solution of the macrocycle.

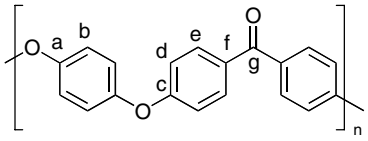
Tetracyclic tris(1,3-dithiane) **13**



13

To a stirred solution of PEEK cyclic trimer (0.144 g, 0.17 mmol) in dichloromethane (20 mL) was added 1,2-propanedithiol (0.108 g, 1.00 mmol) followed by boron trifluoride diethyl etherate (0.078 g, 0.55 mmol) under an atmosphere of nitrogen. After 24 h at room temperature the deep red solution was diluted to 50 mL with dichloromethane and washed with water. The organic layer was dried with MgSO4 and evaporated. The tetracyclic compound **13** (0.155 g, 82% yield) was recovered by column chromatography (dichloromethane/ petroleum ether 30-40 °C; 5:1) as a white powder, ν_{max}/cm^{-1} 3042 (C-H), 2908 (C-H), 1603 (C-C), 1493 (C-C), 1227 (C-O-C), 1193 (C-H); m/z (MALDI-ToF) 1135 $[M+H]^+$, calc. 1135.2317; δ_H (250 MHz, $CDCl_3$) 2.01 (6 H, br, H_i), 2.78(12 H, br, H_h), 6.88 (12 H, AA'XX', H_d), 7.01 (12 H, s, H_b), 7.58 (12 H, AA'XX'. H_e); δC (62.5 MHz, $CDCl_3$) 24.8 (C_i), 29.8 (C_h), 62.1 (C_g), 117.5 (C_d), 121.5 (C_b), 131.1 (C_f), 137.3 (C_e), 152.7 (C_a), 157.7 (C_c). Anal. calc. for $C_{66}H_{54}O_6S_6$: C, 69.81; H, 4.79; S, 16.94. Found: C, 69.41; H, 4.87; S, 16.72%.

Deprotection of poly(ether-ether-1,3-dithiane) **7** *to regenerate PEEK* **(1)**



1

To a solution of **7** (0.189 g; 0.5 mmol)) in chloroform (20 mL) were added rapidly DMSO (0.78 g; 10.0 mmol) and 2-iodo-methylpropane (0.93 g; 5.0 mmol). After three days at 70 °C, the dark solution was cooled and poured into methanol (100 mL). The beige precipitate was recovered by filtration and was extensively washed with methanol and dried in a vacuum oven at 80 °C. Poly(ether ether ketone) (0.135 g, 94%) was isolated as a pale grey solid, T_g = 143 °C, T_m = 334 °C; δ_H (250 MHz, $CDCl_3$/TFA) 7.10 (4 H, AA'XX', H_d), 7.19 (4 H, s, H_b), 7.84 (4 H, AA'XX', H_e); δC (62.5 MHz, $CDCl_3$/TFA) 117.4 (C_d), 122.6 (C_b), 131.0 (C_f), 133.9 (C_e), 152.2 (C_a), 163.5 (C_c), 200.0 (C_g); GPC (phenol/trichlorobenzene at 115°C): M_n = 31,000, M_w = 78,000; The parent PEEK sample also had M_n = 31,000, M_w = 78,000.