Direct iminization of PEEK

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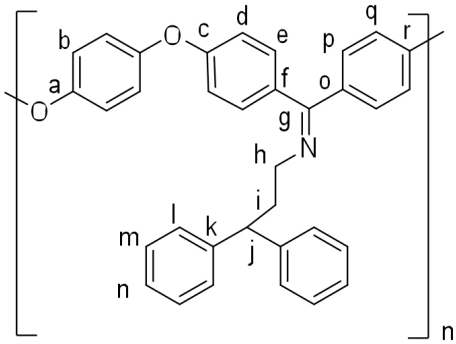
SUPPORTING INFORMATION

Synthesis and characterisation of poly(ether imine)s **1 – 4** including thermal, spectroscopic, GPC and elemental analyses. Gel permeation chromatograms for poly(ether imine)s **1 – 4.** Further analysis of sequence-effects in the ^{13}C NMR spectra of poly(ether imine)s. ^{1}H NMR spectrum of polymer **2**.

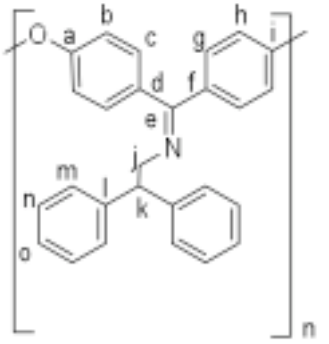
Synthesis of poly(ether imine)s: A sample of PEEK powder (0.577 g, 2.00 mmol) was placed in a reaction tube equipped with a nitrogen inlet and mechanical stirrer, together with diphenyl sulfone (9.0 g, 41 mmol) and 2,2-diphenylethylamine (1.972 g, 10 mmol) The system was stirred under a gentle, continuous purge of dry nitrogen and heated slowly (90 °C h^{-1}) to 315 °C to dissolve the polymer. The temperature was then lowered to 270 °C and the solution was stirred at this temperature for 3 h, giving a clear, viscous, bright yellow solution. The reaction mixture was then poured onto an aluminium tray to cool. The resulting beige solid was dissolved in dichloromethane (100 mL) and the polymer recovered as a pale yellow powder by precipitation in methanol (300 mL). Traces of diphenyl sulfone were removed by extracting the polymer in refluxing methanol for 1 h, and the product poly(ether imine), **1**, was then filtered off and dried at 80 °C (0.83 g, 89% yield). Aanalogous poly(ether imine)s **2**, **3** and **4** were obtained under the same conditions by reactions, respectively, of PEEK with 3,3-diphenylpropylamine, PEK with 2,2-diphenylethylamine, and PEK with 3,3-diphenylpropylamine.

Characterization data for poly(ether imine)s:

*Polymer **2***. IR (film from chloroform) ν_{max}/cm^{-1}: 3025 (C-H_{Ar}), 2934 (C-H), 1613 (C=N), 1491 (C-C), 1222 (C-O-C), 1164 (C-O-C); ^{1}H NMR (250 MHz, $CDCl_3$): δ_H (ppm) 7.61-7.56 (2H, m, H_p), 7.30-6.91 (20H, m, H_b, H_d, H_e, H_q, H_l, H_m, H_n), 4.14-4.08 (1H, tr, H_j, J = 7.5 Hz), 3.37-3.31 (2H, t, H_h, J = 7.5 Hz), 2.46-2.37 (2H, m, H_i); ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\__c$ (ppm) 167.3 (C_g), 159.8 (C_r), 158.1 (C_c), 152.8 (C_a), 145.2 (C_k), 135.5 (C_o), 131.5 (C_f), 130.5 (C_p), 129.9 (C_e), 128.8 (C_l), 128.4 (C_m), 126.3 (C_n), 121.3 (C_b), 118.1 (C_d, C_q), 52.3 (C_h), 49.1 (C_j), 37.3 (C_i); η_{inh} ($CHCl_3$) 0.32 dL g^{-1}; T_g (onset) = 112 °C; GPC (RI, THF, 25 °C): M_n= 21 kD, M_w = 45 kD; Calcd. for $[C_{34}H_{27}NO_2]_n$: C 84.80, H 5.65, N 2.91; Found: C 84.69, H 5.63, N 2.82%.

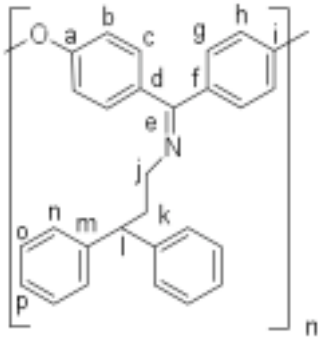


*Polymer **3***. IR (film from chloroform) ν_{max}/cm^{-1}: 3064 (C-H_{Ar}), 3018 (C-H), 1625 (C=N), 1593 (C=C_{Ar}), 1496 (C-C), 1214 (C-O-C), 1166 (C-O-C); ^{1}H NMR (250 MHz, $CDCl_3$): δ_H (ppm) 7.50-7.38 (2H, m, H_g),



7.25-6.84 (16H, m, H_b, H_c, H_h, H_m, H_n, H_o), 4.57-4.54 (1H, br, H_k), 4.11-4.04 (2H, d, H_j, J = 7.5 Hz); ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\_c$ (ppm) 167.2 (C_e), 158.3 (C_i), 157.0 (C_a), 143.4 (C_l), 135.8 (C_d), 131.7 (C_f), 130.2 (C_g), 129.8 (C_c), 128.5 (C_m), 128.3 (C_n), 126.3 (C_o), 118.8 (C_b, C_h), 58.9 (C_j), 52.6 (C_k); η_{inh} ($CHCl_3$) 0.24 dL g^{-1}; T_g (onset) = 130 °C; GPC (RI, THF, 25 °C): M_n= 22 kD, M_w = 42 kD.

*Polymer **4***. IR (film from chloroform) ν_{max}/cm^{-1}: 3019 (C-H_{Ar}), 2940 (C-H), 1616 (C=N), 1593 (C=C_{Ar}), 1496 (C-C), 1216 (C-O-C), 1166 (C-O-C); ^{1}H NMR (250 MHz, $CDCl_3$): δ_H (ppm) 7.67-7.57 (2H, m, H_g),



7.25-6.97 (16H, m, H_b, H_c, H_h, H_m, H_n, H_o), 4.14-4.10 (1H, br, H_k), 3.38-3.34 (2H, m, H_j), 2.43 (2H, br, H_k); ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\_c$ (ppm) 167.2 (C_e), 158.7 (C_i), 157.1 (C_a), 145.1 (C_l), 136.0 (C_d), 132.0 (C_f), 130.5 (C_g), 129.9 (C_c), 128.8 (C_n), 128.4 (C_o), 126.5 (C_p), 118.8 (C_b, C_h), 52.0 (C_j), 48.8 (C_l), 37.0 (C_k); η_{inh} ($CHCl_3$) 0.25 dL g^{-1}; T_g (onset) = 109 °C; GPC (RI, THF, 25 °C): M_n= 17 kD, M_w = 36 kD.

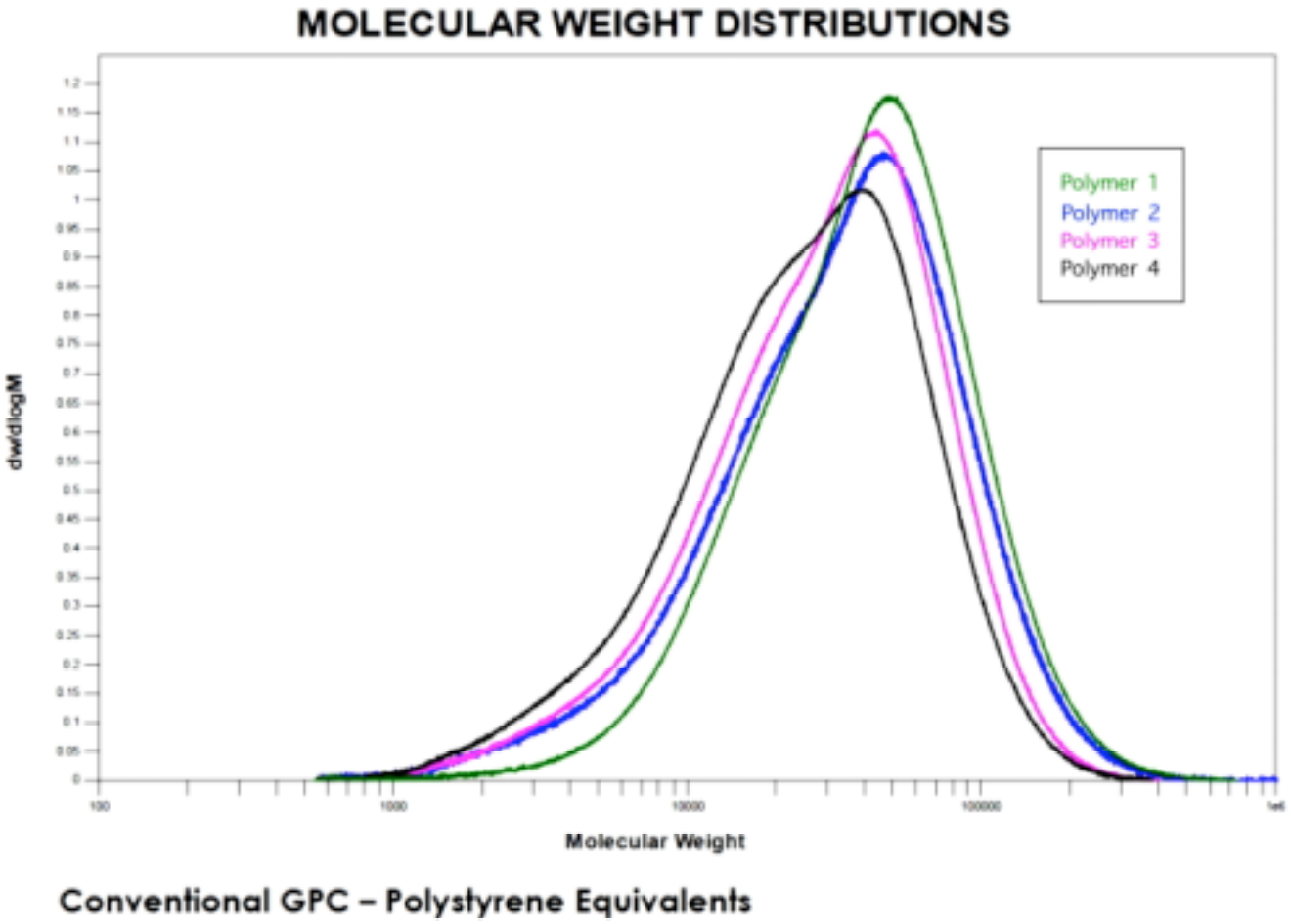


Figure S1. Gel permeation chromatograms of poly(ether imine)s **1** – **4** (THF as solvent, RI detection).

Further analysis of ^{13}C NMR resonance multiplicities for poly(ether imine) 1

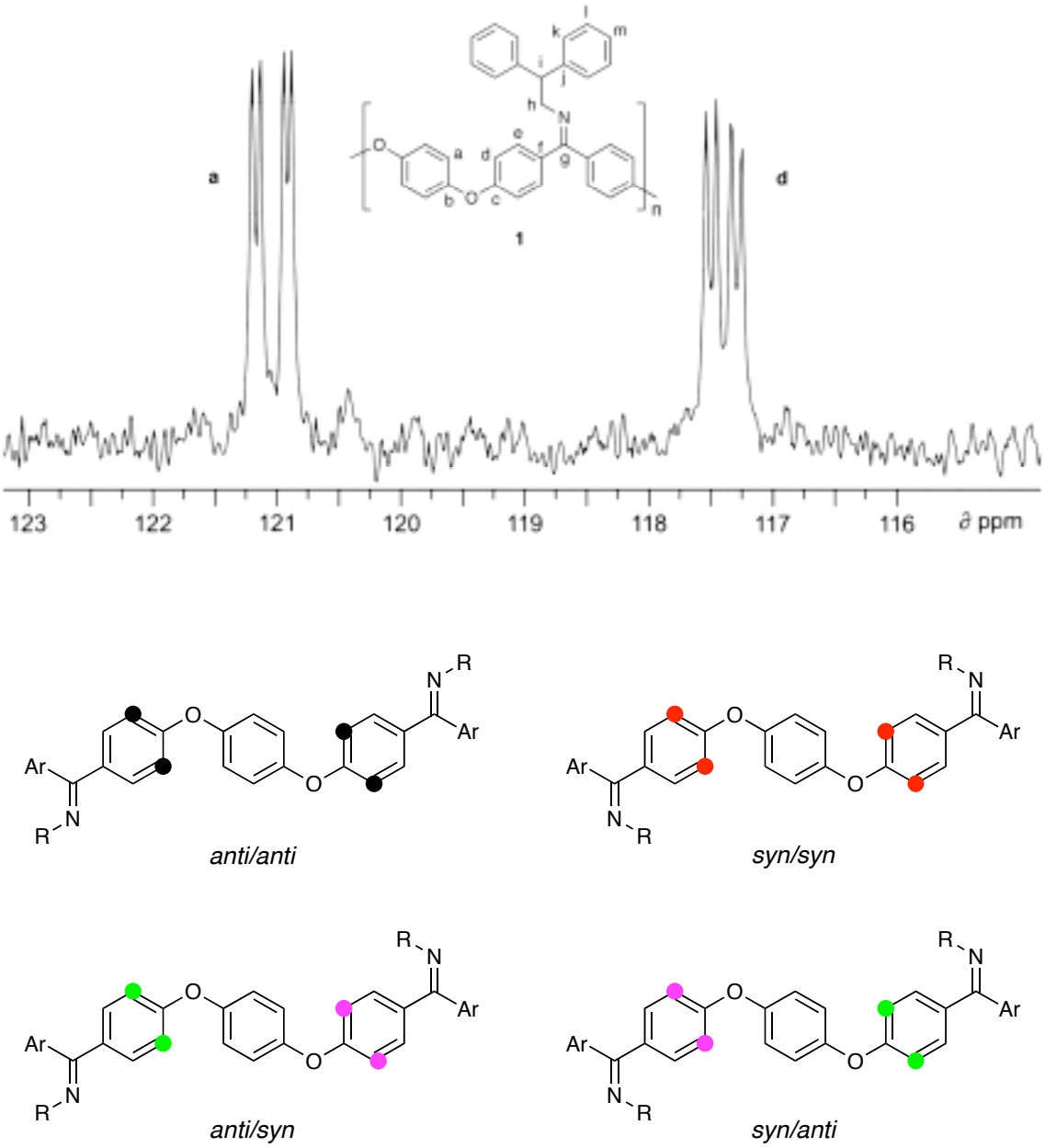


Figure S2. The different environments of carbon atom "C_d" in the monomer sequences found in polymers **1** and **2**. Colours indicate magnetically equivalent positions, and show why four ^{13}C resonances of equal intensity are observed for the carbon atoms (C_d) *ortho* to oxygen in the "benzophenone" residue of polymers **1** and **2**, as shown in the spectrum above.

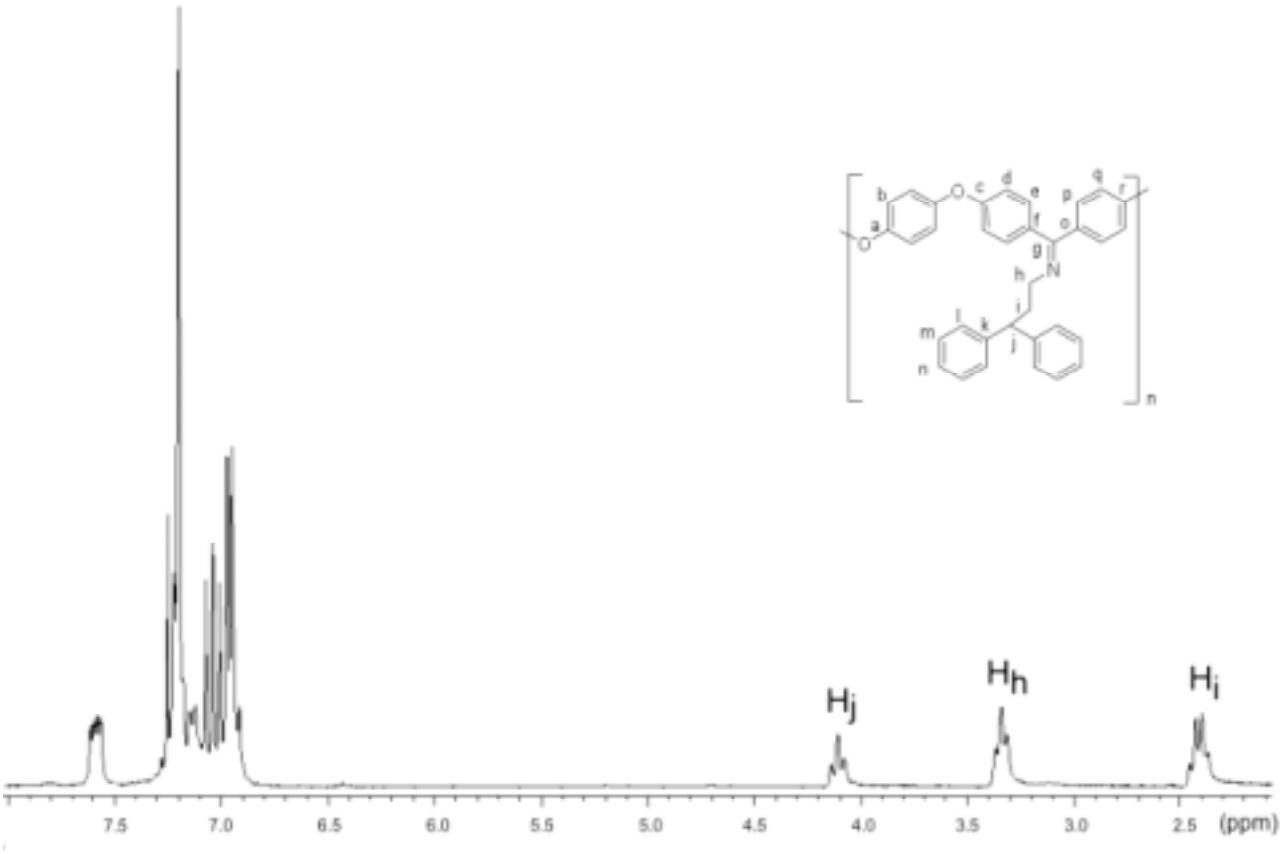


Figure S3. The ^{1}H NMR spectrum of poly(ether imine) **2** (250 MHz, $CDCl_3$). The well-resolved resonances in the aliphatic region are assigned to the different side-chain protons on the basis of multiplicities and integrated relative intensities.