

Direct iminization of PEEK

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Accepted Version

Manolakis, I., Cross, P. and Colquhoun, H. (2011) Direct iminization of PEEK. Macromolecules, 44 (19). pp. 7864-7867. ISSN 0024-9297 doi: 10.1021/ma201606q Available at https://centaur.reading.ac.uk/24209/

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Published version at: http://pubs.acs.org/doi/full/10.1021/ma201606q

To link to this article DOI: http://dx.doi.org/10.1021/ma201606q

Publisher: American Chemical Society

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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 ¹³C NMR spectra of poly(ether imine)s. ¹H NMR spectrum of polymer 2.

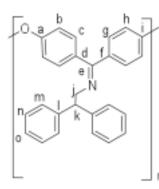
Synthesis of poly(ether imine)s: A sample of PEEK powder (0.577 g, 2.00 mmol) was placed in a reaction tube equipped with a nitrogen inlet and mechanical stirrer, together with diphenyl sulfone (9.0 g, 41 mmol) and 2,2-diphenylethylamine (1.972 g, 10 mmol) The system was stirred under a gentle, continuous 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) v_{max}/cm^{-1} : 3025 (C-H_{Ar}), 2934 (C-H), 1613 (C=N), 1491 (C-C), 1222 (C-O-C), 1164 (C-O-C); ¹H NMR (250 MHz, CDCl₃): 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_j); ¹³C-NMR (62.5 MHz, CDCl₃): _c (ppm) 167.3 (C_σ), 159.8 (C_r), 158.1 (C_σ), 152.8

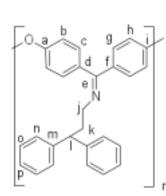
 (C_a) , 145.2 (C_k) , 135.5 (C_o) , 131.5 (C_f) , 130.5 (C_p) , 129.9 (C_e) , 128.8 (C_l) , 128.4 (C_m) , 126.3 (C_n) , 121.3 (C_b) , 118.1 (C_d, C_q) , 52.3 (C_h) , 49.1 (C_j) , 37.3 (C_i) ; η_{inh} (CHCl₃) 0.32 dL g⁻¹; T_g (onset) = 112 °C; GPC (RI, THF, 25 °C): M_n = 21 kD, M_w = 45 kD; Calcd. for $[C_{34}H_{27}NO_2]_n$: 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); ¹H NMR (250 MHz, CDCl₃): $\delta_{\rm H}$ (ppm) 7.50-7.38 (2H, m, H_g),



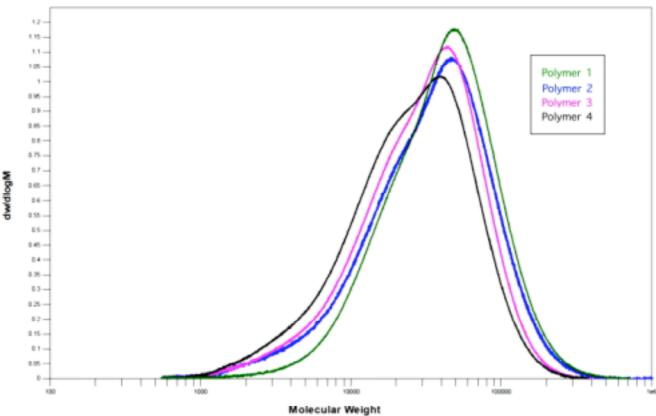
7.25-6.84 (16H, m, H_b, H_c, H_h, H_m, H_n, H_o), 4.57-4.54 (1H, br, H_k), 4.11-4.04 (2H, d, H_j, J = 7.5 Hz); 13 C-NMR (62.5 MHz, CDCl₃): $_{-c}$ (ppm) 167.2 (C_e), 158.3 (C_i), 157.0 (C_a), 143.4 (C_l), 135.8 (C_d), 131.7 (C_f), 130.2 (C_g), 129.8 (C_c), 128.5 (C_m), 128.3 (C_n), 126.3 (C_o), 118.8 (C_b, C_h), 58.9 (C_j), 52.6 (C_k); η_{inh} (CHCl₃) 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); ¹H NMR (250 MHz, CDCl₃): $\delta_{\rm H}$ (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); ¹³C-NMR (62.5 MHz, CDCl₃): $_{-c}$ (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} (CHCl₃) 0.25 dL g⁻¹; T_g (onset) = 109 °C; GPC (RI, THF, 25 °C): M_n = 17 kD, M_w = 36 kD.

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

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

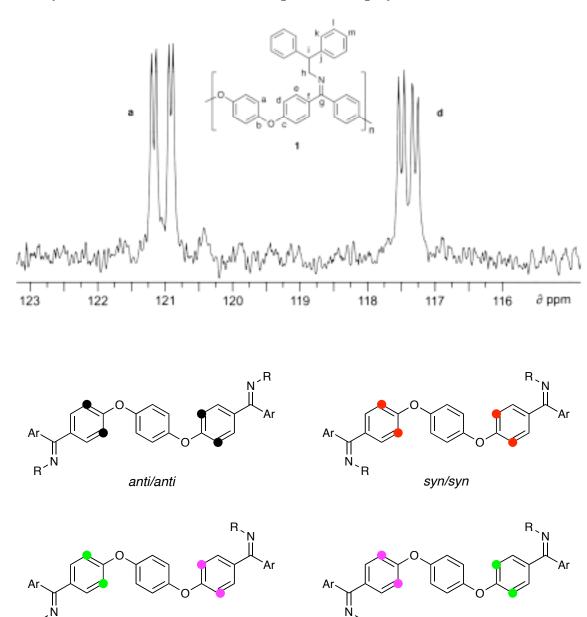


Figure S2. The different environments of carbon atom " C_d " in the monomer sequences found in polymers **1** and **2**. Colours indicate magnetically equivalent positions, and show why four ¹³C resonances of equal intensity are observed for the carbon atoms (C_d) *ortho* to oxygen in the "benzophenone"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

syn/anti

anti/syn

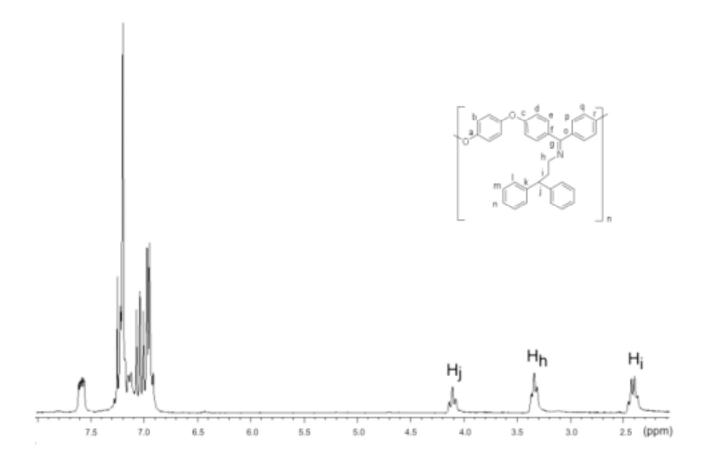


Figure S3. The ¹H NMR spectrum of poly(ether imine) **2** (250 MHz, CDCl₃). The well-resolved resonances in the aliphatic region are assigned to the different side-chain protons on the basis of multiplicities and integrated relative intensities.