University of Reading

Direct iminization of PEEK

Article

Accepted Version

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

It is advisable to refer to the publisher's version if you intend to cite from the work. See Guidance on citing.
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

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the End User Agreement.

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

Direct Iminization of PEEK

Ioannis Manolakis,[†] *Paul Cross*[§] *and Howard M. Colquhoun**[†]

Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK; Cytec Engineered Materials Ltd, Wilton Centre, Redcar, Teesside, TS10 4RF, UK

EMAIL: h.m.colquhoun@rdg.ac.uk

[†] University of Reading [§] Cytec Engineered Materials

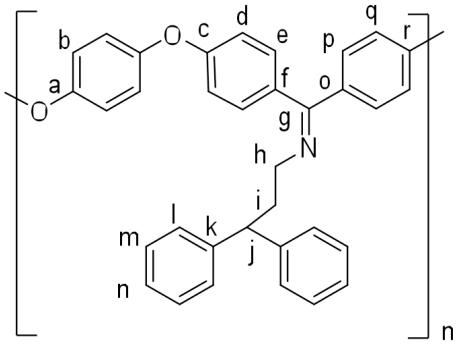
SUPPORTING INFORMATION

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**.

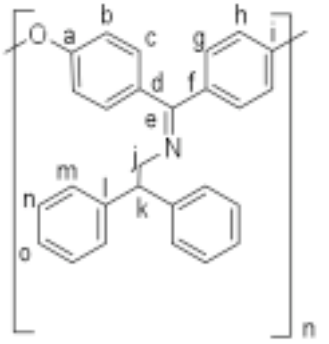
Synthesis of poly(ether imine)s: A sample of PEEK powder (0.577 g, 2.00 mmol) was placed in a reaction tube equipped with a nitrogen inlet and mechanical stirrer, together with diphenyl sulfone (9.0 g, 41 mmol) and 2,2-diphenylethylamine (1.972 g, 10 mmol) The system was stirred under a gentle, continuous 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%.

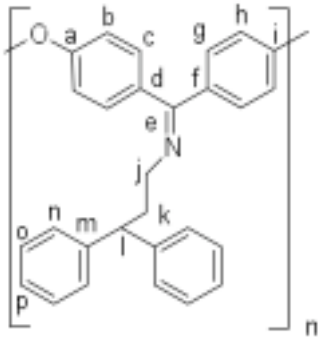


*Polymer **3***. IR (film from chloroform) ν_{max}/cm^{-1}: 3064 (C-H_{Ar}), 3018 (C-H), 1625 (C=N), 1593 (C=C_{Ar}), 1496 (C-C), 1214 (C-O-C), 1166 (C-O-C); ^{1}H NMR (250 MHz, $CDCl_3$): δ_H (ppm) 7.50-7.38 (2H, m, H_g),



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.

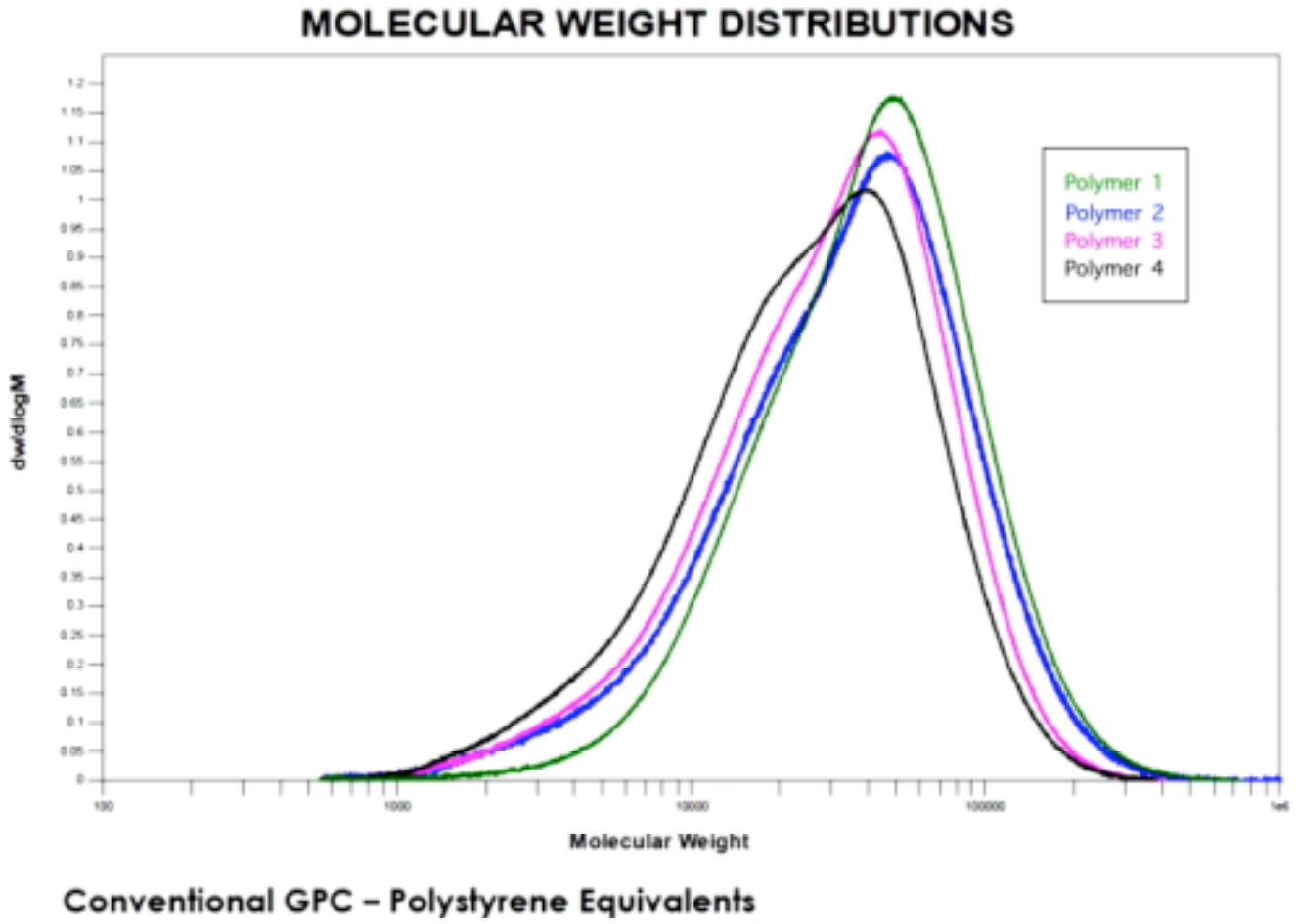


Figure S1. Gel permeation chromatograms of poly(ether imine)s **1** – **4** (THF as solvent, RI detection).

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

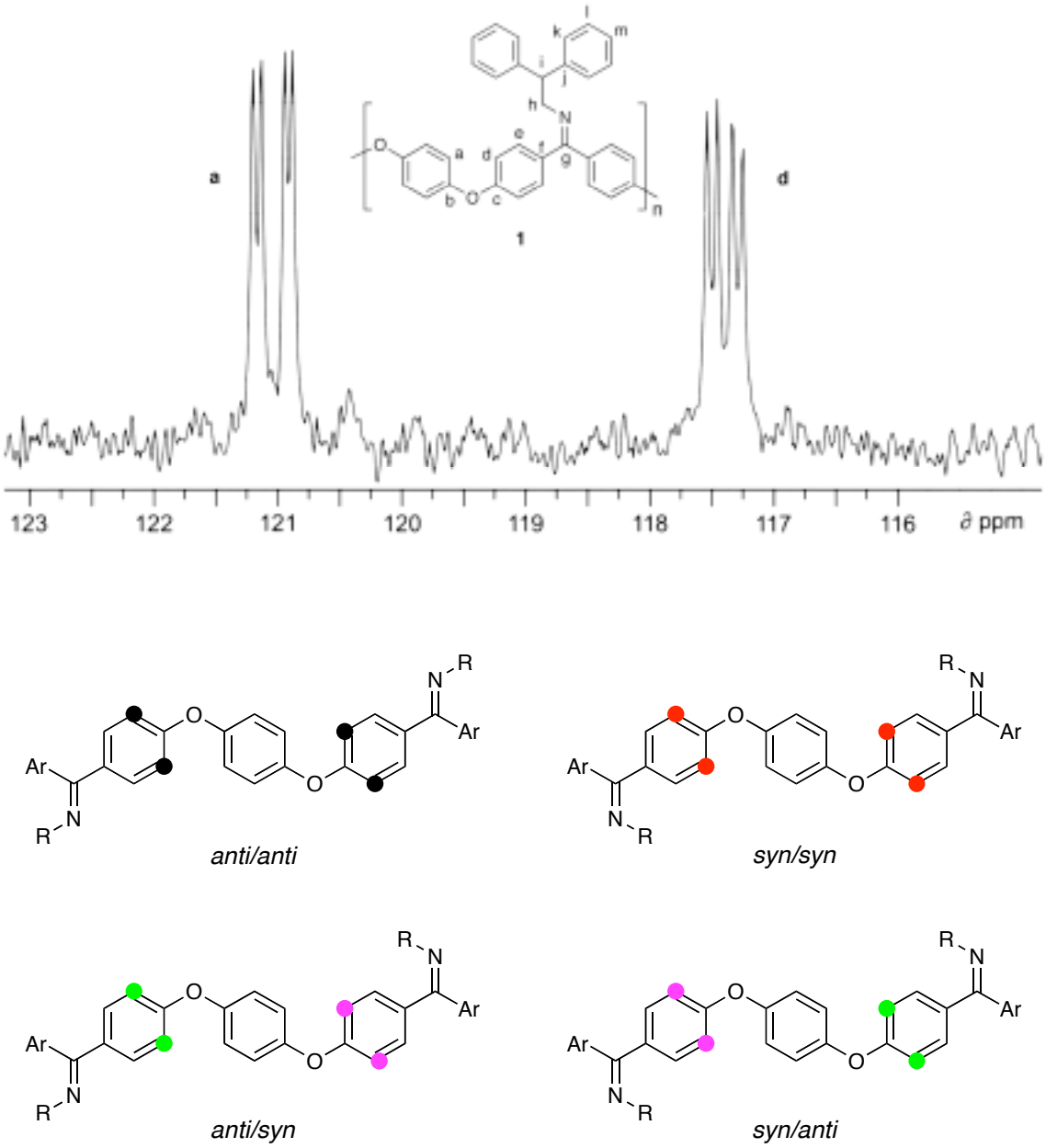


Figure S2. The different environments of carbon atom "C_d" in the monomer sequences found in polymers **1** and **2**. Colours indicate magnetically equivalent positions, and show why four ^{13}C resonances of equal intensity are observed for the carbon atoms (C_d) *ortho* to oxygen in the "benzophenone"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

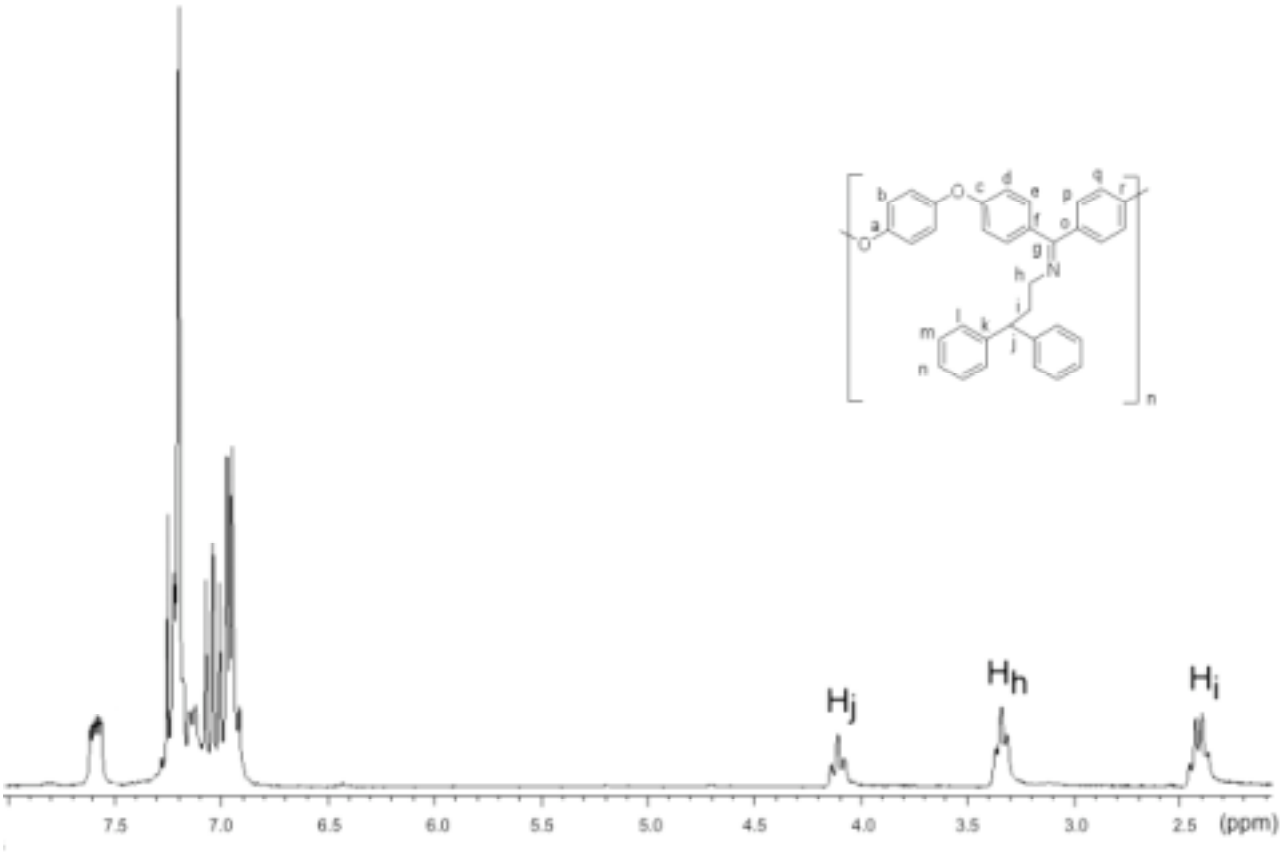


Figure S3. The ^{1}H NMR spectrum of poly(ether imine) **2** (250 MHz, $CDCl_3$). The well-resolved resonances in the aliphatic region are assigned to the different side-chain protons on the basis of multiplicities and integrated relative intensities.