Exchange reactions of poly(arylene ether ketone) dithioketals with aliphatic diols: formation and deprotection of poly(arylene ether ketal)s

Article

Supplemental Material

Manolakis, I., Cross, P. and Colquhoun, H. (2017) Exchange reactions of poly(arylene ether ketone) dithioketals with aliphatic diols: formation and deprotection of poly(arylene ether ketal)s. Macromolecules, 50 (24). pp. 9561-9568. ISSN 0024-9297 doi: 10.1021/acs.macromol.7b02203 Available at https://centaur.reading.ac.uk/73954/

To link to this article DOI: http://dx.doi.org/10.1021/acs.macromol.7b02203

Publisher: American Chemical Society

Supporting Information

Exchange reactions of poly(arylene ether ketone) dithioketals with aliphatic diols: formation and deprotection of poly(arylene ether ketal)s

Ioannis Manolakis, Paul Cross and Howard M. Colquhoun*

CONTENTS

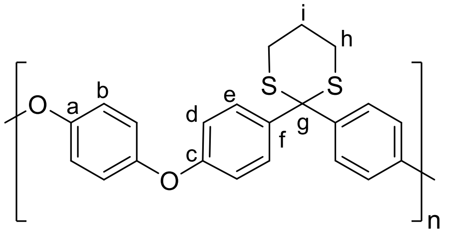
INFORMATION **PAGE NO.**

1. Materials and Instrumentation

Starting materials and solvents were used as received unless otherwise stated otherwise. Ethane-1,2-diol, propane-1,2-diol, propane-1,3-diol, 2,2-diethylpropane1,3-diol, ethane1,2-dithiol, propane-1,3-dithiol, boron trifluoride diethyl etherate, and *N*-bromosuccinimide were obtained from Fisher UK. Samples of composite-grade polymers (PEEK and PEKK) were provided by Cytec Aerospace Materials. Other polyketones (PEK and PEKEKK) were provided as research samples by ICI plc. Ethane-1,2-diol and propane-1,3-diol were purified by vacuum distillation. Proton NMR (250 MHz), ^{13}C NMR (62.5 MHz) and 2D (C-H) correlation spectra were recorded on a Bruker DPX 250 MHz spectrometer using $CDCl_3$ or $CDCl_3$/TFA as solvent, with TMS as internal standard. Melting points and glass transition temperatures were determined under a nitrogen atmosphere by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC20 instrument at a heating rate of 10 °C min^{-1}. Polymer infrared spectra were recorded on a Perkin Elmer FT1700 IR spectrophotometer with polymer samples as thin films from chloroform solution or as KBr pellets. Composite IR spectra were recorded using a Perkin Elmer Spotlight 400 IR-imaging system. Gel permeation chromatography (GPC) of poly(ether dithioketal)s and poly(ether ketal)s was conducted on a Polymer Labs GPC 220 system, with chloroform as eluent and both refractive index (RI) and light scattering (LS) detection. The refractive index detector was calibrated using polystyrene standards. GPC analyses for PEEK samples were provided by RAPRA Ltd (Shawbury, UK) using phenol/trichlorobenzene as eluent. Scanning electron microscopy (SEM) was carried out on gold-coated specimens using a Cambridge 360 Stereoscan instrument. X-ray diffractograms were recorded on an Oxford Diffraction Gemini Ultra-S CCD diffractometer using Cu-Kα radiation.

2. Synthesis of poly(ether dithioketal)s

*Synthesis of PEEK-1,3-dithiane (**2**):* A sample of PEEK (0.577 g, 2.0 mmol) was dissolved in a mixture of dichloromethane (30 mL) and trifluoroacetic acid (3 mL) with vigorous stirring under nitrogen. A cloudy yellow solution was formed. The system was purged with nitrogen for approximately 30 min and 1,3-propanedithiol (0.649 g, 6.0 mmol) was then added, followed by boron trifluoride diethyl etherate (0.284 g, 2.0 mmol). A color change to dark red was observed and the solution slowly became completely clear. After 24 h the reaction mixture was poured into methanol (60 mL), giving a white precipitate which was filtered off, extracted with methanol, filtered off again and then dried at room temperature overnight. The product was recovered as a white powder (0.732 g, 97% yield for PEEK-1,3-dithiane **2**).



2

IR (film): ν_{max}/cm^{-1}: 2952 (-C-H), 2907 (-C-H), 1601 (-C=C-), 1491 (-C=C-), 1225 (-C-O-C-), 1192 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.65-7.54 (4H, AA'XX', H_e), 7.02 (4H, s, H_b), 6.97-6.86 (4H, AA'XX', H_d), 2.80-2.76 (4H, br, H_h), 2.00 (2H, br, H_i); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 157.6 (C_a), 152.8 (C_c), 137.3 (C_f), 131.3 (C_e), 121.4 (C_b), 117.9 (C_d), 62.3 (C_g), 29.9 (C_h), 24.8 (C_i); η_{inh} ($CHCl_3$) = 0.48 dL g^{-1}; T_g (onset) = 179° C; GPC (RI, $CHCl_3$): M_n = 24.0, M_w = 65.5 kDa; GPC (LS, $CHCl_3$): M_n = 18.1, M_w = 57.0 kDa; Elemental analysis for $C_{22}H_{18}O_2S_2$: Calculated: C 69.81, H 4.79, S 16.94; Found: C 69.21, H 4.77, S 16.43%.

Other poly(ether dithioketal)s: Poly(ether dithioketal)s **3**, **4** and **5** were synthesized as described in references [S1], [S2] and [S3].

3. Time dependence of the poly(dithioketal/ketal) exchange reaction affording PEEK-1,3-dioxolane (6)

Table S1. Effect of reaction time on the formation of poly(ether ketal) **6**

Entry[a]	Reaction time [min]	% Yield	Mol% ketal ^{1}H NMR	T_g (onset) [^oC]	η_{inh} in $CHCl_3$ [dL g^{-1}]
1	5	98	95	139	0.39
2	5	96	90	138	0.41
3	15	98	84	139	0.41
4	30	91	81	138	0.39
5	45	99	77	139	0.42
6	60	92	67	139	0.44
7	60	96	55	143	[b]

a) Poly(ether dithioketal) **2** as starting material in each case; b) Insoluble in $CHCl_3$

4. Characterisation data for PEEK-1,3-dioxolane (6) obtained from NBS-promoted reaction of PEEK-dithiane (2) with ethane-1,2-diol

The ^{13}C-NMR resonances for polymers **2** and **6** are listed in Table S2, and the corresponding spectra are shown below. Carbon resonances arising from residual ketonic units present in these polymers were too weak to be resolved. It is interesting to note that even at 45% ketone content, no melting transition was evident in the DSC thermogram of polymer **6**. However, the "45% ketone" polymer was insoluble in $CHCl_3$, suggesting the presence of trace levels of crystallinity, not detectable by DSC. Moreover, a shift in T_g towards the corresponding PEEK value (~145 ^oC) was observed once the ketone percentage increased beyond 40%.

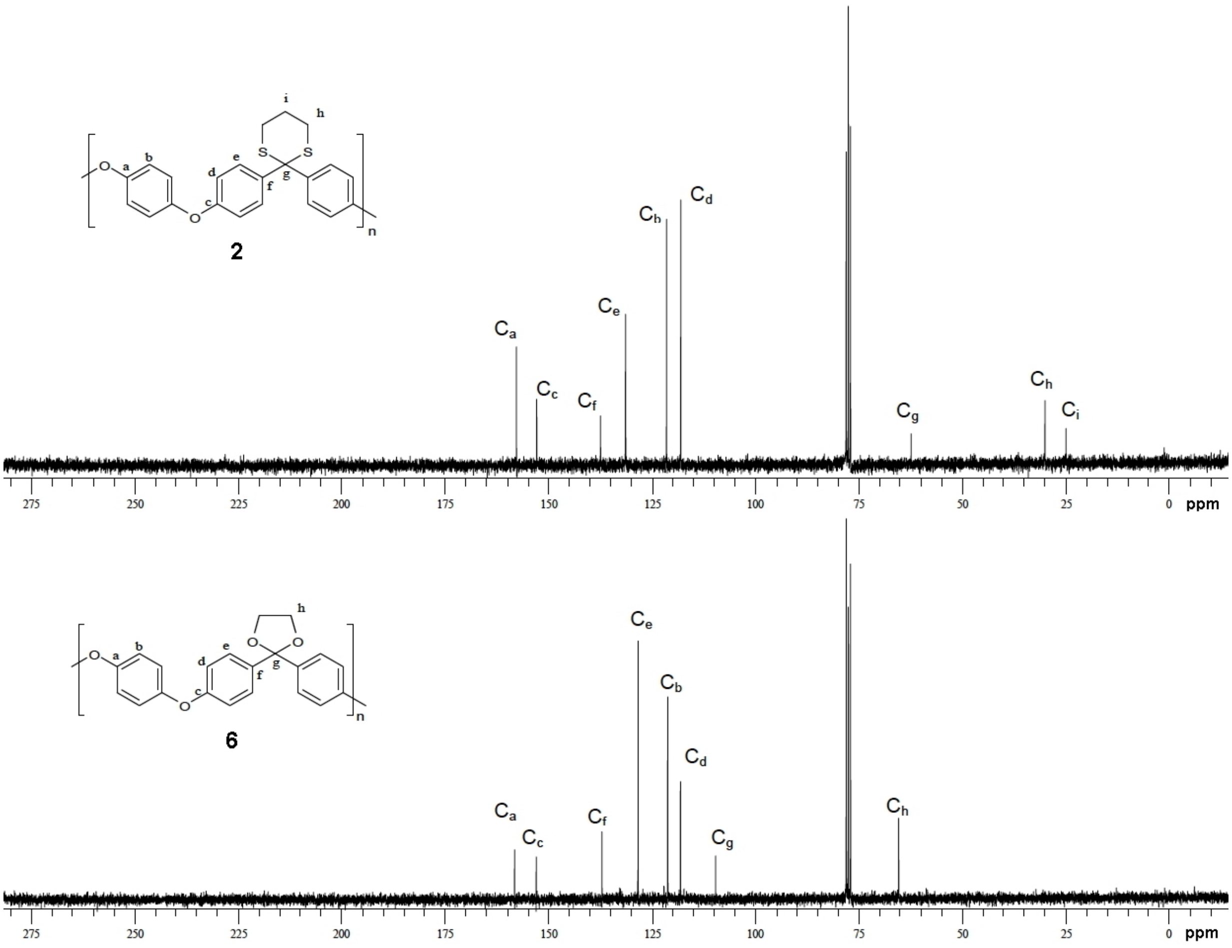


Figure S1. ^{13}C-NMR spectra of PEEK-1,3-dithiane (**2**) and PEEK-1,3-dioxolane (**6**)

Table S2. ^{13}C-NMR resonances (ppm) of PEEK-1,3-dithiane **2** and PEEK-1,3-dioxolane **6**[a]

Polymer	**C_a**	**C_b**	**C_c**	**C_d**	**C_e**	**C_f**	**C_g**	**C_h**	**C_i**
PEEK-1,3-dithiane (**2**)	157.6	121.4	152.8	117.9	131.3	137.3	62.3	29.9	24.8
PEEK-1,3-dioxolane (**6**)	158.1	121.1	152.9	118.0	128.2	137.0	109.5	65.3	

a) Assignments based on previously reported spectra of poly(ether dithioketal)s [S1,S2,S3]

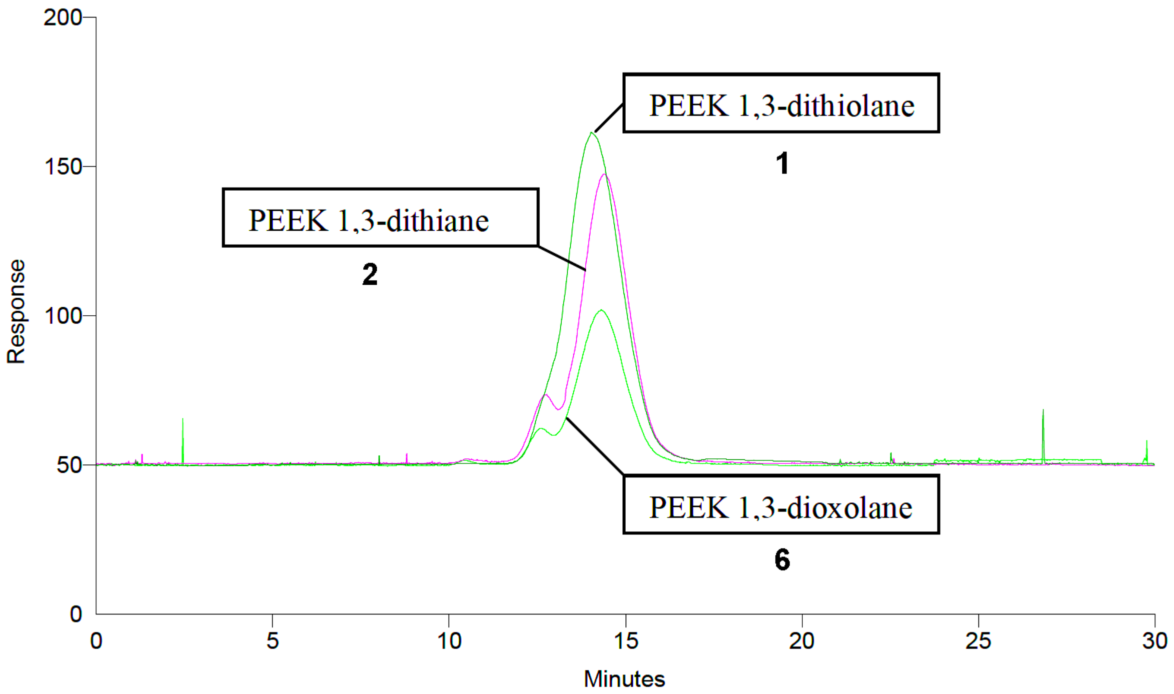


Figure S2. GPC-LS chromatograms ($CHCl_3$ eluent, LS detection) for PEEK-1,3-dithiolane (**1**), PEEK-1,3-dithiane (**2**) and PEEK-1,3-dioxolane (**6**) derived from **2**. Note the high-MW component revealed by light-scattering for all three polymers. Refer to Table 1 and Charts 2 and 3 in the main paper.

5. Carbon fiber composite data

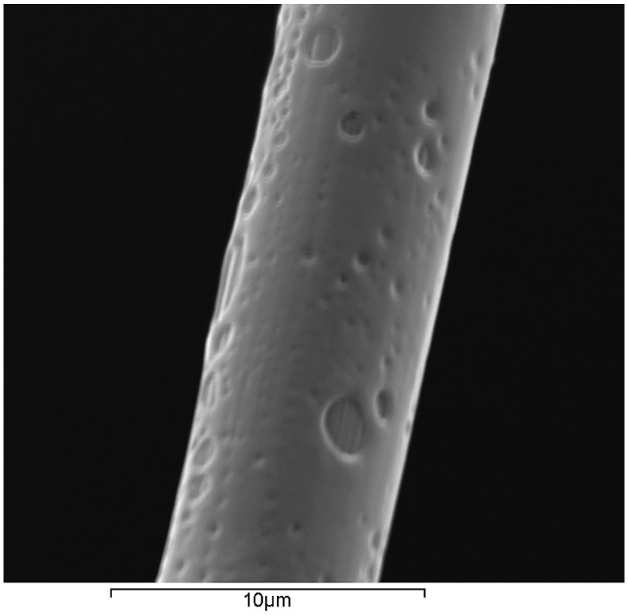


Figure S3. Scanning electron micrograph of a single coated carbon fiber from a fiber-bundle impregnated with poly(ether ether ketal) **6** (5% w/v chloroform solution).

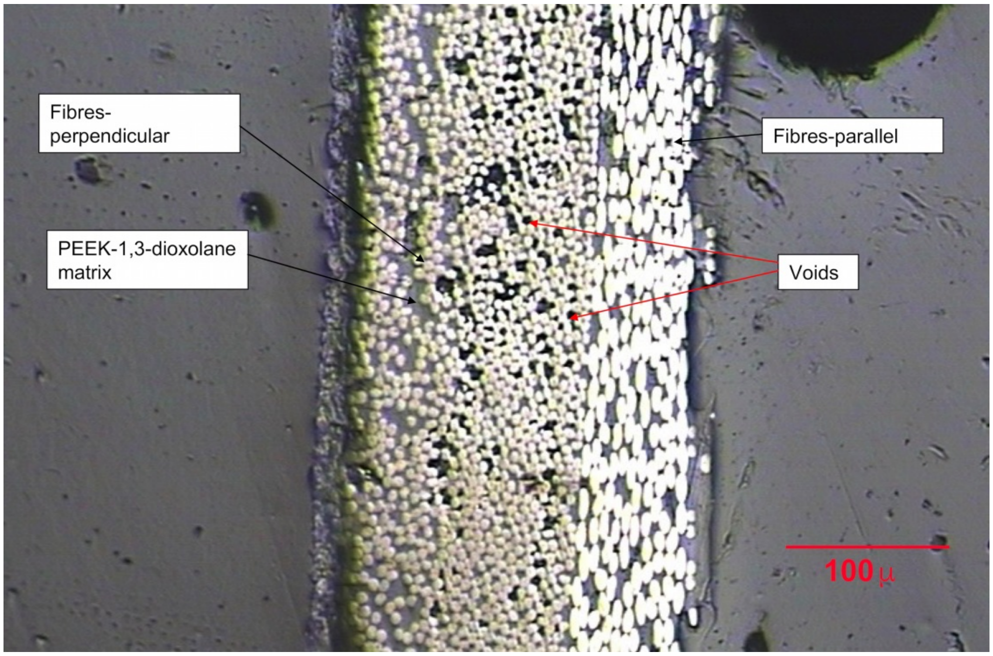


Figure S4. Optical micrograph of a hot-pressed (370 °C) sample in cross-section of a composite formed by impregnation of poly(ether ether ketal) **6** into a woven carbon fiber fabric

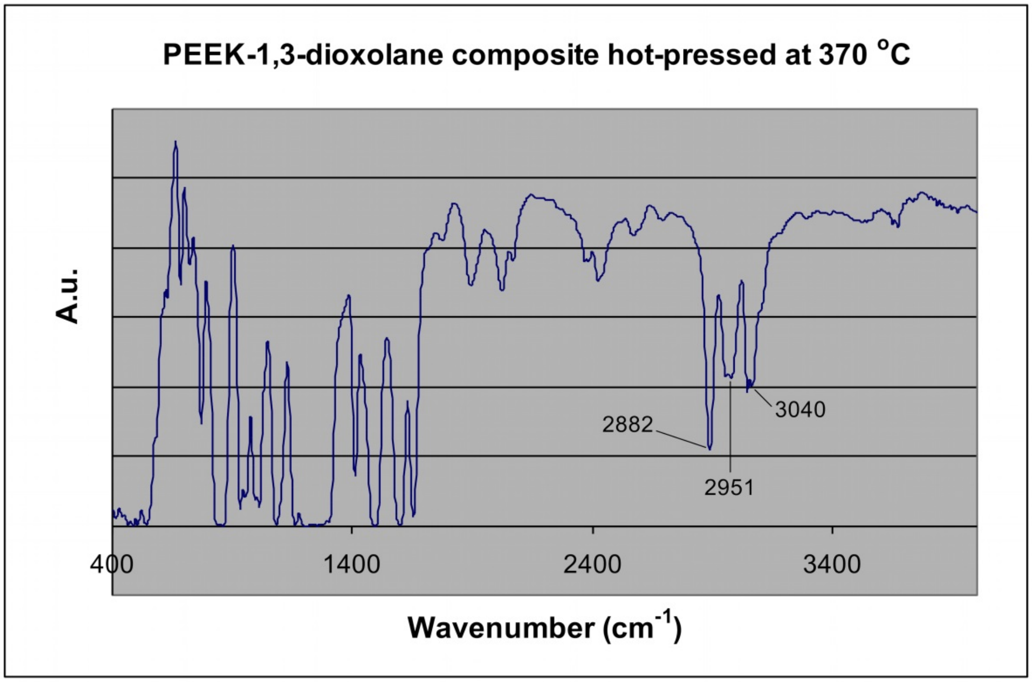


Figure S5. FT-IR reflectance spectrum, taken using an IR microcope, of a hot-pressed (370 °C, 30 bar) specimen of the composite from impregnation of poly(ether ether ketal) **6** into a woven carbon-fiber fabric. Absorptions assignable to both aromatic νC-H (3040 cm^{-1}) and aliphatic νC-H (2951 and 2882 cm^{-1}) are clearly evident.

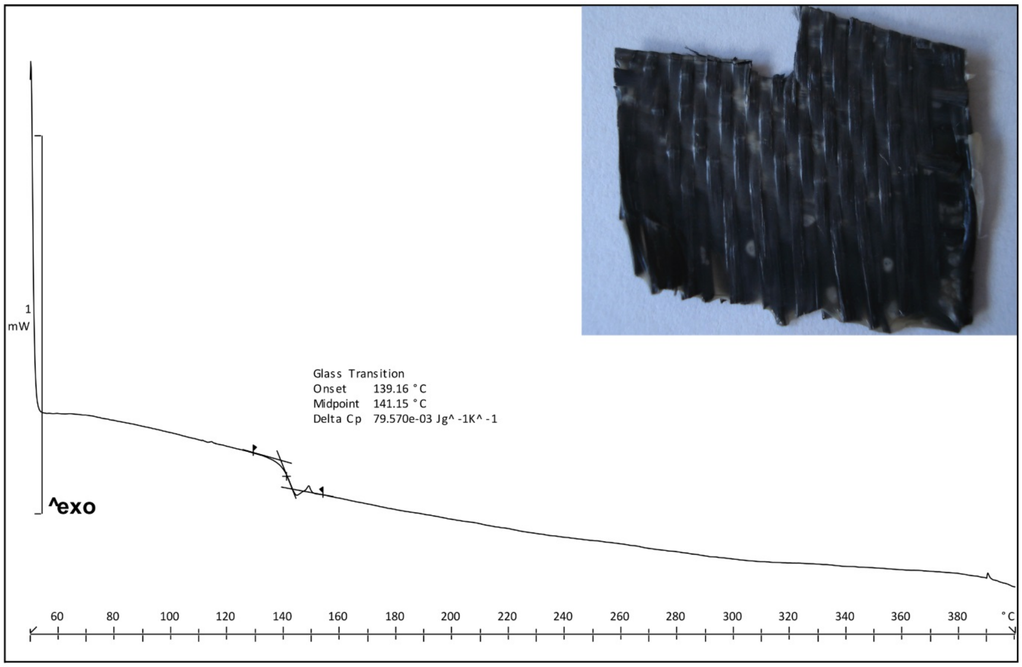
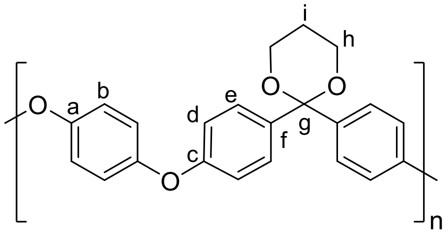


Figure S6. DSC thermogram of a specimen (inset) of the composite formed by solution impregnation of poly(ether ether ketal) **6** into a woven carbon-fiber fabric.

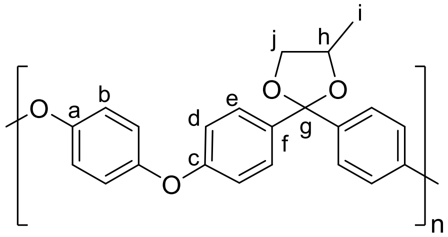
6. Characterisation data for poly(ether ketal)s

Poly(ether ether 1,3-dioxane) **(7)**



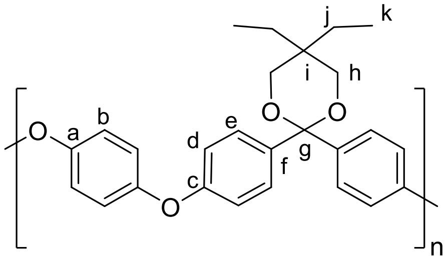
IR ($CHCl_3$ film) ν_{max}/cm^{-1}: 2966 (-C-H-), 2926 (-C-H-), 1603 (-C-C-), 1493 (-C-C-), 1225 (-C-O-C-), 1194 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.50-7.42 (4H, m, H_e), 6.99-6.91 (8H, m, H_b, H_d), 4.04-4.01 (4H, br, H_h), 1.80 (2H, br, H_i); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 157.8 (C_a), 152.9 (C_c), 137.4 (C_f), 128.5 (C_e), 121.1 (C_b), 118.3 (C_d), 101.2 (C_g), 62.0 (C_h), 26.0 (C_i); T_g (onset) = 155 °C.

Poly(ether ether 5-methyl-1,3-dioxolane) **(8)**



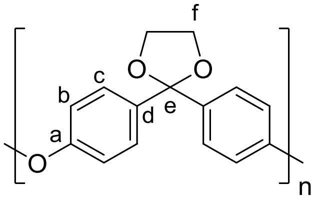
IR ($CHCl_3$ film) ν_{max}/cm^{-1}: 2966 (-C-H-), 2922 (-C-H-), 1603 (-C-C-), 1493 (-C-C-), 1224 (-C-O-C-), 1197 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.49-7.40 (4H, m, H_e), 6.99-6.89 (8H, m, H_b, H_d), 4.32-4.25 (1H, m, H_h), 4.15-4.09 (1H, m, H_j), 3.63-3.57 (1H, m, H_j), 1.36-1.34 (3H, d, J = 6 Hz, H_i); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 158.0 (C_a), 152.9 (C_c), 137.8 (C_f), 128.3 (C_e), 121.1 (C_b), 118.0 (C_d), 109.6 (C_g), 73.3 (C_h), 71.7 (C_j), 19.1 (C_i); η_{inh} ($CHCl_3$) = 0.39 dL·g^{-1}; T_g (onset) = 139 °C; GPC (RI, $CHCl_3$): M_n = 26.9, M_w = 62.4 kDa.

Poly(ether ether 5,5-diethyl-1,3-dioxane) **(9)**



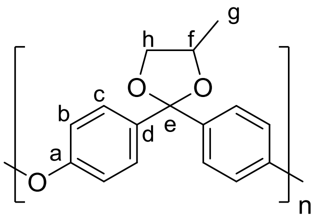
IR ($CHCl_3$ film) ν_{max}/cm^{-1}: 2974 (-C-H-), 2922 (-C-H-), 1602 (-C-C-), 1493 (-C-C-), 1226 (-C-O-C-), 1193 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.47-7.40 (4H, m, H_e), 6.99-6.83 (8H, m, H_b, H_d), 3.65 (4H, s, H_h), 1.47-1.42 (4H, m, H_j), 0.83-0.77 (6H, m, H_k); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 157.8 (C_a), 152.8 (C_c), 132.7 (C_f), 128.8 (C_e), 121.2 (C_b), 118.1 (C_d), 101.4 (C_g), 69.7 (C_h), 35.3 (C_i), 23.9 (C_j), 7.44 (C_k); η_{inh} ($CHCl_3$) = 0.45 dL·g^{-1}; T_g (onset) = 145 ^{o}C; GPC (RI, $CHCl_3$): M_n = 28.0, M_w = 62.0 kDa.

Poly(ether 1,3-dioxolane) **(10)**



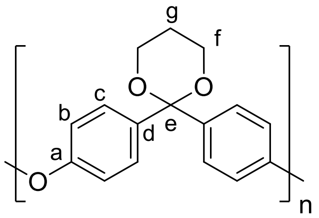
IR ($CHCl_3$ film) ν_{max}/cm^{-1}: 3017 (-C-H-), 2896 (-C-H-), 1595 (-C-C-), 1498 (-C-C-), 1215 (-C-O-C-), 1163 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.53-7.41 (4H, m, H_c), 6.97-6.92 (4H, m, H_b), 4.05 (4H, s, H_f); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 157.3 (C_a), 137.4 (C_d), 128.2 (C_c), 118.8 (C_b), 109.5 (C_e), 65.3 (C_f); η_{inh} ($CHCl_3$) = 0.48 dL·g^{-1}; T_g (onset) = 154 ^{o}C; GPC (RI, $CHCl_3$): M_n = 35.1, M_w = 76.2 kDa.

Poly(ether 5-methyl-1,3-dioxolane) (11)



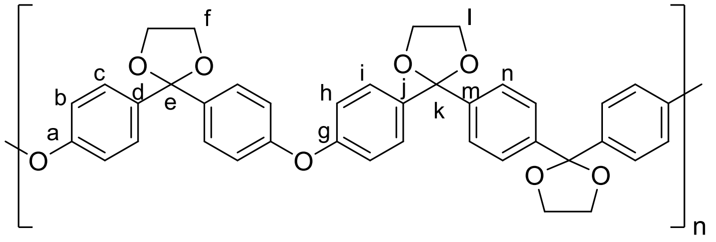
IR ($CHCl_3$ film) v_{max}/cm^{-1}: 2974 (-C-H-), 2915 (-C-H-), 1596 (-C-C-), 1499 (-C-C-), 1241 (-C-O-C-), 1165 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.51-7.40 (4H, m, H_c), 6.97-6.90 (4H, m, H_b), 4.34-4.25 (1H, m, H_f), 4.16-4.09 (1H, m, H_h), 3.67-3.57 (1H, m, H_h), 1.40-1.34 (3H, m, H_g); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 157.2 (C_a), 132.6 (C_d), 128.2 (C_c), 118.8 (C_b), 109.6 (C_e), 73.3 (C_f), 71.7 (C_h), 19.1 (C_g); η_{inh} ($CHCl_3$) = 0.49 dL·g^{-1}; T_g (onset) = 156 ^{o}C; GPC (RI, $CHCl_3$): M_n = 35.1, M_w = 79.5 kDa.

Poly(ether 1,3-dioxane) (12)



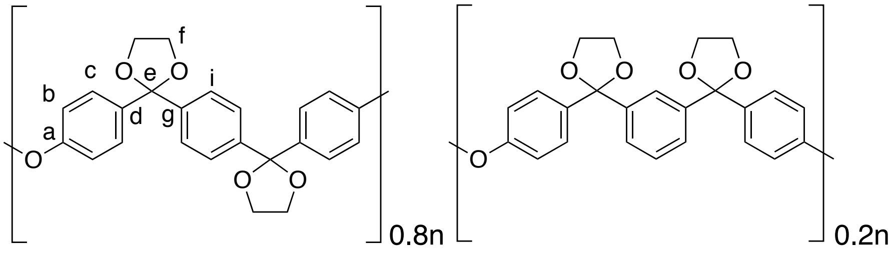
IR ($CHCl_3$ film) v_{max}/cm^{-1}: 2966 (-C-H-), 2929 (-C-H-), 1595 (-C-C-), 1497 (-C-C-), 1243 (-C-O-C-), 1199 (-C-O-C-); ^{1}H-NMR (250 MHz, $CDCl_3$): δ_H (ppm) = 7.50-7.42 (4H, m, H_c), 6.99-6.93 (4H, m, H_b), 4.06-4.00 (4H, m, H_f), 1.85-1.80 (4H, br, H_g); ^{13}C-NMR (62.5 MHz, $CDCl_3$): δ_c (ppm) = 157.0 (C_a), 132.6 (C_d), 128.5 (C_c), 119.1 (C_b), 101.1 (C_e), 62.1 (C_f), 26.0 (C_g); η_{inh} ($CHCl_3$) = 0.50 dL·g^{-1}; T_g (onset) = 176 ^{o}C; GPC (RI, $CHCl_3$): M_n = 36.0, M_w = 80.9 kDa.

Poly(ether 1,3-dioxolane ether 1,3-dioxolane 1,3-dioxolane) **(13)**



IR (CHCl$_3$ film) v_{max}/cm^{-1}: 2981 (-C-H-), 2900 (-C-H-), 1595 (-C-C-), 1500 (-C-C-), 1243 (-C-O-C-), 1166 (-C-O-C-); ^{1}H-NMR (250 MHz, CDCl$_3$): δ_H (ppm) = 7.55-7.41 (12H, m, H$_c$, H$_i$, H$_n$), 7.03-6.84 (8H, m, H$_b$, H$_h$), 4.11-4.04 (12H, m, H$_f$, H$_l$); ^{13}C-NMR (62.5 MHz, CDCl$_3$): δ_c (ppm) = 157.3 (C$_a$, C$_g$), 142.3 (C$_m$), 137.3 (C$_d$, C$_j$), 128.5 (C$_c$, C$_i$), 126.4 (C$_n$), 118.8 (C$_b$, C$_h$), 109.5 (C$_k$, C$_e$), 65.3 (C$_f$, C$_l$); η_{inh} (CHCl$_3$) = 0.52 dL·g^{-1}; T$_g$ (onset) = 170 ^{o}C; GPC (RI, CHCl$_3$): M$_n$ = 32.8, M$_w$ = 74.0 kDa.

Poly(ether 1,3-dioxolane 1,3-dioxolane) (80/20 meta/para) **(14)**



IR (CHCl$_3$ film) v_{max}/cm^{-1}: 2988 (-C-H-), 2899 (-C-H-), 1597 (-C-C-), 1500 (-C-C-), 1243 (-C-O-C-), 1167 (-C-O-C-); ^{1}H-NMR* (250 MHz, CDCl$_3$): δ_H (ppm) = 7.51-7.36 (8H, m, H$_c$), 7.03-6.84 (6H, m, H$_b$), 4.08-4.01 (8H, m, H$_f$); ^{13}C-NMR* (62.5 MHz, CDCl$_3$): δ_c (ppm) = 157.3 (C$_a$), 142.4 (C$_g$), 137.4 (C$_d$), 128.2 (C$_c$), 126.4 (C$_h$), 118.9 (C$_b$), 109.5 (C$_e$), 65.3 (C$_f$); η_{inh} (CHCl$_3$) = 0.48 dL·g^{-1}; T$_g$ (onset) = 147 ^{o}C; GPC (RI, CHCl$_3$): M$_n$ = 25.5, M$_w$ = 74.1.

*Resonances are assigned only for the *para*-substituted component of this copolymer.

Table S2. Elemental analyses of PEEK-1,3-dithiane **2** and PEEK-1,3-dioxolane **6**

Polymer		**%C (calcd.)**	**%H (calcd.)**	**%S (calcd.)**	**%C (found)**	**%H (found)**	**%S (found)**
2	PEEK-1,3-dithiane $[C_{22}H_{18}O_2S_2]_n$	69.81	4.79	16.94	69.21	4.77	16.43
6	PEEK-1,3-dioxolane $[C_{21}H_{16}O_4]_n$	75.89	4.85	–	75.85	4.78	< 0.10

Table S3. Characterization data for ketals (other than the dioxolane) of PEEK

Polymer	**%Yield**	**% Ketal ^{1}H NMR**	**T_g onset [°C]^a**	**M_n (RI) [kDa]^b**	**M_w/M_n RI^b**	**η_{inh} [dL g^{-1}]^c**
7	94	76	155	–	–	–
8	95	79	139	26.9	2.32	0.41
9	87	65	145	28.0	2.21	0.45

[a] By DSC; [b] By GPC in chloroform at 35 °C; [c] In chloroform at 25 °C

Table S4. Poly(ether ketal)s derived from PEK-1,3-dithiane **3**

Polymer		**%Yield**	**%Ketal ^{1}H NMR**	**η_{inh} [dL g^{-1}]^b**	**M_n RI [kDa]^c**	**M_w/M_n RI^c**	**T_g onset^d [°C]**
3	PEK-1,3-dithiane^a	–	–	0.32	37.0	2.21	203
10	PEK-1,3-dioxolane	94	85	0.48	35.1	2.17	154
11	PEK-1,3-(5-methyl) dioxolane	93	78	0.49	36.0	2.25	156
12	PEK-1,3-dioxane	91	80	0.50	35.1	2.26	176

[a] Starting material; [b] In chloroform at 25 °C; [c] By GPC in chloroform at 35 °C; [d] By DSC

Table S5. Poly(ether ketal)s derived from poly(ether dithioketal)s of PEKEKK (all-*para*) and PEKK (80/20 *para*/*meta* – see Chart 1)

Polymer		**% Yield**	**η_{inh} [dL g^{-1}]^{b}**	**M_n RI [kDa]^{c}**	**M_w/M_n RI^{c}**	**T_g [°C] onset^{d}**
4	PEKEKK-1,3-dithiane	SM^{a}	0.35	21.5	3.11	221
13	PEKEKK-1,3-dioxolane	76	0.52	32.8	2.26	170
5	PEKK-1,3-dithiane	SM^{a}	0.27	12.0	4.23	202
14	PEKK-1,3-dioxolane	93	0.48	25.5	2.91	147

$^{a)}$ Starting material; $^{b)}$ In chloroform at 25 °C; $^{c)}$ GPC in $CHCl_3$ at 35 °C; $^{d)}$ DSC

Table S6. Characterisation data for PEEK, first as its 1,3-dithiane derivative and then after ketalisation of the latter by exchange with ethane-1,2-diol, deprotection with trifluoroacetic acid, and finally re-protection with propane-1,3-dithiol.

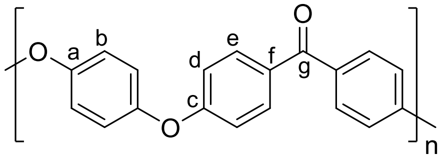
Entry	**Polymer**	**% Dithioketal by ^{1}H NMR**	**T_g onset [°C]^{a}**	**M_n RI [kDa]^{a}**	**M_w/M_n RI^{b}**	**η_{inh} [dL g^{-1}]^{c}**
1	PEEK-1,3-dithiane (starting material)	98	178	28.4	2.15	0.32
2	PEEK-1,3-dithiane (final product)	99	174	28.1	2.15	0.33

$^{a)}$ By DSC; $^{b)}$ By GPC in chloroform at 35 °C; $^{c)}$ In chloroform at 25 °C

7. Deprotection of poly(ether ether ketal) 6

Hydrolysis with trifluoroacetic acid

A sample of PEEK-1,3-dioxolane **6** (0.106 g, 0.319 mmol) was dissolved in dichloromethane (20 mL) under vigorous stirring. Trifluoroacetic acid (1 mL) was then added. A color change from light pink to orange was immediately observed. The reaction was continued for 30 minutes. The reaction mixture was poured into cold methanol (50 mL), giving a white precipitate. The latter was filtered off, extracted with water, filtered off, extracted with methanol, filtered off and then dried under vacuum at 90 °C for 4 hours, to give 0.091 g (99% yield) of the deprotected polymer.



IR (KBr disc) v_{max}/cm^{-1}: 1653 (-C=O), 1598 (-C-C-), 1490 (-C-C-), 1222 (-C-O-C-), 1186 (-C-CO-C-); ^{1}H-NMR (250 MHz, $CDCl_3$/TFA): δ_H (ppm) = 7.91-7.84 (4H, AA'XX', H_e), 7.23 (4H, s, H_b), 7.14-7.09 (4H, AA'XX', H_d); ^{13}C-NMR (62.5 MHz, $CDCl_3$/TFA): δ_c (ppm) = 200.8 (C_g), 163.5 (C_c), 152.2 (C_a), 134.0 (C_e), 130.8 (C_f), 122.6 (C_b), 117.4 (C_d); η_{inh} (H_2SO_4) = 0.67 dL·g^{-1}; T_g (onset) = 147 °C, T_m = 333 °C.

Hydrolysis with concentrated hydrochloric acid

A sample of PEEK-1,3-dioxolane **6** (0.190 g, 0.572 mmol) was dispersed in concentrated (37%) hydrochloric acid (25 mL) and vigorously stirred under reflux for 6 hours. The off-white powder was filtered off, extracted with water, filtered off, extracted with acetone, filtered off again and then dried at room temperature for 2 days, giving 0.127 g (77% yield) of the deprotected polymer.

IR (KBr disc) ν_{max}/cm^{-1}: 1653 (-C=O), 1600 (-C-C-), 1489 (-C-C-), 1222 (-C-O-C-), 1185 (-C-CO-C-); ^{1}H-NMR (250 MHz, $CDCl_3$/TFA): δ_H (ppm) = 7.95-7.91 (4H, AA'XX', H_e), 7.28 (4H, s, H_b), 7.21-7.18 (4H, AA'XX', H_d); ^{13}C-NMR (62.5 MHz, $CDCl_3$/TFA): δ_c (ppm) = 201.1 (C_g), 162.3 (C_c), 152.3 (C_a), 134.1 (C_e), 130.7 (C_f), 122.6 (C_b), 117.3 (C_d); η_{inh} (H_2SO_4) = 0.61 dL·g^{-1}; T_g (onset) = 146 °C, T_m = 341 °C; GPC (RI, phenol/1,2,4-trichlorobenzene): M_n = 28.7, M_w = 77.2 kDa.

8. References to Supporting Information

S1. Colquhoun, H. M.; Drew, M. G. B.; Hodge, P.; Paoloni, F. P. V.; McGrail, P. T. *Chem. Commun.* **2007**, *32*, 3365.

S2. Colquhoun, H. M.; Hodge, P.; Paoloni, F. P. V.; McGrail, P. T.; Cross, P. *Macromolecules* **2009**, *42*, 1955.

S3. Paoloni, F. P. V., Ph.D. Thesis, University of Reading, 2007.