

## A thermotropic poly(ether ketone) based on the *p*-quaterphenyl unit: evidence for a smectic C phase

Fatai O. Oladoyinbo,<sup>a</sup> David F. Lewis,<sup>a</sup> David J. Blundell,<sup>b</sup> and Howard M. Colquhoun\*<sup>a</sup>

<sup>a</sup> *Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK.*

<sup>b</sup> *Department of Physics, Keele University, Keele, Staffordshire, ST5 5BG, UK*

### ELECTRONIC SUPPORTING INFORMATION

<b><u>Information</u></b>	<b><u>Page</u></b>
Synthesis and characterisation of intermediate <b>9</b> and polymers <b>14</b> , <b>15</b> , <b>16</b> , <b>19</b> and <b>20</b>	S2
<b>Figure S1.</b> Effects of cooling rate on the thermal transitions exhibited by polymer <b>8</b>	S5
<b>Figure S2.</b> Optical micrographs of polymer <b>8</b> , viewed between crossed polarizers	S6
<b>Figure S3.</b> Tensile testing data for polymer <b>8</b> before and after uniaxial orientation (fivefold extension)	S7

## Synthesis and characterisation of intermediates and polymers

### *(4'-Bromo-[1,1'-biphenyl]-4-yl)(4-fluorophenyl)methanone (9)*

A mixture of anhydrous  $\text{AlCl}_3$  (5.99 g, 0.045 mol), 4-bromobiphenyl (10.0 g, 0.043 mol) and 1,2-dichlorobenzene (60 mL) was stirred for 20 min under nitrogen and 4-fluorobenzoyl chloride (6.48 g, 0.041 mol) was then added over 40 min while the reaction temperature was maintained at 34 °C. The temperature was raised to 65 °C and the reaction was stirred overnight, after which it was cooled to room temperature and poured into a mixture of ice-water (150 mL) and 1M aqueous HCl (500 mL). The resulting white precipitate was filtered off, washed copiously with water and hexane, and dried to give a crude product (8.05 g). Recrystallisation from toluene/petroleum spirit (bp 100-120 °C), 30/90 mL, followed by recrystallisation from acetone/2-butanone (90/30 mL), yielded white, crystalline 4-bromo-4'-(4''-fluorobenzoyl)biphenyl (**9**); (7.82 g, 54%). Mp 181 °C; HRMS-ESI;  $(\text{C}_{19}\text{H}_{12}\text{BrFO})_{\text{calc}} = 355.0056$ ; found  $m/z = 355.0128$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.91–7.81 (m, 4H), 7.70–7.64 (d, 2H), 7.64–7.58 (d, 2H), 7.55–7.47 (d, 2H), 7.22–7.14 (app. t, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 132.7, 132.6, 132.1, 130.7, 128.9, 126.9, 115.7, 115.4; IR ( $\nu_{\text{max}}$   $\text{cm}^{-1}$ ) 3068 ( $\nu_{\text{CH}_{\text{Ar}}}$ ), 1643 ( $\nu_{\text{C=O}}$ ), 1599 ( $\nu_{\text{C-C}_{\text{Ar}}}$ ), 1236 ( $\nu_{\text{C-F}}$ ), 1150  $\text{cm}^{-1}$  ( $\nu_{\text{C-Br}}$ ).

### *Polymers 14, 15 and 16*

High-temperature polycondensations of 4,4'-hexafluoroisopropylidenediphenol (**10**, HFDP, 1.00 equivalent) with a 3 mol% excess of each of the three monomers **11**, **12** and **13** were carried out in diphenyl sulfone at 300 °C in the presence of sodium carbonate at approximately 10 wt% concentration of polymer. In each case the reaction mixture remained translucent throughout the polymerisation indicating that the product was fully soluble in diphenylsulfone. After cooling, polymers **14** and **15** were extracted with methanol, and polymer **16** with acetone (three extractions in each case) to remove the diphenylsulfone.

Sodium fluoride and residual carbonate were extracted three times with boiling water, and the polymers were finally rinsed with methanol and dried under vacuum at 100 °C. Polymers **14**, **15** and **16** were readily soluble in polar solvents such as chloroform and NMP and their inherent viscosities were measured in NMP. The synthesis and characterisation of polymer **16** are detailed in reference [22], where a sample of inherent viscosity 1.29 dL g<sup>-1</sup> was found by GPC to have  $M_w/M_n = 170,000/56,000$  daltons. Characterisation data for polymers **14**, **15** and **16** obtained in the present work are given below.

**Polymer 14:** Yield = 5.12 g (93%);  $\eta_{inh}$  (NMP) = 0.69 dL g<sup>-1</sup>;  $T_g = 171$  °C; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 160.2, 156.4, 140.1, 132.6, 129.9, 129.7, 129.6, 128.4, 119.1, 118.3. IR ( $\nu_{max}$ ) 3090, 1656, 1592, 1496, 1240, 1204, 1170, 1135, 967, 923, 834 cm<sup>-1</sup>.

**Polymer 15:** Yield = 6.17 g (85%);  $\eta_{inh}$  (NMP) = 0.45 dL g<sup>-1</sup>;  $T_g = 185$  °C; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 190.6, 160.2, 156.1, 140.1, 136.6, 132.5, 130.6, 127.2, 118.9, 118.3, 99.7. IR ( $\nu_{max}$ ) 3090, 1653, 1593, 1498, 1240, 1204, 1170, 967, 925, 831, 758, 683 cm<sup>-1</sup>.

**Polymer 16:** Yield = 3.51 g (80%);  $\eta_{inh}$  (NMP) = 0.45 dL g<sup>-1</sup>;  $T_g = 205$  °C; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 162.9, 162.4, 161.9, 161.6; IR ( $\nu_{max}$ ) 3090, 1653, 1594, 1499, 1243, 1205, 1172, 968, 824, 764 cm<sup>-1</sup>.

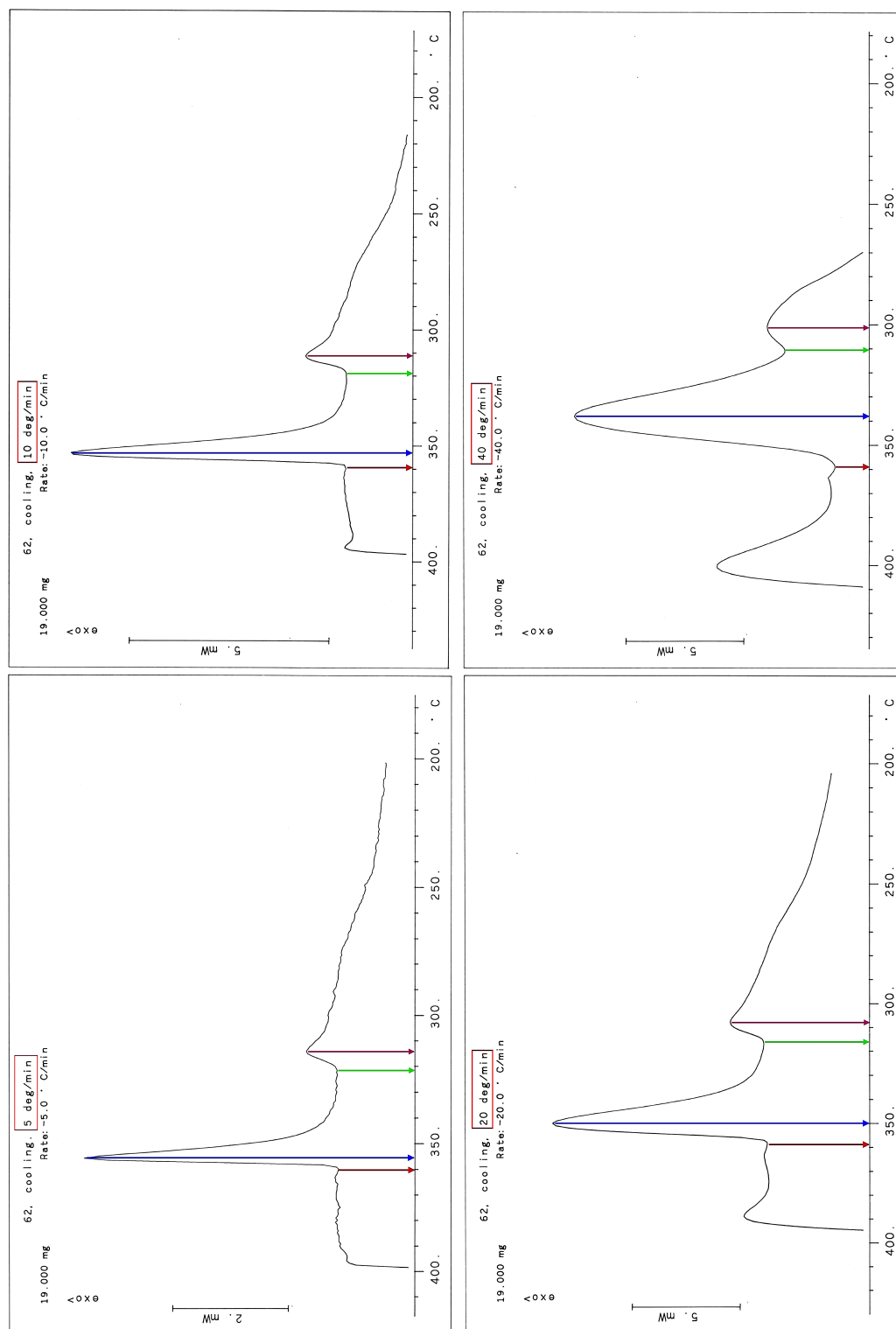
### *Copolymers 19 and 20*

Copolymer **19** (1:1 molar ratio of difluoro-monomers; Scheme 3) was obtained by statistical co-polycondensation of the *p*-quaterphenyl-based monomer **7** (1.500 g, 2.72 mmol) and 1,3-phenylenebis((4-fluorophenyl)methanone) (**18**) (0.996 g, 2.99 mmol) with HFDP (**10**, 1.832 g, 5.45 mmol) and anhydrous Na<sub>2</sub>CO<sub>3</sub> (0.635 g, 5.99 mmol) at 300 °C in diphenyl sulfone (25 g). A 5 mol% excess of difluoro-monomers over biphenol was used to control the MW. Copolymer **20** (2:1 molar ratio of monomers **7** and **18** respectively) was prepared

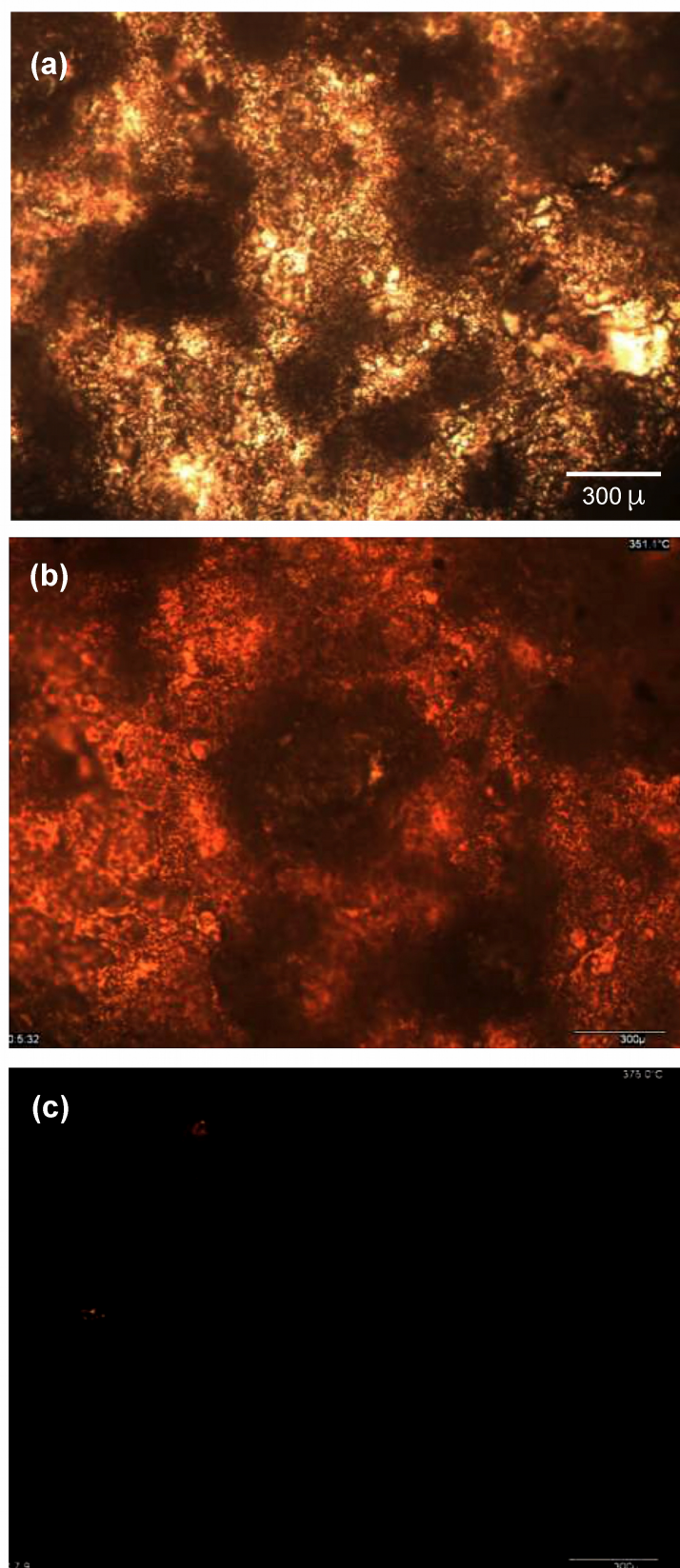
analogously. The synthesis and isolation procedures for copolymers **19** and **20** were as described for homopolymer **8** (see main paper).

**Copolymer 19 (1:1):** Yield = 3.40 g (85%);  $\eta_{\text{inh}}$  (triflic acid) = 0.81 dL g<sup>-1</sup>; mesophase – isotropic transition (heating) at 330 °C; <sup>13</sup>C NMR (100 MHz, CF<sub>3</sub>SO<sub>3</sub>H, co-axial CDCl<sub>3</sub>)  $\delta$  (ppm) 162.7, 162.3, 161.8, 161.4, 155.6, 132.2, 131.7, 131.4, 127.9, 127.7, 127.1, 126.9, 119.7, 119.5, 118.3, 118.0, 117.9, 115.6, 112.7, 109.9; IR ( $\nu_{\text{max}}$ ) 3090, 1593 ( $\nu_{\text{CO}}$ ), 1499, 1242, 1205, 1173, 929, 818. 767 cm<sup>-1</sup>.

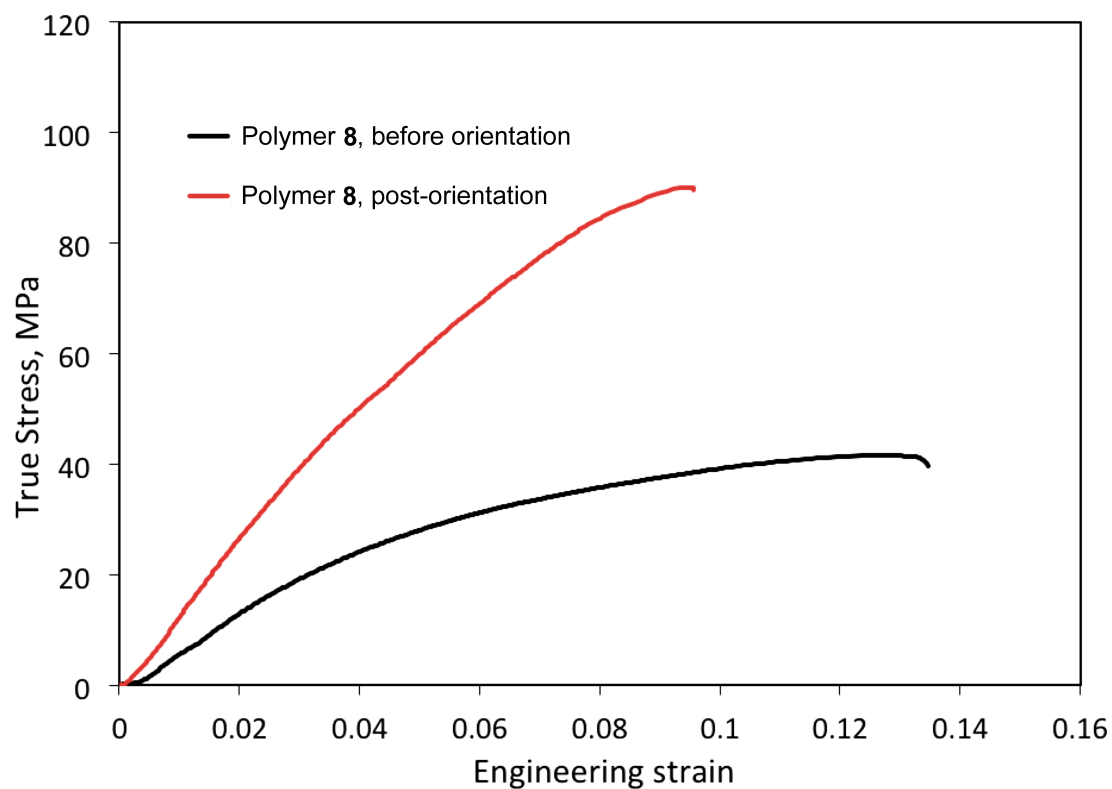
**Copolymer 20 (2:1):** Yield = 3.58 g (86%);  $\eta_{\text{inh}}$  (H<sub>2</sub>SO<sub>4</sub>) = 0.89 dL g<sup>-1</sup>; mesophase–isotropic transition (heating) at 338 °C; <sup>13</sup>C NMR (100 MHz, CF<sub>3</sub>SO<sub>3</sub>H, co-axial CDCl<sub>3</sub>)  $\delta$  (ppm) 162.7, 162.3, 161.9, 161.4, 155.9, 137.2, 135.0, 133.7, 132.1, 131.2, 127.8, 127.7, 127.1, 119.7, 119.5, 118.3, 118.0, 117.9, 115.6, 112.7, 109.9; IR ( $\nu_{\text{max}}$ ) 3090, 1593 ( $\nu_{\text{CO}}$ ), 1499, 1242, 1205, 1172, 968, 817, 766 cm<sup>-1</sup>.



**Figure S1.** Effects of cooling rate on the thermal transitions exhibited by polymer **8**. The onset-temperature of the isotropic-to-mesophase transition (red arrow) is essentially unaffected, shifting by no more than a degree as the cooling rate increases from 5 °C min<sup>-1</sup> to 40 °C min<sup>-1</sup>. The peak of this transition (blue arrow) moves some 17 °C to lower temperature over the same range of cooling rates. The onset of the broad, lower-temperature multiple endotherm (green arrow) falls by some 14 °C under the same conditions.



**Figure S2.** Optical micrographs of polymer **8**, viewed between crossed polarizers. (a) Film of polymer quench-cooled in ice water from 400 °C and then viewed at 40 °C. (b) The same sample heated and held at 350 °C. (c) The same sample further heated and held at 375 °C.



**Figure S3.** Tensile testing data (room temperature) for polymer **8** before and after uniaxial orientation (fivefold extension) and annealing (300 °C, 8h).