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# Controlled variation of monomer sequence distribution in the synthesis of aromatic poly(ether ketone)s

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and Howard M Colquhoun<sup>1</sup>

High Performance Polymers  
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## Abstract

The effects of varying the alkali metal cation in the high-temperature nucleophilic synthesis of a semi-crystalline, aromatic poly(ether ketone) have been systematically investigated, and striking variations in the sequence distributions and thermal characteristics of the resulting polymers were found. Polycondensation of 4,4'-dihydroxybenzophenone with 1,3-bis(4-fluorobenzoyl)benzene in diphenylsulphone as solvent, in the presence of an alkali metal carbonate  $M_2CO_3$  ( $M = Li, Na, K,$  or  $Rb$ ) as base, affords a range of different polymers that vary in the distribution pattern of two-ring and three-ring monomer units along the chain. Lithium carbonate gives an essentially alternating and highly crystalline polymer, but the degree of sequence randomization increases progressively as the alkali metal series is descended, with rubidium carbonate giving a fully random and non-thermally crystallizable polymer. Randomization during polycondensation is shown to result from reversible cleavage of the ether linkages in the polymer by fluoride ions, and an isolated sample of alternating sequence polymer is thus converted to a fully randomized material on heating with rubidium fluoride.

## Keywords

Polymer synthesis, nucleophilic aromatic substitution, sequence randomization, poly(ether ketone)s, crystallinity, tailor-made polymers

## Introduction

Composite materials for aerospace applications have traditionally been based on thermosetting matrix polymers such as the epoxies and bismaleimides,<sup>1,2</sup> but in more recent years the potential advantages of thermoplastic matrices (increased speed of fabrication and greater toughness) have begun to be realized,<sup>3</sup> notably with the introduction of long-fibre composites based on semi-crystalline engineering polymers such as poly(1,4-phenylene sulphide)<sup>4</sup> and the aromatic poly(ether ketone)s (PEKs), poly(ether ether ketone) (PEEK)<sup>5</sup> and poly(ether ketone ketone) (PEKK; Figure 1).<sup>6</sup>

The high crystalline melting points ( $T_m$ ) of PEKs (typically 340–380°C) result in the retention of significant mechanical strength and stiffness even at temperatures well above their glass transition temperatures ( $T_g$ s).<sup>7</sup> However, such  $T_m$ s also require correspondingly high composite fabrication temperatures – up to 420°C.<sup>3,8</sup> In the present article, we report a study of a lower melting but still crystallizable PEK matrix polymer (N1) derived from the nucleophilic polycondensation of 4,4'-dihydroxybenzophenone with

1,3-bis(4-fluorobenzoyl)benzene (Figure 2). The synthesis of this polymer ( $T_g = 152^\circ\text{C}$ ;  $T_m = 285^\circ\text{C}$ ) has been briefly noted in a conference paper,<sup>9</sup> and its combination of a  $T_g$  somewhat higher than that of PEEK ( $T_g = 143^\circ\text{C}$ ;  $T_m = 343^\circ\text{C}$ ) and a very much lower  $T_m$  – potentially enabling more facile processing – suggested to us that it would be worth investigating further as a possible composite matrix.

The polymer that might naively be expected from the above polycondensation would comprise an alternating sequence of two-ring and three-ring monomer residues. A rigorously alternating structure of this type has been obtained from the *electrophilic* polycondensation of

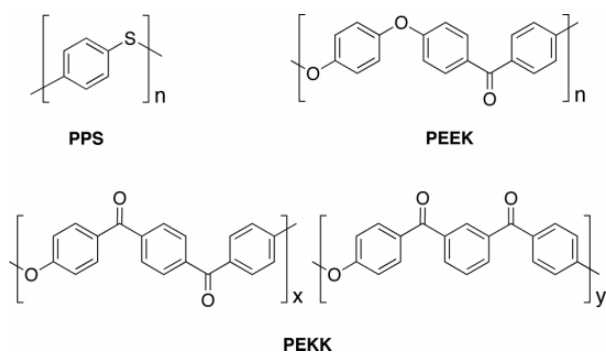
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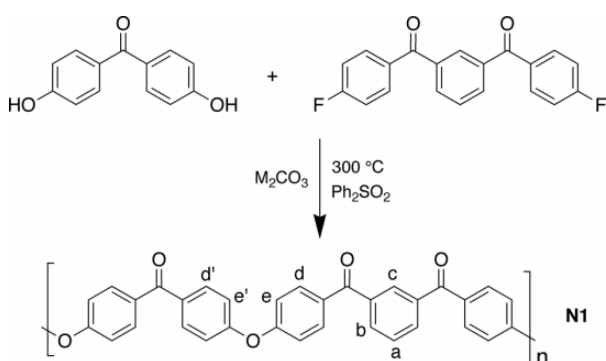
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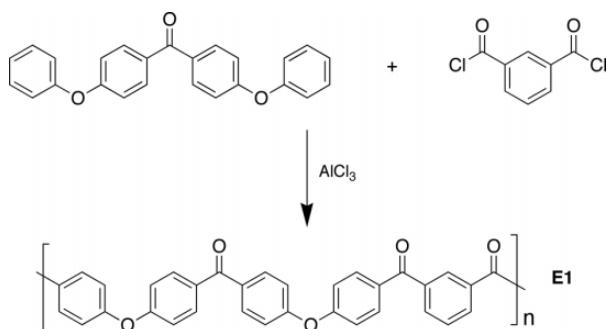
Email: h.m.colquhoun@rdg.ac.uk



**Figure 1.** Some thermoplastic aromatic matrix polymers used in carbon fibre composites.



**Figure 2.** Synthesis of polymer **N1**, also symbolized as PEKEK $m$ K. ( $M$  in  $M_2CO_3$  = alkali metal). Atom labels refer to  $^1H$  NMR assignments; see Experimental section.  $^1H$  NMR: proton nuclear magnetic resonance; PEKEK $m$ K: poly(ether ketone ether ketone)s containing meta-phenyl links.



**Figure 3.** Synthesis of polymer **E1**.<sup>10</sup> Note that the structures shown for **N1** (Figure 1) and **E1** are merely different representations of the same polymer chain sequence.

4,4'-diphenoxybenzophenone with isophthaloyl chloride (Figure 3).<sup>10,11</sup> The resulting semi-crystalline polymer (**E1**) shows thermal characteristics ( $T_g = 147^\circ C$ ;  $T_m = 310^\circ C$ ) similar to that of the 'nucleophilic' polymer **N1** ( $T_g = 152^\circ C$ ;  $T_m = 285^\circ C$ ), though the  $T_m$  of **E1** is noticeably higher. This difference in  $T_m$  may well be significant, as we now report that the nucleophilic synthesis, involving

the use of an alkali metal carbonate as base, affords polymers with a range of different  $T_m$  and degrees of crystallinity depending on the nature of the alkali metal cation. This variability is shown to relate to the degree of sequence randomization during polycondensation, an effect resulting from reversible cleavage of the ether linkages during the growth of the polymer chain.<sup>12,13</sup>

## Experimental

### Materials, instrumentation and analysis

Monomers, solvents, alkali metal carbonates and other reagents were obtained from Sigma Aldrich (UK) and were used without further purification. Inherent viscosities ( $\eta_{inh}$ ) were measured at 25 °C with 0.1% w/v polymer solutions in 96% sulphuric acid ( $H_2SO_4$ ) using a Schott Instruments CT 52 viscometer (Mainz, Germany). No insoluble gel fractions were present in any of the polymers described. Phase transitions (glass transitions, cold crystallizations and melting points) were identified from the second heating cycles of differential scanning calorimetry (DSC) traces using a TA DSC Q2000 instrument (New Castle, Delaware, USA; 4–12 mg samples,  $10^\circ C \text{ min}^{-1}$  under nitrogen atmosphere). A slight excess of alkali metal carbonate was used in each polycondensation to ensure quantitative conversion of the bisphenol to bisphenoxide. Yields of polymers were essentially quantitative and were diminished only by mechanical losses during the milling stage. Proton ( $^1H$ ) and carbon ( $^{13}C$ ) nuclear magnetic resonance (NMR) spectra were obtained on Bruker Nanobay 400 MHz or 700 MHz NMR spectrometers (Billerica, Massachusetts, USA) using polymer solutions in (deuterated chloroform;  $CDCl_3$ /hexafluoro-2-propanol;  $(CF_3)_2CHOH$  (6:1 v/v) or  $CDCl_3$ /trifluoro acetic acid ( $CF_3COOH$ ) (6:1 v/v). Mass spectra (electrospray ionization (ESI)) were obtained from 0.1% (w/v) sample solutions in methanol using a ThermoScientific LTQ Orbitrap XL instrument (Waltham, Massachusetts, United States) equipped with an ACCELA LC autosampler.

### Synthesis and characterization

**Polymer N1a.** A mixture of 1,3-bis(4-fluorobenzoyl)benzene (4.60 g, 14.28 mmol), 4,4'-dihydroxybenzophenone (3.00 g, 14.00 mmol), sodium carbonate ( $Na_2CO_3$ ; 1.63 g, 15.4 mmol) and diphenylsulphone (35 g) was heated with stirring to 300 °C under argon atmosphere. After 3 h, the polymer solution was poured onto a sheet of aluminium and allowed to cool. The resulting solid was ground to a powder in an ultracentrifugal mill and then stirred in acetone (200 mL) at room temperature for 30 min. The powder was filtered off, washed with acetone and dried. The powder was next extracted with 4 × 200 mL of refluxing acetone, and then overnight in a Soxhlet extractor with refluxing acetone. The powder was extracted with 5 × 200 mL of boiling water and

then finally with 4 × 200 mL of refluxing acetone. The resulting, purified material was dried at 110°C under vacuum overnight, affording polymer **N1a** (5.65 g, 81.3% yield).  $T_g = 149^\circ\text{C}$ ;  $T_m = 300^\circ\text{C}$ ;  $\eta_{\text{inh}}(\text{H}_2\text{SO}_4) = 0.62 \text{ dL g}^{-1}$ ; IR  $\nu_{\text{max}} \text{ cm}^{-1}$ : 2997 (C–H), 1655 (C=O), 1588 (C–C), 1238 (C–O–C), 1161 (C–O–C);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  8.18 (s, 1H<sub>c</sub>), 8.07 (d,  $J = 7.6 \text{ Hz}$ , 2H<sub>b</sub>), 7.91 (m, 8H<sub>d,d'</sub>), 7.75 (t,  $J = 7.6 \text{ Hz}$ , 1H<sub>a</sub>), 7.26 (d,  $J = 8.0 \text{ Hz}$ , 8H<sub>e,e'</sub>) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  199.08, 198.77, 161.35, 160.47, 137.45, 134.22, 133.08, 132.84, 132.60, 131.57, 130.80, 129.00, 119.10, 118.81 ppm.

**Polymer N1b.** This polymer was obtained using the procedure described for polymer **N1a**, but with potassium carbonate (2.13 g, 15.4 mmol) replacing  $\text{Na}_2\text{CO}_3$  to give polymer **N1b** (6.00 g, 86.3%).  $T_g = 151^\circ\text{C}$ ;  $\eta_{\text{inh}}(\text{H}_2\text{SO}_4) = 0.78 \text{ dL g}^{-1}$ ; IR  $\nu_{\text{max}} \text{ cm}^{-1}$  2985 (C–H), 1656 (C=O), 1591 (C–C), 1240 (C–O–C), 1163 (C–O–C);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  8.19 (s, 1H), 8.08 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.92 (m, 8H), 7.76 (t,  $J = 7.6 \text{ Hz}$ , 1H), 7.26 (d,  $J = 8.0 \text{ Hz}$ , 8H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  199.37, 199.00, 161.42, 161.13, 160.82, 160.54, 134.25, 133.05, 132.84, 132.82, 132.60, 131.75, 131.57, 130.83, 129.00, 119.75, 118.79 ppm.

**Polymer N1c.** The same procedure as described for polymer **N1a** was used, but replacing  $\text{Na}_2\text{CO}_3$  with rubidium carbonate (3.56 g, 15.4 mmol) and using a 5 mol% excess of 1,3-bis(4-fluorobenzoyl)benzene (4.74 g, 14.70 mmol) to control molecular weight (MW), afforded polymer **N1c** (5.35 g, 77.0%).  $T_g = 153^\circ\text{C}$ ;  $\eta_{\text{inh}}(\text{H}_2\text{SO}_4) = 0.73 \text{ dL g}^{-1}$ ; IR  $\nu_{\text{max}} \text{ cm}^{-1} = 3000$  (C–H), 1654 (C=O), 1588 (C–C), 1497 (C–C), 1236 (C–O–C), 1160 (C–O–C);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  8.12 (s, 1H), 8.01 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.86 (m, 8H), 7.70 (t,  $J = 7.6 \text{ Hz}$ , 1H), 7.21 (d,  $J = 8 \text{ Hz}$ , 8H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  199.04, 198.72, 161.36, 161.07, 160.76, 160.47, 137.47, 134.22, 133.07, 132.84, 132.63, 132.46, 131.78, 131.59, 130.80, 129.00, 119.10, 118.89 ppm.

**Polymer N1d.** Polymer **N1a** (2.20 g), rubidium fluoride (1.49 g, 14.28 mmol) and diphenylsulphone (35 g) were heated with stirring at 300°C under argon for 2 h. Using the same workup procedure as described for polymer **N1a** afforded polymer **N1d** as a tan powder (1.05 g, 47.0%),  $T_g = 153^\circ\text{C}$ ;  $\eta_{\text{inh}}(\text{H}_2\text{SO}_4) = 0.44 \text{ dL g}^{-1}$ ; IR  $\nu_{\text{max}} \text{ cm}^{-1}$  2982 (C–H), 1655 (C=O), 1589 (C–C), 1497 (C–C), 1238 (C–O–C);  $^1\text{H NMR}$  (100 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  8.13 (s, 1H), 8.01 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.87 (m, 8H), 7.70 (t,  $J = 7.6 \text{ Hz}$ , 1H), 7.20 (d,  $J = 8.0 \text{ Hz}$ , 8H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  197.56, 197.39, 161.00, 160.73, 160.43, 160.14, 137.57, 134.00, 133.07, 132.81, 131.89, 131.71, 130.85, 129.78, 128.94, 119.10, 118.90 ppm.

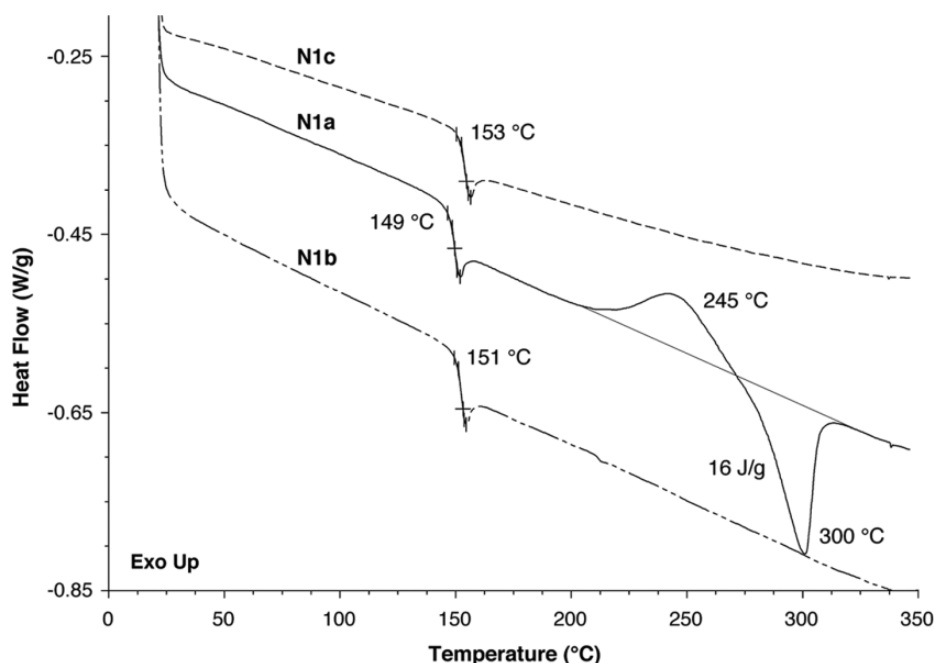
**Polymer N1e.** The same procedure as described for polymer **N1a** was used, but replacing  $\text{Na}_2\text{CO}_3$  with lithium carbonate (1.13 g, 15.4 mmol) and using an additional 2 × 200 mL of boiling water at the extraction stage to ensure removal of lithium fluoride (LiF). This gave polymer **N1e** (5.53 g, 78.2%).  $T_g = 143^\circ\text{C}$ ;  $T_m = 304^\circ\text{C}$ ;  $\eta_{\text{inh}}(\text{H}_2\text{SO}_4) = 0.40 \text{ dL g}^{-1}$ ; IR  $\nu_{\text{max}} \text{ cm}^{-1} = 1653$  (C=O), 1588 (C–C), 1496 (C–C), 1235 (C–O–C), 1161 (C–O–C);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  8.13 (s, 1H), 8.01 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.87 (t, 8H), 7.70 (t,  $J = 7.6 \text{ Hz}$ , 1H), 7.20 (dd,  $J = 8, 4 \text{ Hz}$ , 8H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.75, 196.63, 160.46, 159.63, 137.13, 133.45, 132.57, 132.31, 131.32, 130.40, 129.32, 128.45, 118.61, 118.36 ppm.

**Bisphenol 2.** A solution of 4-hydroxy-3-methylbenzoic acid (3.00 g, 19.7 mmol) and *o*-cresol (2.27 g, 21 mmol) in a mixture of trifluoromethanesulphonic anhydride (3.36 mL, 20 mmol) and trifluoromethanesulphonic acid (30 mL) was stirred under nitrogen for 18 h. The solution was then added dropwise with stirring into 800 mL of cold water. The precipitate was filtered off, washed repeatedly with boiling water, then with a 0.01M sodium hydroxide solution, and finally with cold water until a neutral filtrate was obtained. The solid was dried in a vacuum oven at 90°C for 5 h to afford bisphenol **2** as a colourless powder (3.20 g, 67%). Melting point (m.p.; DSC) 248°C (literature 247–248°C)<sup>14</sup>; FTIR  $\nu_{\text{max}} \text{ cm}^{-1}$  3424 (O–H), 3229 (O–H), 1639 (C=O), 1579 (C–C), 1373 (C–O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3/\text{CF}_3\text{COOH}$  6:1 v/v)  $\delta$  7.65 (d,  $J = 2.0 \text{ Hz}$ , 2H), 7.58 (dd,  $J = 2.0, 8.4 \text{ Hz}$ , 2H), 6.91 (d,  $J = 8.4 \text{ Hz}$ , 2H), 2.31 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3/\text{CF}_3\text{COOH}$ ):  $\delta$  200.36, 158.81, 134.68, 131.75, 129.26, 124.74, 115.06, 15.51. ESI-MS  $m/z = 243.1016$  [M+H], 243.1021 calculated.

**Polymer 3.** A mixture of bisphenol **2** (2.42 g, 10 mmol), 1,3-bis(4-fluorobenzoyl)benzene (3.28 g, 10.2 mmol),  $\text{Na}_2\text{CO}_3$  (1.16 g, 11.0 mmol) and diphenylsulphone (35 g) was heated with stirring to 300°C under argon atmosphere. The workup procedure for polymer **N1a** was followed to afford polymer **3** (3.40 g, 64%).  $T_g = 168^\circ\text{C}$ ,  $\eta_{\text{inh}}(\text{H}_2\text{SO}_4) = 0.44 \text{ dL g}^{-1}$ ;  $\nu_{\text{max}} \text{ cm}^{-1}$  1736 (C–H), 1657 (C=O), 1584 (C–C), 1496 (C–C), 1233 (C–O–C);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3/\text{CF}_3\text{COOH}$  6:1 v/v)  $\delta$  8.18 (s, 1H), 8.06 (d,  $J = 7.6 \text{ Hz}$ , 2H), 7.91 (d,  $J = 7.2 \text{ Hz}$ , 4H), 7.82 (s, 2H), 7.71 (m, 3H), 7.24 (d,  $J = 5.6 \text{ Hz}$ , 1H), 7.11 (m, 5H) 2.34 (s, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3/(\text{CF}_3)_2\text{CHOH}$  6:1 v/v)  $\delta$  215.24, 198.85, 197.87, 161.56, 157.54, 137.26, 133.66, 133.02, 132.88, 130.71, 130.54, 129.90, 128.58, 119.19, 115.80, 117.16, 29.83 ppm.

## Results and discussion

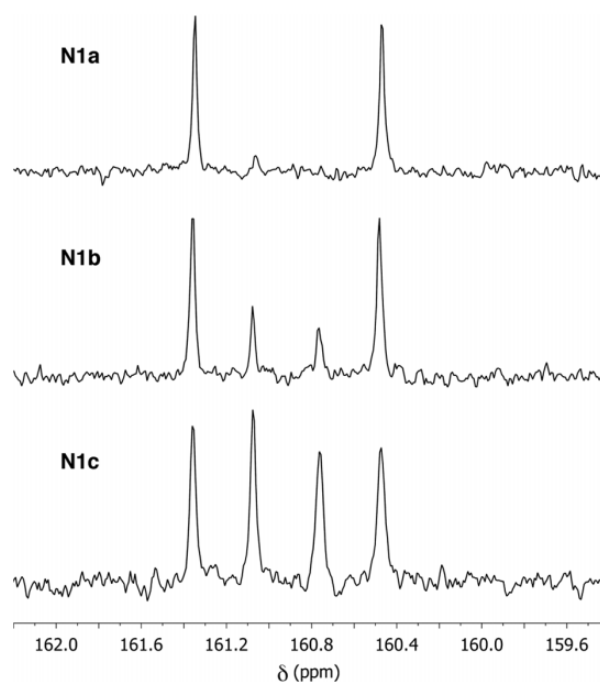
Polycondensation of 4,4'-dihydroxybenzophenone with 1,3-bis(4-fluorobenzoyl)-benzene, in diphenylsulphone as



**Figure 4.** DSC scans (2nd heating,  $10^{\circ}\text{C min}^{-1}$ ) for polymers **N1a**, **N1b** and **N1c**. DSC: differential scanning calorimetry.

solvent, at  $300^{\circ}\text{C}$  in the presence of an alkali metal carbonate  $M_2\text{CO}_3$  as base (Figure 2;  $M = \text{Na, K, or Rb}$ ), afforded high-molecular-weight PEK **N1a**, **N1b** and **N1c** respectively, with inherent viscosities in the range  $0.6\text{--}0.8 \text{ dL g}^{-1}$ . A slight molar excess of the difluoroketone was used to control the final MW. Following exhaustive extraction of diphenylsulphone and inorganic salts, the polymers were dried and analysed by DSC. After heating to  $350^{\circ}\text{C}$ , the samples were cooled at  $10^{\circ}\text{C min}^{-1}$ , but none showed evidence of crystallization on cooling from the melt. However, on reheating at the same rate (Figure 4), polymer **N1a** underwent a glass transition (onset at  $149^{\circ}\text{C}$ ), followed by a cold crystallization exotherm peaking at  $245^{\circ}\text{C}$ , and finally a crystal melting endotherm at  $300^{\circ}\text{C}$ . The other two polymers (**N1b** and **N1c**) showed only glass transitions at  $151$  and  $153^{\circ}\text{C}$ , respectively.

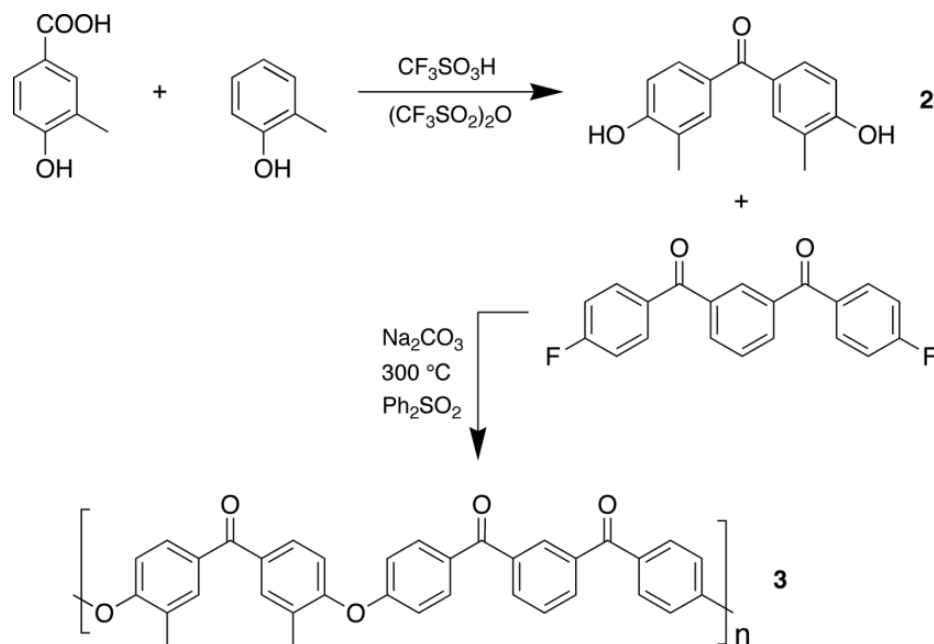
It seemed possible that the observed variation in crystallizability between the three polymers could result from differences in their sequence distributions since transesterification with sequence randomization is known to occur during the nucleophilic synthesis of aromatic polyethers in which both monomer residues in the chain are activated towards nucleophilic attack adjacent to the ether linkage.<sup>12,13</sup> This possibility was confirmed by  $^{13}\text{C}$  NMR analysis (Figure 5), which showed useful diagnostic resonances in the range  $\delta = 160\text{--}162 \text{ ppm}$ , corresponding to the aromatic carbons attached directly to ether oxygens. Polymer **N1a** shows only two peaks in this region, corresponding to the two different carbons of this type that would be expected in the simple alternating structure  $(\text{EKEK}m\text{K})_n$  (c.f. polymer **E1**), whereas polymers **N1b**



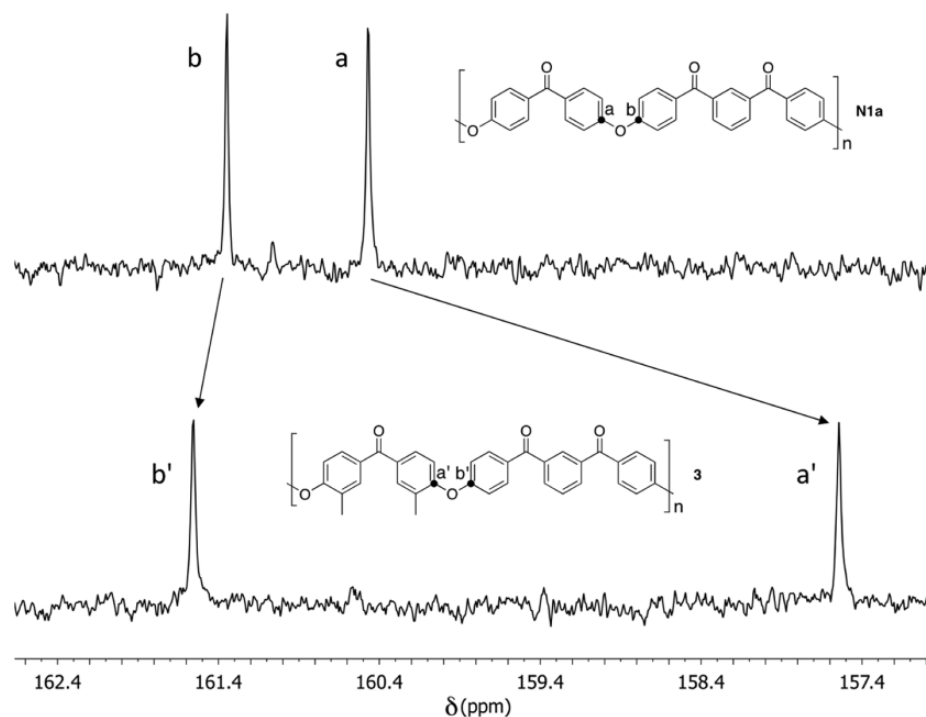
**Figure 5.**  $^{13}\text{C}$  NMR resonances in the C–O–C region for polymers **N1a**, **N1b** and **N1c**.  $^{13}\text{C}$  NMR: carbon nuclear magnetic resonance.

and **N1c** show two additional ‘inner’ peaks in the  $^{13}\text{C}$ –O–C region, with the relative intensity of these increasing substantially from **N1b** to **N1c** (Figure 5).

In order to aid the assignment of  $^{13}\text{C}$ –O–C peaks to the specific two-ring and three-ring residues, a dimethyl-substituted polymer (**3**), analogous to **N1a**, was synthesized.



**Figure 6.** Synthesis of bisphenol **2** and its derived PEK **3**. PEK: poly(ether ketone).

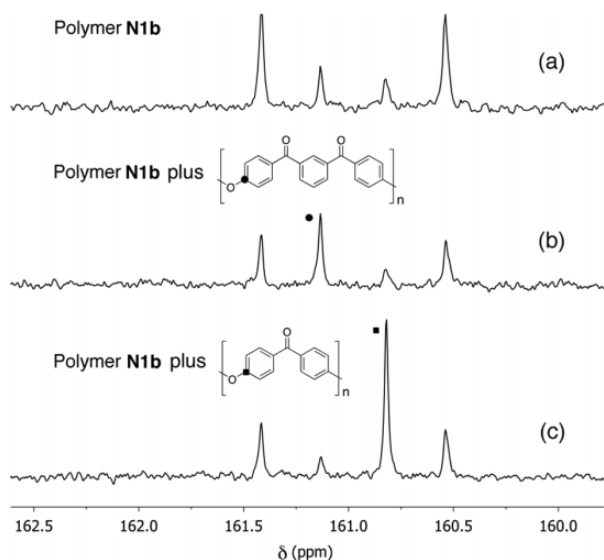


**Figure 7.**  $^{13}\text{C}$  NMR resonances in the C–O–C region for polymers **N1a** and **3**.  $^{13}\text{C}$  NMR: carbon nuclear magnetic resonance.

Direct condensation of *o*-cresol with 4-hydroxy-3-methylbenzoic acid in trifluoromethanesulphonic (triflic) acid gave very pure 3,3'-dimethyl-4,4'-dihydroxybenzophenone (**2**).<sup>14</sup> This condensed with 1,3-bis(4-fluorobenzoyl)benzene in the presence of  $\text{Na}_2\text{CO}_3$  (Figure 6) to give polymer **3**.

In the  $^{13}\text{C}$  NMR spectrum of polymer **3**, two  $^{13}\text{C}$ –O–C resonances are still evident, but the lower field  $^{13}\text{C}$ –O–C peak is shifted only very slightly (ca. 0.25 ppm) relative to its position in the spectrum of **1a**, whereas the other peak moves substantially upfield by some 2.9 ppm (Figure 7). This result strongly suggests that the lower field resonance





**Figure 8.**  $^{13}\text{C}$  NMR resonances in the C–O–C region for (a) polymer **N1b**, and the same polymer doped with either (b) PEKmkK or (c) PEK.  $^{13}\text{C}$  NMR: carbon nuclear magnetic resonance; PEKmkK: poly(ether ketone) containing meta-phenylene links.

represents the  $^{13}\text{C}$ –O–C carbon associated with the three-ring residue – which is chemically unchanged in the dimethyl polymer **3** – and that the strongly shifted, higher field resonance can be assigned to the two-ring residue, in which the methyl substituents are *ortho* to its  $^{13}\text{C}$ –O–C carbons.

The  $^{13}\text{C}$  NMR spectra of polymers **N1b** and **N1c** however show two additional inner peaks in the  $^{13}\text{C}$ –O–C region (Figure 5). The increased multiplicity of peaks suggests sequence randomization could be occurring, and indeed the new peaks proved assignable to sequences comprising two adjacent two-ring residues and two adjacent three-ring residues. These assignments were achieved by doping samples of polymer **N1b** with the homopolymers PEK<sup>7</sup> and PEKmkK<sup>9</sup>, which resulted in the enhancement of the intensities of the higher field and lower field inner peaks, respectively (Figure 8).

The  $^{13}\text{C}$  NMR spectrum of polymer **N1c**, produced using rubidium carbonate, showed even more extensive sequence randomization than in **N1b**, now with four peaks of equal intensity in the  $^{13}\text{C}$ –O region (Figure 5). Analysis of the probability distribution for the three possible dimer sequences around the ether linkages in polymer **N1** shows that a completely random polymer would contain KEK, KEKmkK and KmKEKmkK sequences in the relative proportions 1:2:1. This distribution would indeed give rise to four  $^{13}\text{C}$  NMR resonances of equal intensity (1:1:1:1) in this region of the spectrum since the unsymmetrical KEKmkK sequence contains two inequivalent C–O–C carbons. A similar calculation indicates that the intensity ratios observed in the spectrum of polymer **N1b** (ca. 3:1:1:3)

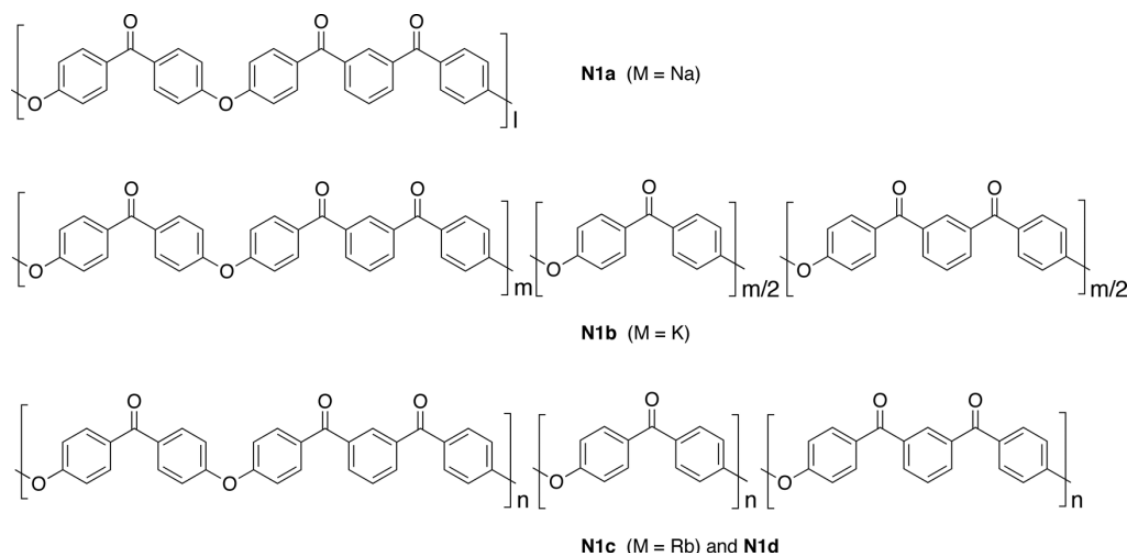
correspond to approximately 50% randomization, relative to a fully alternating sequence. It is worth noting that the original report of polymer **N1** indicated that it was synthesized using a mixture of sodium and potassium carbonates and that its melting point was 285°C,<sup>9</sup> significantly lower than that that observed for polymer **N1a**. It thus seems very probable that a significant degree of sequence randomization of **N1** had also occurred in that work. In fact, even **N1a** is unlikely to be 100% alternating as its melting point (300°C) is still slightly lower than that of the “electrophilic” polymer **E1** (305°C). Moreover, the  $^{13}\text{C}$  NMR spectrum of **N1a**, shown in Figure 5, reveals a very weak but still detectable inner resonance corresponding to the symmetric, non-alternating sequence KmKEKmkK. The relationships between polymers **N1a**–**N1d**, identified in the present work, are summarized in Figure 9.

A number of possible mechanisms have been proposed for transesterification during the synthesis of aromatic PEKs, but all depend on reversible, nucleophilic cleavage of the ether linkages (Figure 10). Candidate nucleophiles in the system include the carbonate and fluoride anions, and indeed potassium carbonate has previously been shown to induce a small degree of sequence randomization in an aromatic PEK, albeit requiring very high reaction temperatures (340°C) and long reaction times (6 h).<sup>15</sup> The fluoride ion can be a very strong nucleophile in dipolar aprotic solvents,<sup>16,17</sup> but its effectiveness in the present context would depend both on the solubility of the fluoride salt involved and on the extent of pairing with its counterion in solution. The larger the counterion, the weaker the ion pairing and the more soluble the salt, so RbF should be much more effective than sodium fluoride, with potassium fluoride somewhere in between ( $r_{\text{ionic}} = 1.16, 1.52, 1.66 \text{ \AA}$  for 6-coordinate  $\text{Na}^+, \text{K}^+, \text{and Rb}^+$ , respectively).<sup>18</sup> This is fully consistent with our experimental results for sequence randomization in the synthesis of **N1**.

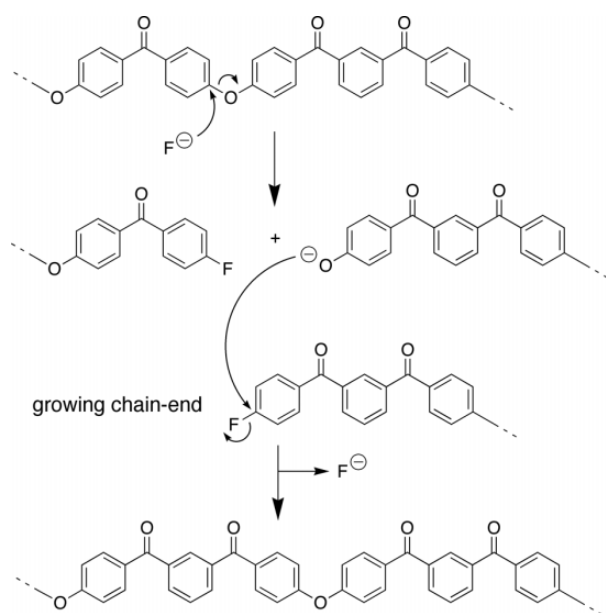
In the present work, sequence randomization catalysed by fluoride ion was demonstrated conclusively by treatment of the alternating polymer **N1a** with RbF in diphenylsulphone, at the same concentrations, temperature and time as in polymer synthesis. The result was completely clear-cut, with the diagnostic  $^{13}\text{C}$ –O–C resonances for the product **N1d** changing from two equal intensity resonances in **N1a** (alternating structure) to four equal intensity resonances (random sequence structure), exactly as found in polymer **N1c**.

As a final test of the proposed mechanism for sequence randomization, the polycondensation shown in Figure 2 was carried out using lithium carbonate as base. The extremely low solubility of lithium fluoride in organic solvents<sup>19</sup> should strongly inhibit fluoride-catalysed transesterification and indeed, as shown in Figure 11, resonances arising from sequence randomization were scarcely discernable in the  $^{13}\text{C}$  NMR spectrum of the resulting polymer (**N1e**).



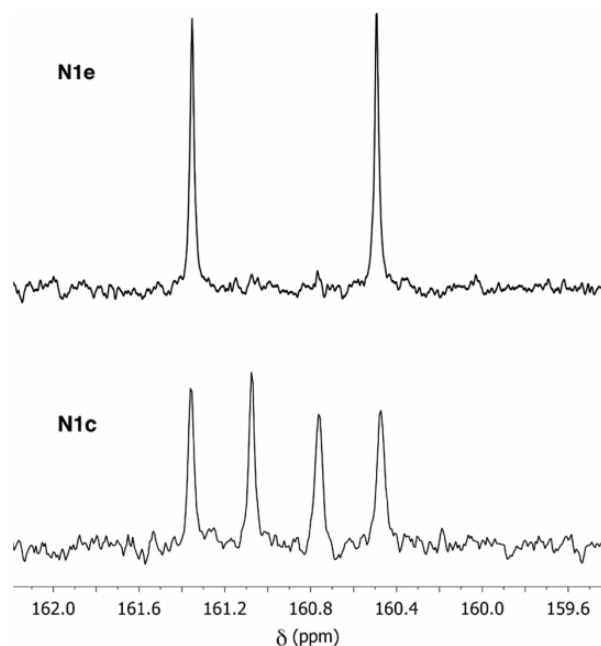


**Figure 9.** Representations of the chain sequences in polymers **N1a** (almost entirely alternating), **N1b** (semi-randomized) and **N1c** (fully randomized), arising from the use of different alkali metal carbonates  $M_2CO_3$  in the nucleophilic polycondensation shown in Figure 1. Treatment of **N1a** with RbF results in its conversion to polymer **N1d**, having the same, fully random, sequence as **N1c**. RbF: rubidium fluoride.



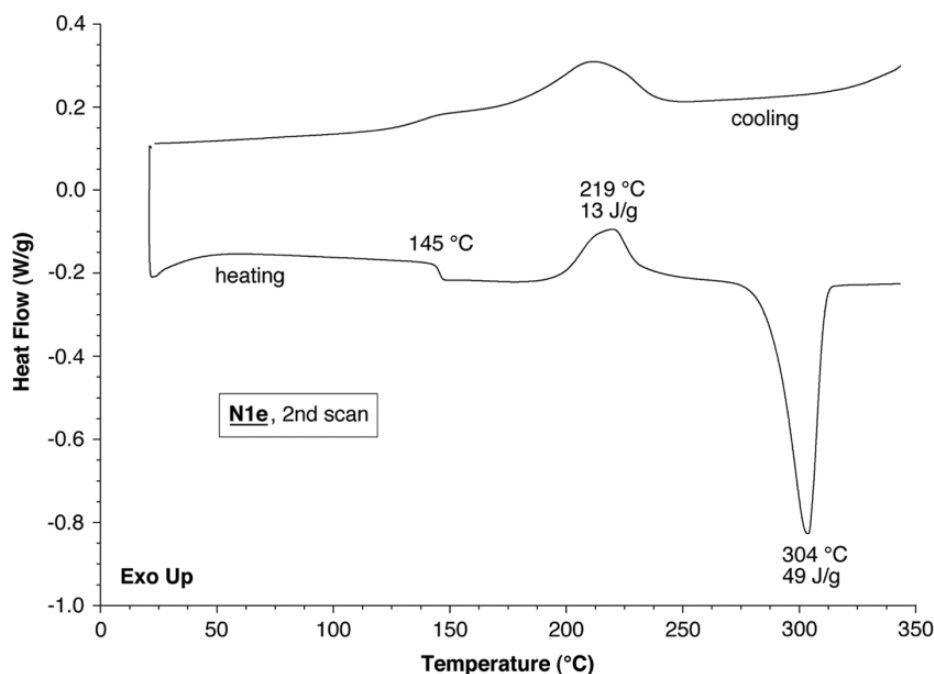
**Figure 10.** Partial mechanism for fluoride-catalysed sequence randomization in the synthesis of polymer **NI**. The initial chain cleavage by fluoride can occur at either the two-ring or three-ring monomer residue, and the fluoro end-group resulting from this reaction can subsequently regenerate a fluoride anion by reaction with a phenoxide monomer or end-group.

As shown in Figure 12, polymer **N1e** also crystallized from the melt ( $T_c = 215^\circ\text{C}$ ) – unlike the other polymers described in this work – and showed a slightly higher  $T_m$  value than **N1b** (304 vs.  $300^\circ\text{C}$ ) and a much higher degree of crystallinity ( $\Delta H_m = 49$  vs.  $16\text{ J g}^{-1}$ ), presumably the consequences of a more perfectly alternating chain sequence.



**Figure 11.**  $^{13}\text{C}$  NMR resonances in the C–O–C region for polymers **N1c** (fully randomized) and **N1e**, illustrating the virtual absence of sequence-randomization in the latter polymer.  $^{13}\text{C}$  NMR: carbon nuclear magnetic resonance.

An intriguing observation is that, although DSC analysis customarily discounts the first heating scan, a consistent feature of the first (but not subsequent) DSC heating scans for polymers **N1a**, **N1b**, and **N1c** is the presence of a melting endotherm at ca.  $174^\circ\text{C}$  – in addition to a conventional polymer melting peak in the range  $230$ – $300^\circ\text{C}$  – that



**Figure 12.** DSC scans (2nd heating and subsequent cooling scan,  $10^{\circ}\text{C min}^{-1}$ ) for polymer **N1e**. DSC: differential scanning calorimetry.

increases in intensity with the degree of sequence randomization. The lower melting peak is however essentially absent from the DSC trace of the fully alternating polymer **N1e**. This correlation seems to imply the existence of a low-melting crystalline phase in the ‘as-isolated’ polymers that is associated specifically with the packing of *random* sequences. This could be possible, in principle, because the three ‘parent’ polymers (KEK $m$ K, KEK and K $m$ KEK $m$ K) have almost identical unit cells in cross-section perpendicular to the chain direction (orthorhombic,  $a = 7.67 \pm 0.05$ ,  $b = 6.04 \pm 0.07$  Å, two chains per cell).<sup>10,20,21</sup> Moreover, the X-ray powder patterns from ‘as-isolated’ samples of polymers **N1c** and **N1d** indicate substantial degrees of crystallinity, despite the high levels of sequence randomization. Crystallization of random sequence copolymers is not of course unknown when the comonomer residues are isomorphous, but it is not yet clear how isomorphism arises in the present system. Computational modelling studies are under way in our laboratory to investigate this problem further.

## Conclusions

Sequence randomization, via transesterification, during the nucleophilic synthesis of an aromatic PEK involving fluoride displacement from a bis(4-fluoroaryl)ketone can be controlled by varying the alkali metal cation ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Rb}^+$ ) present during polycondensation. The degree of transesterification increases with the ionic radius of the alkali metal involved, and a proposed mechanism in which

fluoride ions reversibly cleave the growing polymer chain is substantiated by a direct demonstration of sequence randomization in the presence of RbF. The crystallizability of the polymer from the melt declines markedly as the degree of sequence randomization increases, although crystallization of the more highly randomized polymers from solution in diphenylsulphone affords an unusually low-melting crystalline phase whose nature remains to be established.

## Authors’ Note

Underlying data for this article may be requested from the corresponding author.

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