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

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

**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 diphenylsulfone 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 2-ring and 3-ring monomer units along the chain. Lithium carbonate gives an essentially alternating and highly crystalline polymer, but the degree of sequence-randomisation increases progressively as the alkali metal series is descended, with rubidium carbonate giving a fully random and non-thermally-crystallisable polymer. Randomisation 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 randomised material on heating with rubidium fluoride.

**Keywords:** polymer synthesis; nucleophilic aromatic substitution; sequence-randomisation; 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 bis(maleimides),[1,2] but in more recent years the potential advantages of thermoplastic matrices (increased speed of fabrication and greater toughness) have begun to be realized,[3] notably with the introduction of long-fibre composites based on semi-crystalline engineering polymers such as poly(1,4-phenylene sulfide) (PPS)[4] and the aromatic poly(ether ketone)s PEEK[5] and PEKK (Figure 1).[6]

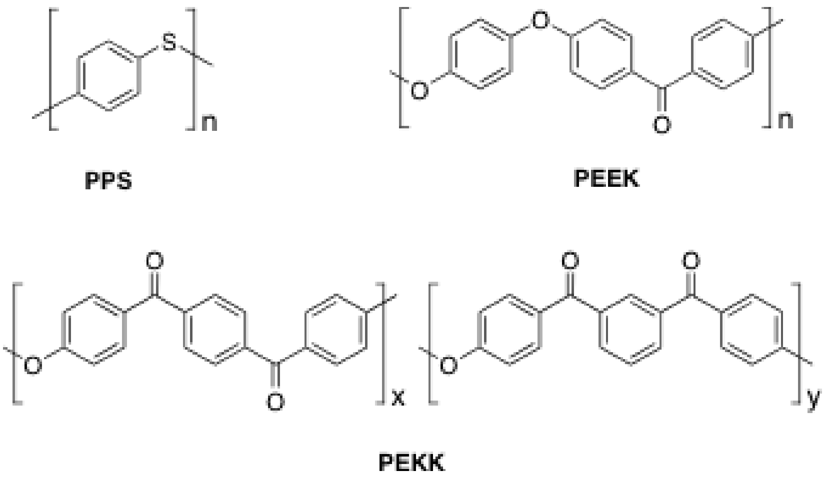
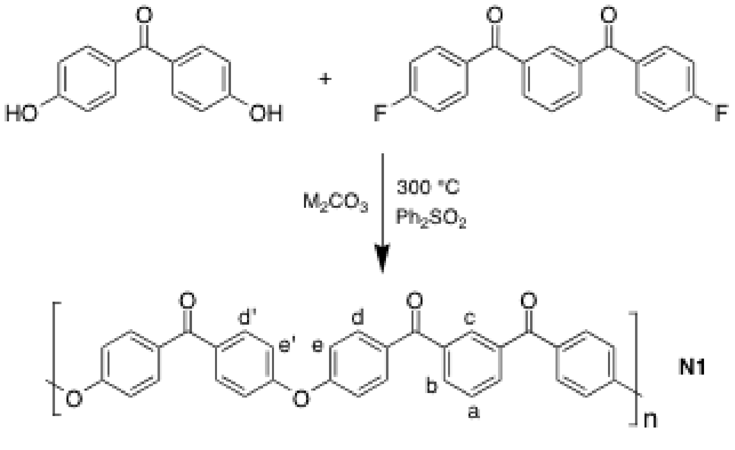


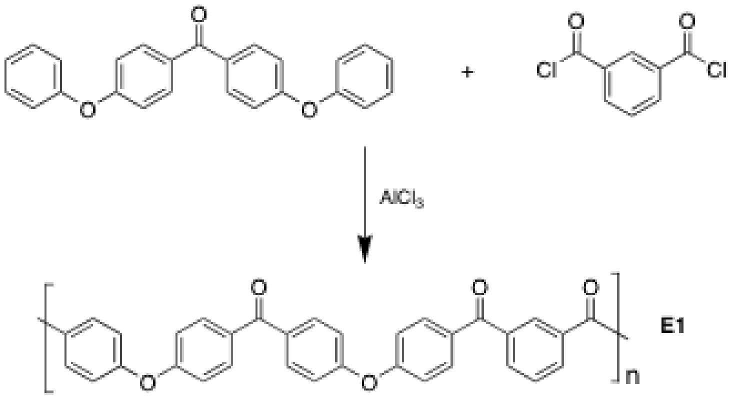
**Figure 1.** Some thermoplastic aromatic matrix polymers used in carbon fibre composites

The high crystalline melting points ($T_m$) of poly(ether ketone)s (typically 340 – 380 °C) result in retention of significant mechanical strength and stiffness even at temperatures well above their glass transition temperatures ($T_g$).[7] However, such melting points also require correspondingly high composite-fabrication temperatures – up to 420 °C.[3,8] In the present paper, we report a study of a lower-melting but still crystallisable poly(ether ketone) matrix polymer (**N1**) derived from the nucleophilic polycondensation of 4,4'-dihydroxybenzophenone with 1,3-bis(4-fluorobenzoyl)benzene (Scheme 1). The synthesis of this polymer ($T_g$ 152 °C; $T_m$ 285 °C) has been briefly noted in a conference paper,[9] and its combination of a $T_g$ somewhat higher than that of PEEK ($T_g$ 143 °C; $T_m$ 343 °C) and a very much lower melting point – potentially enabling more facile processing – suggested to us that it would be worth investigating further as a possible composite matrix.



**Scheme 1.** Synthesis of polymer **N1**, also symbolised as PEKEK*m*K. (M in $M_2CO_3$ = alkali metal). Atom labels refer to $^1$H NMR assignments; see Experimental section.

The polymer that might naively be expected from the above polycondensation would comprise an alternating sequence of 2-ring and 3-ring monomer residues. A rigorously alternating structure of this type has been obtained from the *electrophilic* polycondensation of 4,4'-diphenoxybenzophenone with isophthaloyl chloride (Scheme 2).[10,11] The resulting semi-crystalline polymer (**E1**) shows thermal characteristics ($T_g$ 147 °C; $T_m$ 310 °C) similar to that of the "nucleophilic" polymer **N1** ($T_g$ 152 °C; $T_m$ 285 °C), though the melting point of **E1** is noticeably higher. This difference in melting point may well be significant, as we now report that the nucleophilic synthesis, involving use of an alkali metal carbonate as base, affords polymers with a range of different melting points and degrees of crystallinity depending on the nature of the alkali metal cation. This variability is shown to relate to the degree of sequence-randomisation during polycondensation, an effect resulting from reversible cleavage of the ether linkages during growth of the polymer chain.[12,13]



**Scheme 2.** Synthesis of polymer **E1** [10]. Note that the structures shown for **N1** (in Scheme 1) and **E1** are merely different representations of the same polymer chain sequence.

## 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% sulfuric acid using a Schott Instruments CT 52 viscometer. No insoluble gel fractions were present in any of the polymers described. Phase transitions (glass transitions, cold crystallisations and melting points) were identified from the second heating cycles of differential scanning calorimetry (DSC) traces using a TA DSC Q2000 instrument (4-12 mg samples, 10 °C $min^{-1}$ under a nitrogen atmosphere). A slight excess of alkali metal carbonate was used in each polycondensation to ensure quantitative conversion of the bis-phenol to bis-phenoxide. Yields of polymers were essentially quantitative and were diminished only by mechanical losses during the milling stage. $^{1}H$ and $^{13}C$ NMR spectra were obtained on Bruker Nanobay 400 MHz or 700 MHz NMR spectrometers using polymer solutions in $CDCl_3/(CF_3)_2CHOH$ (6:1 v/v) or $CDCl_3/CF_3COOH$ (6:1 v/v). Mass spectra (ESI) were obtained from 0.1% (w/v) sample solutions in methanol using a Thermo Scientific LTQ OrbiTrap XL instrument equipped with an ACCELA LC Autosampler.

## Synthesis and characterisation

**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), $Na_2CO_3$ (1.63 g, 15.4 mmol) and diphenylsulfone (35 g) was heated with stirring to 300 °C under argon. 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 x 200 mL of refluxing acetone, and then overnight in a Soxhlet extractor with refluxing acetone. The powder was extracted with 5 x 200 mL of boiling water and then finally with 4 x 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 °C; $T_m$ = 300 °C; $\eta_{inh}$ ($H_2SO_4$) = 0.62 dL $g^{-1}$; IR $\nu_{max}/cm^{-1}$: 2997 (C-H), 1655 (C=O), 1588 (C-C), 1238 (C-O-C), 1161 (C-O-C); $^1H$ NMR (400 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 8.18 (s, $1H_c$), 8.07 (d, $J$ = 7.6 Hz, $2H_b$), 7.91 (m, $8H_{d,d'}$), 7.75 (t, $J$ = 7.6 Hz, $1H_a$), 7.26 (d, $J$ = 8.0 Hz, $8H_{e,e'}$) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v)) δ 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 sodium carbonate to give polymer **N1b** (6.00 g, 86.3%). $T_g$ = 151 °C; $\eta_{inh}$ ($H_2SO_4$) = 0.78 dL $g^{-1}$; IR $\nu_{max}$/$cm^{-1}$ 2985 (C-H), 1656 (C=O), 1591 (C-C), 1240 (C-O-C), 1163 (C-O-C); $^1$H NMR (400 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 8.19 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.92 (m, 8H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 8H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 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 sodium carbonate 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 MW, afforded polymer **N1c** (5.35 g, 77.0%). $T_g$ = 153 °C; $\eta_{inh}$ ($H_2SO_4$) = 0.73 dL $g^{-1}$; IR $\nu_{max}$/$cm^{-1}$ = 3000 (C-H), 1654 (C=O), 1588 (C-C), 1497 (C-C), 1236 (C-O-C), 1160 (C-O-C); $^1$H NMR (400 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 8.12 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.86 (m, 8H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8 Hz, 8H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 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), RbF (1.49 g, 14.28 mmol) and diphenylsulfone (35 g) were heated with stirring at 300 °C under argon for 2 hours. Using the same work-up procedure as described for polymer **N1a** afforded polymer **N1d** as a tan powder (1.05 g, 47.0%), $T_g$ = 153 °C; $\eta_{inh}$ ($H_2SO_4$) = 0.44 dL $g^{-1}$; IR $\nu_{max}/cm^{-1}$ 2982 (C-H), 1655 (C=O), 1589 (C-C), 1497 (C-C), 1238 (C-O-C); $^1H$ NMR (100 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 8.13 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.87 (m, 8H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 8H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 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 sodium carbonate with lithium carbonate (1.13 g, 15.4 mmol) and using an additional 2 x 200 mL of boiling water at the extraction stage to ensure removal of lithium fluoride. This gave polymer **N1e** (5.53 g, 78.2%). $T_g$ = 143 °C; $T_m$ = 304 °C; $\eta_{inh}$ ($H_2SO_4$) = 0.40 dL $g^{-1}$; IR $\nu_{max}/cm^{-1}$ = 1653 (C=O), 1588 (C-C), 1496 (C-C), 1235 (C-O-C), 1161 (C-O-C); $^1H$ NMR (400 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 8.13 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.87 (t, 8H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.20 (dd, *J* = 8, 4 Hz, 8H) ppm; $^{13}C$ NMR (100 MHz, CDCl3) δ 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 trifluoromethanesulfonic anhydride (3.36 mL, 20 mmol) and trifluoromethanesulfonic 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 NaOH 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%). M.p. (DSC) 248 °C (lit. 247-248 °C) [14]; FT-IR $\nu_{max}/cm^{-1}$ 3424 (O-H), 3229 (O-H), 1639 (C=O), 1579 (C-C), 1373 (C-O); $^1H$ NMR (400 MHz, $CDCl_3/CF_3COOH$ 6:1 v/v) δ 7.65 (d, $J$ = 2.0 Hz, 2H), 7.58 (dd, $J$ = 2.0, 8.4 Hz, 2H), 6.91 (d, $J$ = 8.4 Hz, 2H), 2.31 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3/CF_3COOH$): δ 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), $Na_2CO_3$ (1.16 g, 11.0 mmol) and diphenylsulfone (35 g) was heated with stirring to 300 °C under argon. The workup procedure for polymer **N1a** was followed to afford polymer **3** (3.40 g, 64%). $T_g$ = 168 °C, $\eta_{inh}$ ($H_2SO_4$) = 0.44 dL $g^{-1}$; $\nu_{max}/cm^{-1}$ 1736 (C-H), 1657 (C=O), 1584 (C-C), 1496 (C-C), 1233 (C-O-C); $^1H$ NMR (400 MHz, $CDCl_3/CF_3COOH$ 6:1 v/v) δ 8.18 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 7.2 Hz, 4H), 7.82 (s, 2H), 7.71 (m, 3H), 7.24 (d, *J* = 5.6 Hz 1H), 7.11 (m, 5H) 2.34 (s, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3/(CF_3)_2CHOH$ 6:1 v/v) δ 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 diphenylsulfone as solvent, at 300 °C in the presence of an alkali metal carbonate $M_2CO_3$ as base (Scheme 1; M = Na, K, or Rb), afforded high molecular weight poly(ether ketone)s **N1a**, **N1b** and **N1c** respectively, with inherent viscosities in the range 0.6 – 0.8 dL $g^{-1}$. A slight molar excess of the difluoroketone was used to control the final MW. Following exhaustive extraction of diphenylsulfone and inorganic salts, the polymers were dried and analysed by DSC. After heating to 350 °C the samples were cooled at 10 °C $min^{-1}$, but none showed evidence of crystallisation on cooling from the melt. However, on re-heating at the same rate (Figure 2), polymer **N1a** underwent a glass transition (onset at 149 °C), followed by a cold-crystallisation exotherm peaking at 245 °C, and finally a crystal melting endotherm at 300 °C. The other two polymers (**N1b** and **N1c**) showed only glass transitions, at 151 and 153 °C respectively.

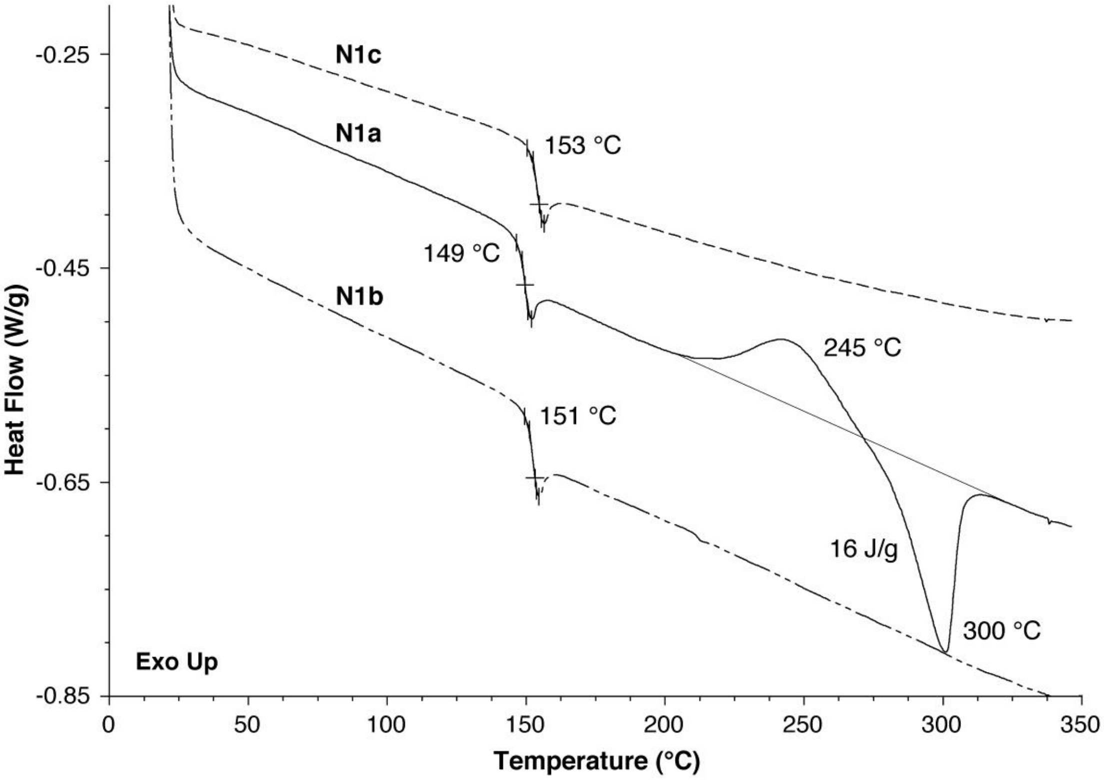


**Figure 2.** DSC scans (2nd heating, 10 °C min$^{-1}$) for polymers **N1a**, **N1b** and **N1c**.

It seemed possible that the observed variation in crystallisability between the three polymers could result from differences in their sequence-distributions, since transetherification with sequence-randomisation 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.[12,13] This possibility was confirmed by $^{13}$C NMR analysis (Figure 3) which showed useful diagnostic resonances in the range $\delta = 160 - 162$ 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 [EKEK*m*K]$_n$ (c.f. polymer **E1**), whereas polymers **N1b** and **N1c** show two additional "inner" peaks in the $^{13}$C–O-C region, with the relative intensity of these increasing substantially from **N1b** to **N1c** (Figure 3).

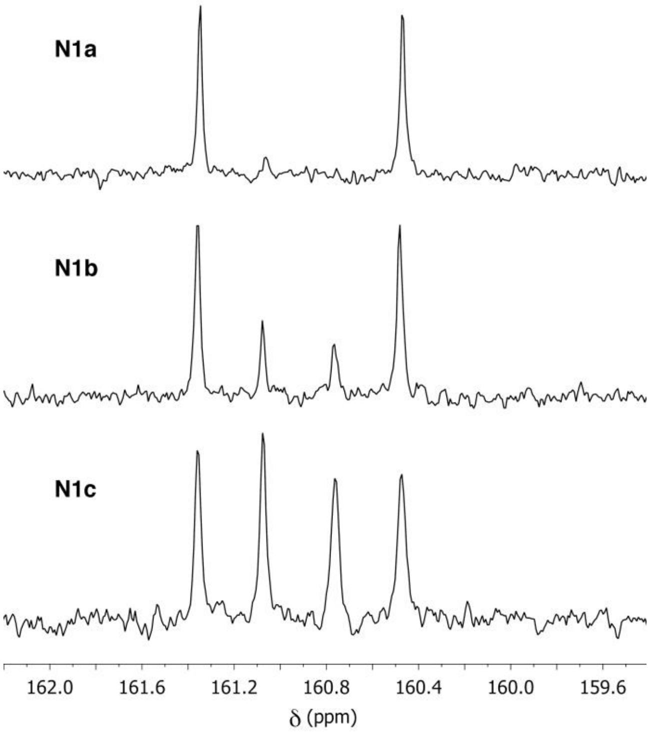
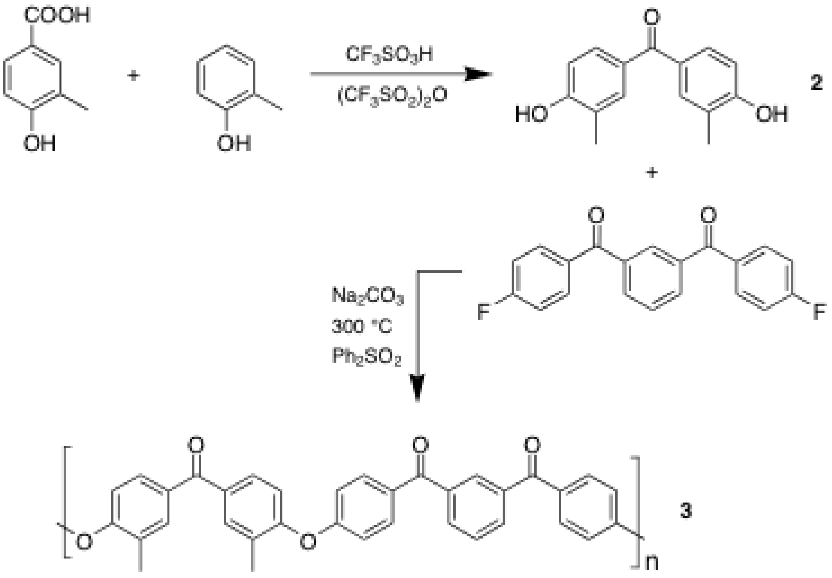


**Figure 3.** $^{13}$C NMR resonances in the C-O-C region for polymers **N1a, N1b** and **N1c**.

In order to aid the assignment of $^{13}$C–O–C peaks to the specific 2-ring and 3-ring residues, a dimethyl-substituted polymer, **3**, analogous to **N1a**, was synthesised. Direct condensation of *o*-cresol with 4-hydroxy-3-methylbenzoic acid in trifluoromethanesulfonic (triflic) acid gave very pure 3,3'-dimethyl-4,4'-dihydroxybenzophenone (**2**).[14] This condensed with 1,3-bis(4-fluorobenzoyl)benzene in the presence of $Na_2CO_3$ (Scheme 3) to give polymer **3**.



**Scheme 3.** Synthesis of bisphenol **2** and its derived poly(ether ketone) **3**.

In the $^{13}$C NMR spectrum of polymer **3**, two $^{13}$C–O-C resonances are still evident, but the lower-field $^{13}$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 4). This result strongly suggests that the lower-field resonance represents the $^{13}$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 subsituents are *ortho* to its $^{13}$C–O-C carbons.

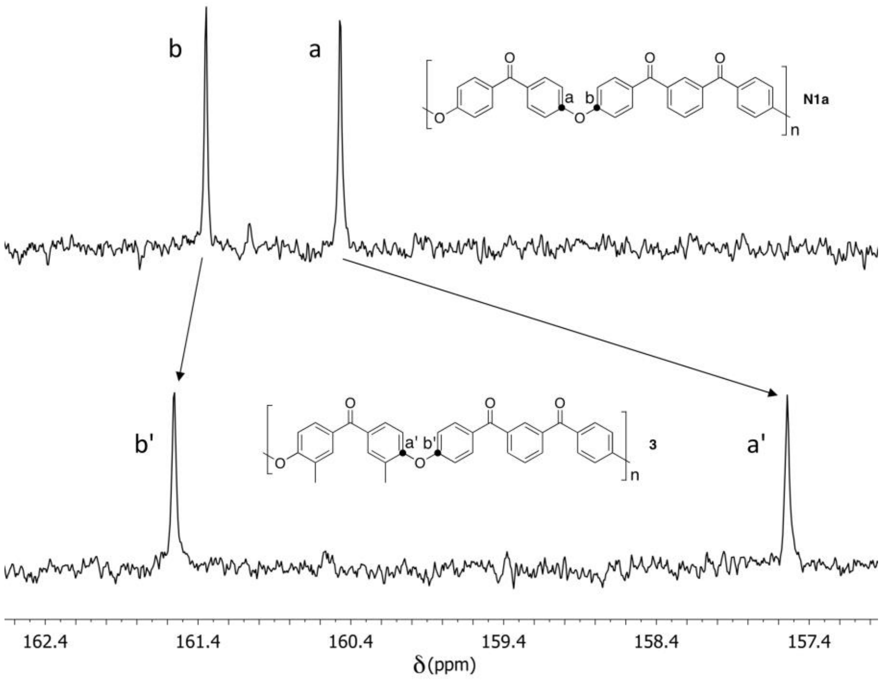


**Figure 4.** $^{13}$C NMR resonances in the C-O-C region for polymers N**1a** and **3**.

The $^{13}$C NMR spectra of polymers **N1b** and **N1c** however show two additional "inner" peaks in the $^{13}$C–O-C region (Figure 3). The increased multiplicity of peaks suggests sequence-randomisation could be occurring, and indeed the new peaks proved assignable to sequences comprising two adjacent 2-ring residues and two adjacent 3-ring residues. These assigments were achieved by doping samples of polymer **N1b** with the homopolymers PEK [15] and PEK*m*K [9] which resulted in enhancement of the intensities of the higher-field and lower-field "inner" peaks respectively (Figure 5).

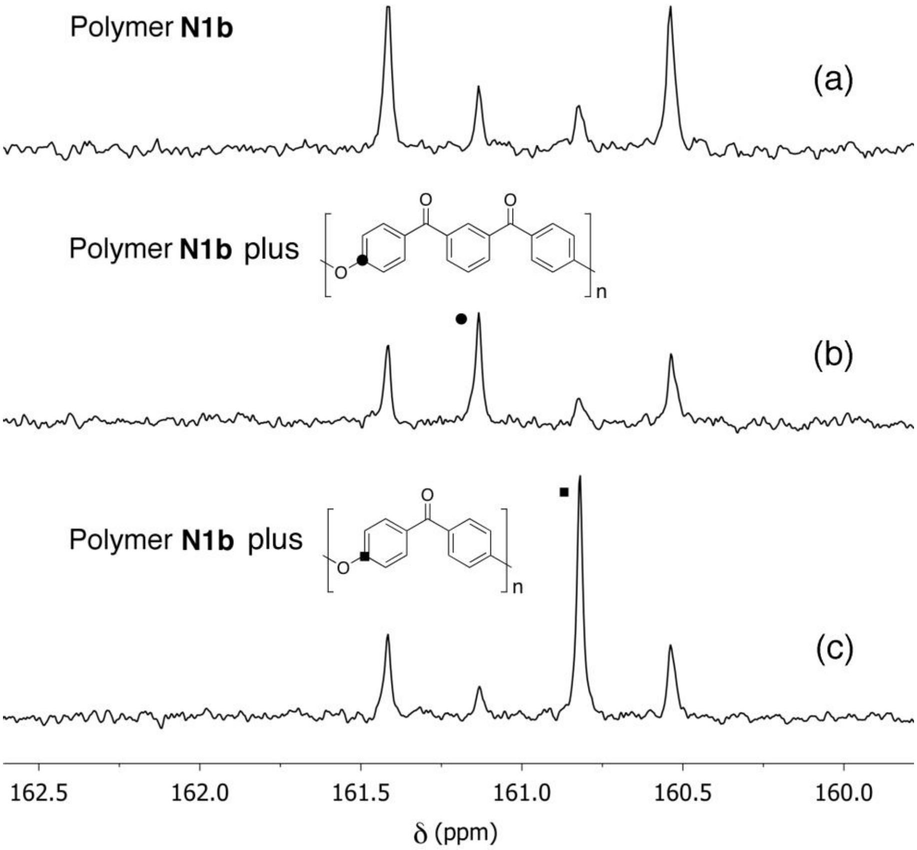
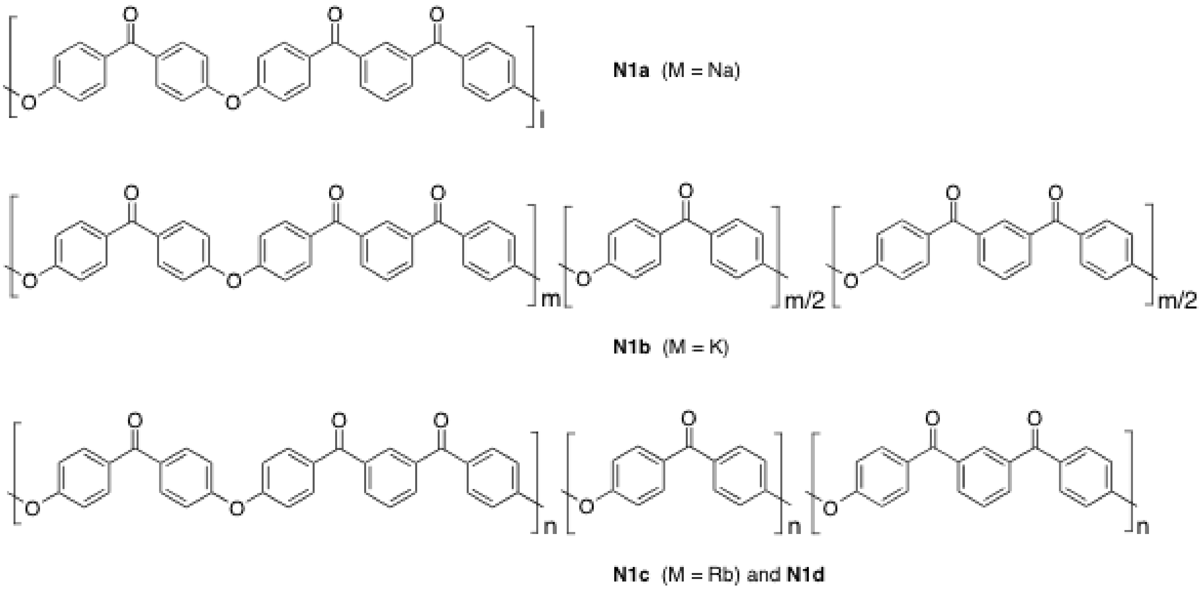


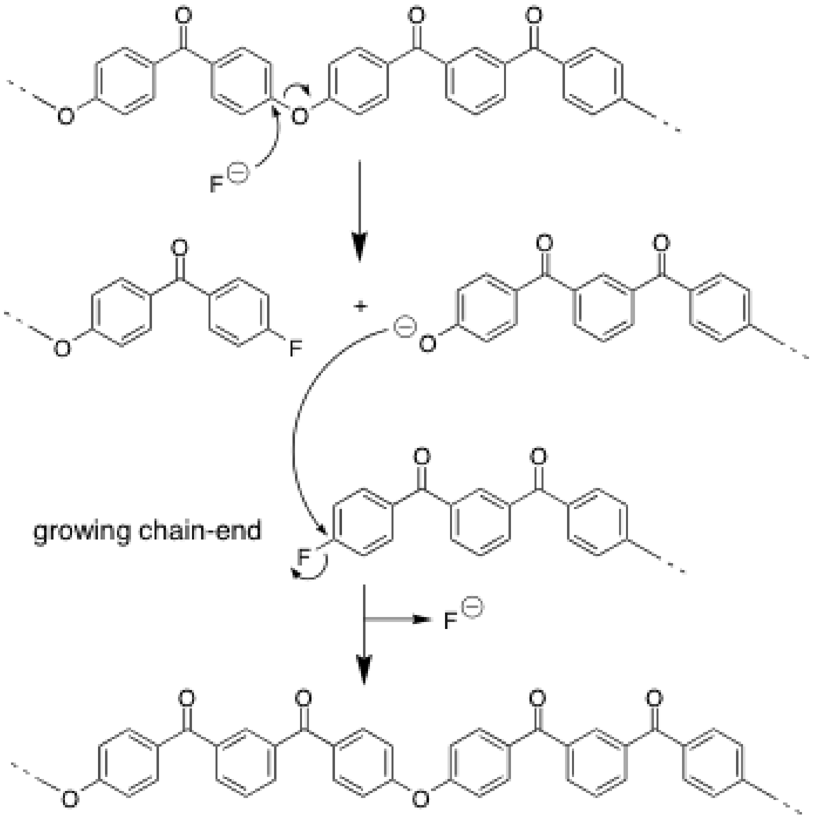
**Figure 5.** $^{13}$C NMR resonances in the C-O-C region for (a) polymer **N1b**, and the same polymer doped with either (b) PEK*m*K or (c) PEK.

The $^{13}$C NMR spectrum of polymer **N1c**, produced using rubidium carbonate, showed even more extensive sequence-randomisation than in **N1b**, now with four peaks of equal intensity in the $^{13}$C–O region (Figure 3). 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, KEK*m*K and K*m*KEK*m*K sequences in the relative proportions 1:2:1. This distribution would indeed give rise to four $^{13}$C NMR resonances of equal intensity (1:1:1:1) in this region of the spectrum, since the unsymmetrical KEK*m*K 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 ca. 50% randomisation, relative to a fully-alternating sequence. It is worth noting that the original report of polymer **N1** indicated that it was synthesised using a mixture of of sodium and potassium carbonates and that its melting point was 285 °C,[9] significantly lower than that that observed for polymer **N1a**. It thus seems very probable that a significant degree of sequence-randomisation 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 $^{13}$C NMR spectrum of **N1a**, shown in Figure 3 reveals a very weak but still detectable "inner" resonance corresponding to the symmetric, non-alternating sequence K*m*KEK*m*K. The relationships between polymers **N1a** – **N1d**, identified in the present work, are summarised in Scheme 4.



**Scheme 4.** Representations of the chain sequences in polymers **N1a** (almost entirely alternating), **N1b** (semi-randomised) and **N1c** (fully randomised), arising from the use of different alkali metal carbonates $M_2CO_3$ in the nucleophilic polycondensation shown in Scheme 1. Treatment of **N1a** with RbF results in its conversion to polymer **M1d**, having the same, fully-random, sequence as **N1c**.

A number of possible mechanisms have been proposed for transetherification during the synthesis of aromatic poly(ether ketone)s, but all depend on reversible, nucleophilic cleavage of the ether linkages (Scheme 5). 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 randomisation in an aromatic poly(ether ketone), albeit requiring very high reaction temperatures (340 °C) and long reaction times (6 h).[16] The fluoride ion can be a very strong nucleophile in dipolar aprotic solvents,[17,18] 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 rubidium fluoride should be much more effective than sodium fluoride, with potassium fluoride somewhere in between ($r_{\mathrm{ionic}}$ = 1.16, 1.52, 1.66 Å for 6-coordinate $Na^+$, $K^+$, and $Rb^+$ respectively).[19] This is fully consistent with our experimental results for sequence-randomisation in the synthesis of **N1**.



**Scheme 5.** Partial mechanism for fluoride catalysed sequence-randomisation in the synthesis of polymer **N1**. 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.

In the present work, sequence-randomisation catalysed by fluoride ion was demonstrated conclusively by treatment of the alternating polymer **N1a** with rubidium fluoride in diphenylsulfone, at the same concentrations, temperature and time as in polymer synthesis. The result was completely clear-cut, with the diagnostic $^{13}$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-randomisation, the polycondensation shown in Scheme 1 was carried out using *lithium* carbonate as base. The extremely low solubility of lithium fluoride in organic solvents[20] should strongly inhibit fluoride-catalysed transetherification and indeed, as shown in Figure 6, resonances arising from sequence randomisation were scarcely discernable in the $^{13}$C NMR spectrum of the resulting polymer (**N1e**).

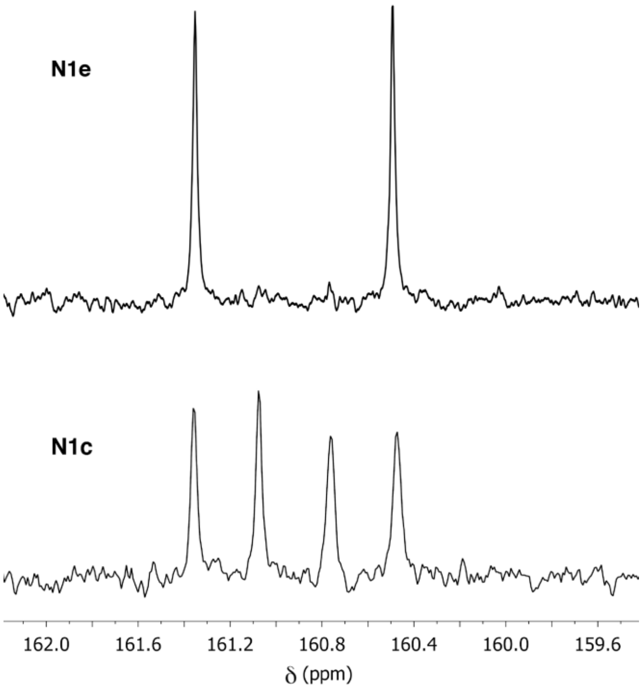


**Figure 6.** $^{13}$C NMR resonances in the C-O-C region for polymers **N1c** (fully randomised) and **N1e**, illustrating the virtual absence of sequence-randomisation in the latter polymer.

As shown in Figure 7, Polymer **N1e** also crystallised from the melt ($T_c$ = 215 °C) – unlike the other polymers described in this work – and showed a slightly higher $T_m$ value than **N1b** (304 vs 300 °C) and a much higher degree of crystallinity ($\Delta H_m$ = 49 vs 16 J/g), presumably the consequences of a more perfectly alternating chain-sequence.

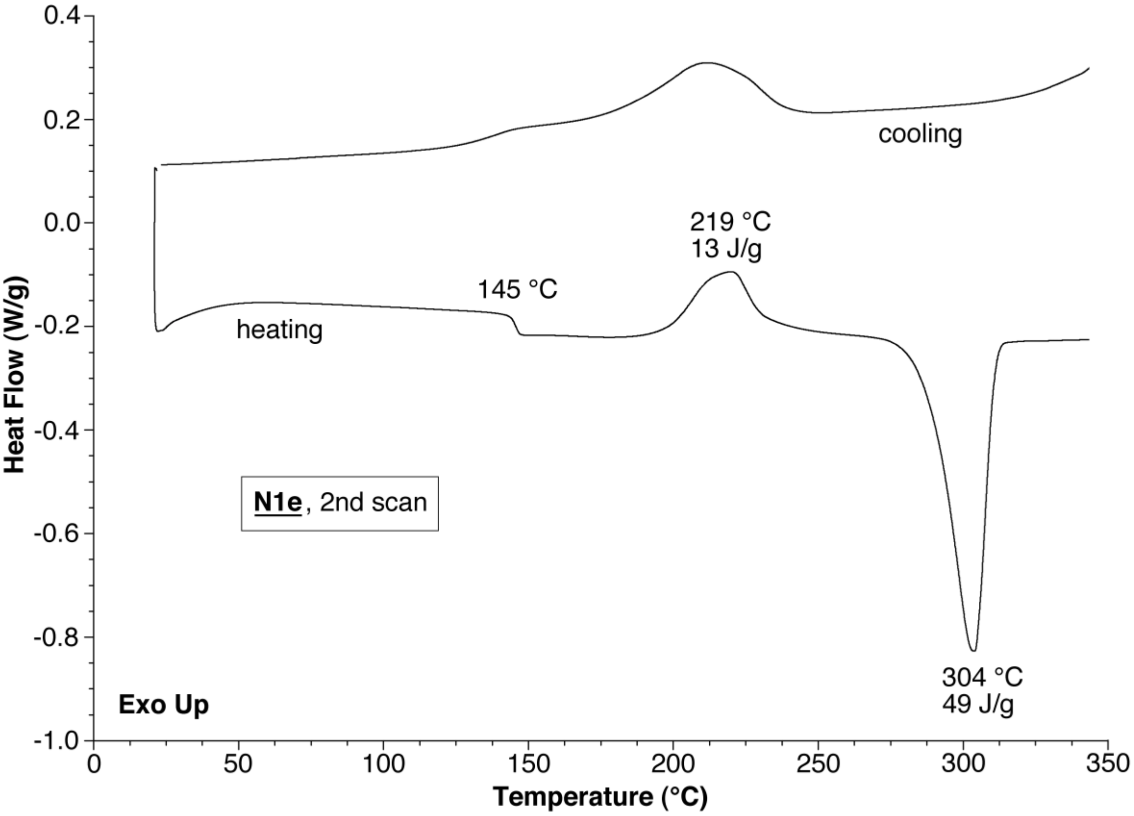


**Figure 7.** DSC scans (2nd heating and subsequent cooling scan, 10 °C $\text{min}^{-1}$) for polymer **N1e**.

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 °C – in addition to a conventional polymer melting peak in the range 230-300 °C – that increases in intensity with the degree of sequence-randomisation. 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 ± 0.05, $b$ = 6.04 ± 0.07 Å, two chains per cell).[10,21,22] 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-randomisation. Crystallisation of random-sequence copolymers is not of course unknown when the comonomer residues are isomorphic, 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-randomisation, via transetherification, during the nucleophilic synthesis of an aromatic poly(ether ketone) involving fluoride displacement from a bis(4-fluoroaryl)ketone can be controlled by varying the alkali metal cation ($Li^+$, $Na^+$, $K^+$, or $Rb^+$) present during polycondensation. The degree of transetherification 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-randomisation in the presence of rubidium fluoride. The crystallisability of the polymer from the melt declines markedly as the degree of sequence-randomisation increases, although crystallisation of the more highly randomised polymers from solution in diphenylsulfone affords an unusually low-melting crystalline phase whose nature remains to be established.

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## UNDERLYING DATA

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

## REFERENCES

1. Morgan RJ. Structure-property relations of epoxies used as composite matrices. *Adv Polym Sci* 1985; **72**: 1-43.

2. Landman D. Advances in the chemistry and applications of bismaleimides. In: Pritchard G (ed) *Developments in Reinforced Plastics.* Vol. 5. London: Elsevier, 1986, pp. 39-81.

3. Cogswell FN. *Thermoplastic Aromatic Polymer Composites*, Oxford: Butterworth-Heinemann, 1992.

4. Diez-Pascual AM and Naffakh M. Inorganic nanoparticle-modified poly(phenylene sulphide)/carbon fiber laminates: thermomechanical behaviour. *Materials* 2013; **6**: 3171-3193.

5. Wood A, Pandey D, Walling J, Lenferink R, Wijskamp S, Day R, Bennett J, Nesbitt A and Methven J. Manufacture of high performance thermoplastic composite structures. In: *SAMPE Conf. Proceedings*, Long Beach, USA, 2008 Vol **53**, 325/1-325/11.

6. Mazur RL, Oliveira PC, Rezende MC and Botelho EC. Environmental effects on viscoelastic behavior of carbon fiber/PEKK thermoplastic composites. *J Reinf Plast Compos* 2014; **33**: 749-757.

7. Staniland PA. Poly(ether ketones). In: Allen G and Bevington JC (eds) *Comprehensive Polymer Science*. Oxford: Pergamon, 1989, Vol. 5. pp. 483-497.

8. Schmitt-Thomas KG, Yang Z-G and Malke R. Failure behavior and performance analysis of hybrid-fiber reinforced PAEK composites at high temperature. *Compos Sci Technol* 1998; **58**: 1509-1518.

9. Staniland PA. Synthesis and properties of novel polyetherketones and polyethersulfones. *Bull Soc Chim Belges* 1989; **98**: 667-676.

10. Qiu Z, Mo Z, Sheng S and Song C. Crystal structure and variation in unit cell parameters with crystallization temperatures of poly (ether ketone ether ketone ketone)s containing *meta*-phenyl links (PEKEK*m*K). *Macromol Chem Phys* 2000; **201**: 2756-2759.

11. Qiu Z and Yang W. Isothermal and nonisothermal melt crystallization kinetics of a novel poly(aryl ether ketone ether ketone ketone) containing a *meta*-phenyl linkage. *J Appl Polym Sci* 2006; **102**: 4775-4779.

12. Colquhoun HM, Dudman CC, Blundell DJ, Bunn A, Mackenzie PD, McGrail PT, Nield E, Rose JB and Williams DJ. An aromatic polyether in which sequence-randomization leads to induction of crystallinity: X-ray structure of the crystalline phase $[-OArCOArArCOAr-]_n$ (Ar = 1,4-phenylene). *Macromolecules* 1993; **26**: 107-111.

13. Rao VL, Sabeena PU, Rao MR and Ninan KN. Synthesis and characterization of poly(ether sulfone) and poly(ether sulfone ketone) copolymers. *J Appl Polym Sci* 1999; **73**: 2113-2121.

14. Hubacher MH. 3,3'-Dimethyl-4,4'-dihydroxybenzophenone. *J Am Chem Soc* 1939; **61**: 2664-2665.

15. Attwood TE, Dawson PC, Freeman J, Hoy LRJ, Rose JB and Staniland PA. Synthesis and properties of polyaryletherketones. *Polymer* 1981; **22**: 1096-1103.

16. Fukawa I, Tanabe T and Hachiya H. Trans-etherification of aromatic polyetherketone and trans-etherification between aromatic polyetherketone and aromatic polyethersulfone. *Polym J* 1992; **24**: 173-186.

17. Finger GC and Kruse CW. Aromatic fluorine compounds. VII. Replacement of aromatic -Cl and -$NO_2$ groups by -F. *J Am Chem Soc* 1956; **78**: 6034-6037.

18. Markezich RL, Zamek OS, Donahue PE and Williams FJ. Reactions of 4-nitrophthalic anhydride with potassium fluoride and potassium nitrite. *J. Org. Chem*. 1977; **42**: 3435-3436.

19. Cotton FA and Wilkinson G. *Advanced Inorganic Chemistry*. 5th ed. Chichester: John Wiley, 1988. pp.1385-1388.

20. Wynn DA, Roth MM and Pollard BD. The solubility of alkali-metal fluorides in non-aqueous solvents with and without crown ethers, as determined by flame emission spectrometry. *Talanta* 1984; **31**: 1036-1040.

21. Dawson PC and Blundell DJ. X-Ray data for poly(aryl ether ketones). *Polymer* 1980; **21**: 577-577.

22. Ho R-M, Cheng SZD, Fisher HP, Eby RK, Hsiao BS and Gardner KH. Crystal morphology and phase identifications in poly(aryl ether ketone)s and their copolymers. 2. Poly(oxy-1,4-phenylenecarbonyl-1,3-phenylenecarbonyl-1,4-phenylene). *Macromolecules* 1994; **27**: 5787-5793.