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

Kate JC Lim¹, Paul Cross², Peter Mills² and Howard M Colquhoun¹

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,¹² 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 sulphide)⁴ and the aromatic poly(ether ketone) (PEKs), poly(ether ether ketone) (PEEK)⁵ and poly(ether ketone ketone) (PEKK; Figure 1).⁶ 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).⁷ However, such $T_m$s also require correspondingly high composite fabrication temperatures – up to 420°C.³⁸ 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 ($T_g = 152°C; T_m = 285°C$) 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 $T_m$ – 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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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.\textsuperscript{12,13}

**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$_2$SO$_4$) 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°C 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 ($^1$H) 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$_3$)$_2$CHOH (6:1 v/v) or CDCl$_3$/trifluoro acetic acid (CF$_3$COOH) (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'-diphenoxybenzophenone (3.00 g, 14.00 mmol), sodium carbonate (Na$_2$CO$_3$; 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

![Figure 1. Some thermoplastic aromatic matrix polymers used in carbon fibre composites.](image)

![Figure 2. Synthesis of polymer N1, also symbolized as PEKEKnK. ($M$ in $M_2$CO$_3$ = alkali metal). Atom labels refer to $^1$H NMR assignments; see Experimental section. $^1$H NMR: proton nuclear magnetic resonance; PEKEKnK: poly(ether ketone ether ketone ketone)s containing meta-phenyl links.](image)

![Figure 3. Synthesis of polymer E1. Note that the structures shown for N1 (Figure 1) and E1 are merely different representations of the same polymer chain sequence.](image)
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). 

Polymer N1b. This polymer was obtained using the procedure described for polymer N1a, but with potassium carbonate (2.13 g, 15.4 mmol) replacing Na2CO3 to give polymer N1b (6.00 g, 86.3%). 

Polymer N1c. The same procedure as described for polymer N1a was used, but replacing Na2CO3 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%). 

Polymer N1d. Polymeric 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%). 

Polymer N1e. The same procedure as described for polymer N1a was used, but replacing Na2CO3 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%). 

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%). 

Polymer 3. A mixture of bisphenol 2 (2.42 g, 10 mmol), 1,3-bis(4-fluorobenzoyl)benzene (3.28 g, 10.2 mmol), Na2CO3 (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%).
solvent, at 300°C in the presence of an alkali metal carbonate $M_2CO_3$ 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 0.6–0.8 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°C, the samples were cooled at 10°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°C), followed by a cold crystallization 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.

It seemed possible that the observed variation in crystallizability between the three polymers could result from differences in their sequence distributions since transetherification 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.$^{12,13}$ This possibility was confirmed by $^{13}$C NMR analysis (Figure 5), 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 (EKEKnK)$_n$ (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 5).

In order to aid the assignment of $^{13}$C–O–C peaks to the specific two-ring and three-ring residues, a dimethylsubstituted polymer (3), analogous to N1a, was synthesized.
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). This condensed with 1,3-bis(4-fluorobenzoyl)benzene in the presence of Na$_2$CO$_3$ (Figure 6) to give polymer 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 7). This result strongly suggests that the lower field resonance...
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). The fluoride ion can be a very strong nucleophile in dipolar aprotic solvents, 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 (rionic = 1.16, 1.52, 1.66 Å for 6-coordinate Na⁺, K⁺, and Rb⁺, respectively). 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 13C-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 should strongly inhibit fluoride-catalysed transesterification and indeed, as shown in Figure 11, resonances arising from sequence randomization were scarcely discernable in the 13C NMR spectrum of the resulting polymer (N1e).
As shown in Figure 12, polymer N1e also crystallized from the melt ($T_c = 215^\circ C$) – unlike the other polymers described in this work – and showed a slightly higher $T_m$ value than N1b ($304$ vs. $300^\circ C$) and a much higher degree of crystallinity ($\Delta H_m = 49$ vs. $16$ J g$^{-1}$), presumably the consequences of a more perfectly alternating chain sequence.

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. $174^\circ C$ – in addition to a conventional polymer melting peak in the range $230$–$300^\circ C$ – that...
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 (KEKmK, KEK and KmKEKmK) 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).\textsuperscript{10,20,21} 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 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 randomization, via transetherification, 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 (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 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.

Declaration of Conflicting Interests

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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, et al. Manufacture of high performance thermoplastic composite structures. In: SAMPE Conf. Proceedings, Long Beach, USA, Vol 53, 2008, 325/1-325/11.
6. Mazur RL, Oliveira PC, Rezende MC, et al. 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. Vol. 5. Oxford: Pergamon, 1989, 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, et al. Crystal structure and variation in unit cell parameters with crystallization temperatures of poly(ether ketone ether ketone ketone)s containing meta-phenyl links (PEKEKmK). 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. Coquelhoum HM, Dudman CC, Blundell DJ, et al. An aromatic polyether in which sequence-randomization leads to induction of crystallinity. X-ray structure of the crystalline phase [-OArCOArCOAr-]n (Ar = 1,4-phenylene). Macromolecules 1993; 26: 107–111.
13. Rao VL, Sabeena PU, Rao MR, et al. 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’-di-hydroxybenzophenone. J Am Chem Soc 1939; 61: 2664–2665.
15. 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.
16. Finger GC and Kruse CW. Aromatic fluorine compounds. VII. Replacement of aromatic –Cl and –NO2 groups by –F. J Am Chem Soc 1956; 78: 6034–6037.
17. Markezich RL, Zamek OS, Donahue PE, et al. Reactions of 4-nitrophthalic anhydride with potassium fluoride and potassium nitrite. J Org Chem 1977; 42: 3435–3436.
18. Cotton FA and Wilkinson G. Advanced Inorganic Chemistry. 5th ed. Chichester: John Wiley, 1988.
19. 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.
20. Dawson PC and Blundell DJ. X-Ray data for poly(aryl ether ketones). Polymer 1980; 21: 577–577.
21. Ho R-M, Cheng SZD, Fisher HP, et al. Crystal morphology and phase identifications in poly(aryl ether ketone)s and their copolymers. 2. Poly(oxy-1,4-phenylene-carbonyl-1,3-phenylene-carbonyl-1,4-phenylene). Macromolecules 1994; 27: 5787–5793.