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Polyetherketones from diarylcarboranes: a new approach to semi-inorganic polymers

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Linear polyetherketones containing both aromatic rings and icosahedral carborane (C_2B_{10}) cages in the main chain have been synthesized by superacid-promoted polycondensation between bis(4-phenoxyphenyl) derivatives of *ortho*- or *meta*-carborane and aromatic or aliphatic dicarboxylic acids. Under strictly anhydrous conditions, polymers of high molecular weight ($M_w > 150\,000$) are readily obtained. These new materials are amorphous and readily soluble in organic solvents, to give solutions from which strong, transparent films may be cast. Poly(aryletherketonecarborane)s are characterized by very high mass-retention (up to 93%) on thermolysis under nitrogen to 850°C, and demonstrate extreme resistance to combustion, losing as little as 3% of their mass on pyrolyis at 850°C in air. A new type of ionomer, based on the $[-C_2B_9H_{10}-]^-$ sub-unit, is obtained by deboronation of poly(aryletherketone-*ortho*-carborane)s under strongly basic conditions. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The extreme thermal stability of icosahedral carboranes has long attracted the interest of polymer chemists seeking to develop new materials for high-temperature applications[1]. However, only one class of polymeric carboranes, the elastomeric poly(carborane-siloxane)s, for example **1** (*Figure 1*), has ever reached commercial production[2]. This situation seems to reflect not only the very high cost of carborane-based starting materials, but also the difficulty of linking carborane cages in such a way that the stability of the carborane unit is not compromised[3].

In view of the high-temperature capabilities of thermoplastic materials such as **2** and **3**, which are based on aromatic structures linked by thermally and oxidatively stable units, i.e. ether, ketone, sulfone, or direct arene–arene bonds[4], we have attempted to develop linear, carborane-based polymers of the same general type. Here we report the synthesis and characterization of high molecular weight poly(aryletherketonecarborane)s derived from 1,2- and 1,7-dicarbadodecaborane (more generally known as *ortho*- and *meta*-carborane). A preliminary account of this work, describing a number of polyetherketones based on *ortho*-carborane, has appeared in communication form[5].

EXPERIMENTAL

Instrumentation and analysis

I.r. spectra of polymers were obtained from solvent-cast films using Perkin Elmer PE 577 and PE 1600FT spectrometers. ^1H, ^{11}B, and ^{13}C n.m.r. spectra were run on Varian Gemini-200 and Bruker AC250/WH360 instruments, and mass spectra were obtained on a VG 7070E spectrometer. Thermogravimetric analyses (t.g.a.) were carried out at $10°C\,min^{-1}$ on a Mettler DTG 760 instrument, evolved gas analyses (e.g.a.) on a Netzsch EG analyser, and differential scanning calorimetry (d.s.c.) measurements at $10°C\,min^{-1}$ heating rate on Mettler DSC 20 and TA 4000 systems. Solution viscosities were measured at 25°C on 0.1% polymer solutions using a Schott-Geräte CT 150 semi-automated viscometer. Gel permeation chromatography (g.p.c.) was carried out using THF solutions on PL-Gel columns (10^5, 10^3, and 10^2 Å, in series) using a Waters 590/R401 refractometer detector, and were calibrated using polystyrene standards. Laser light-scattering studies were carried out in THF solution over the concentration range 0.1–1.2% (w/v) using an Otsuka DLS-700 dynamic light-scattering spectrophotometer.

Starting materials

Decaborane and *ortho*- and *meta*-carborane were obtained from Katchem Ltd (Czech Republic). Trifluoromethanesulfonic acid was obtained from Fluorochem

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Ltd. and was distilled under dry nitrogen before use. Other materials were obtained from Aldrich and unless otherwise indicated were used as received.

Monomers

Dodecanedioic acid was dried at 60°C under vacuum and used without further purification. Biphenyl-4,4'-

Figure 1 Structures of a poly(carboranesiloxane) (**1**), a poly-(aryletherketone) (**2**), and a poly(biarylethersulfone) (**3**)

dicarboxylic acid and 4,4'-oxydibenzoic acid were purified by conversion to the corresponding aroyl chlorides which were then recrystallized from toluene. The aromatic dicarboxylic acids (mp > 350°C) were recovered from their purified aroyl chlorides by hydrolysis in boiling water, and were finally dried at 80°C under vacuum. The diether monomers 1,2-bis(4- phenoxyphenyl)-1,2-dicarbadodecaborane[6], mp 120–122°C (lit. 120–124°C), and 1,7-bis(4-phenoxyphenyl)-1,7-dicarbadodecaborane[7], mp 111–112°C (lit. 111–112°C) were prepared and purified according to the cited references.
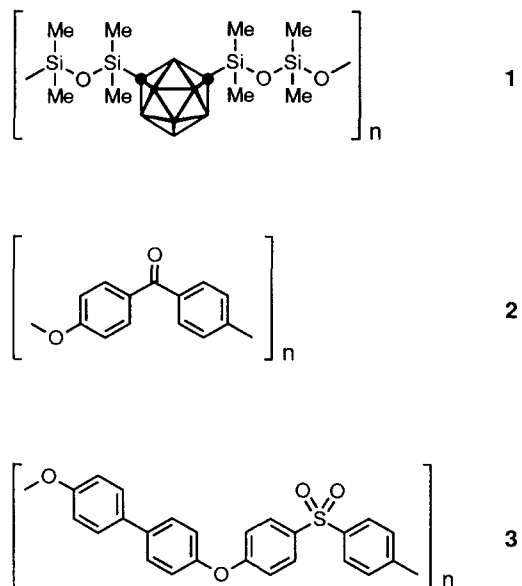
Polymerization procedure—synthesis of polymer 9

In a typical polycondensation, 4,4'-biphenyldicarboxylic acid (0.25 g, 1.03 mmol) and 1,7-bis(4-phenoxyphenyl)-1,7-dicarbadodecaborane (0.50 g, 1.04 mmol) were dissolved in anhydrous trifluoromethanesulfonic acid (9 cm^3) under dry nitrogen, and the reaction mixture was stirred for 20 h to afford a clear, viscous, orange-red solution. This solution was added dropwise with stirring to deionized water (250 cm^3), precipitating the polymer in the form of tough, pale pink beads. After precipitation was complete the beads were filtered off, stirred with 0.25 M sodium hydroxide in 1 : 1 ethanol/water at room temperature for 1 h, and finally stirred in refluxing ethanol for 30 min before filtering and drying under vacuum at 70°C. The resulting pale cream polymer (**9**) was obtained in 91% yield and was characterized by d.s.c. (T_g-onset at 210°C), solution viscometry in N-methyl-pyrrolidone (NMP) ($\eta_{inh} = 0.66 \, \mathrm{dl\,g}^{-1}$), and g.p.c. in

Table 1 Characterization data for poly(etherketonecarborane)s

Polymer structure	No.	η_{inh} (dl g^{-1})	T_g (onset, °C)	M_n/M_w (g.p.c.)
	9	0.66	210	45 900/90 400
	10	0.58	212	37 100/61 500
	11	0.88	183	83 900/170 000
	12	0.41	181	34 300/53 000
	13	0.66	87	48 100/90 300
	14	0.43	98	35 800/72 300

THF (M_n = 46 000; M_w = 90 000; dispersity index 1.97). Polymers **10–14** were prepared, isolated, and characterized using very similar procedures. Analytical data for these materials are given in *Tables 1* and *2*.

Conversion of polymer 10 to polymer 16 via deboronation

Polymer **10** (0.20 g, 0.28 mmol) was stirred under nitrogen in refluxing methanol (2.5 cm^3) containing potassium hydroxide (0.08 g, 1.43 mmol) until all the polymer had dissolved (*ca* 10 days). The solution was diluted with methanol (20 cm^3) and carbon dioxide passed in. The resulting precipitate was removed by filtration and washed with hot methanol (10 cm^3). The washings and filtrate were combined and the solvent removed under vacuum. The resulting solid was dissolved in 10 cm^3 of water/methanol (3 : 1) and the solution filtered before adding aqueous tetra-*n*-butylammonium bromide (0.10 g) dropwise with stirring.

The white precipitate was filtered off, washed with hot water, and dried under vacuum to afford 0.15 g (70%) of polymer **16**. The i.r. spectrum of a film cast from 2-methoxyethanol showed $\nu(CH_{Ar})$ at 3060/3037, $\nu(CH_{Aliph})$ at 2962/2934/2875, $\nu(BH)$ at 2527, and $\nu(C=O)$ at 1647 cm^{-1}. The ^{13}C n.m.r. spectrum (DMSO-d_6) showed resonances at δ 17.5, 23.2, 27.1, and 61.4 (*n*-butyl), 71.6 ($C_{carborane}$), 119.9, 122.7, 130.8, 134.0, 134.6, 135.9, 140.6, 142.1, 146.2, 155.9, 165.5, and 197.4 (C_{Ar}). Solution viscometry (0.1% in NMP) gave η_{inh} = 1.61 dl g^{-1}.

RESULTS AND DISCUSSION

Synthesis

The classical routes to aromatic polyetherketones involve either base-promoted nucleophilic condensation between a fluorobenzophenone and a phenol

Table 2 Spectroscopic and thermogravimetric data for poly(etherketonecarborane)s

| Polymer	I.r. (cast film, cm^{-1})	^{13}C n.m.r. (CDCl$_3$, δ)	Mass (%) retained at 850°C	
			(i) In nitrogen	(ii) In air
9	3066 w, 3016 w (νCH); 2603 s (νBH); 1654 s (νC=O); 1593 s, 1507 s (νCC$_{Ar}$); 1244 s (νC–O)	77.5 ($C_{carborane}$); 118.3, 119.8, 127.6, 130.1, 131.1, 131.6, 132.9, 133.4, 137.7, 144.2, 157.1, 161.1 (C_{Ar}); 195.3 ($C_{carbonyl}$)	92	96
10	3065 w, 3016 w (νCH); 2593 s (νBH); 1655 s (νC=O); 1592 s, 1500 s (νCC$_{Ar}$); 1248 s (νC–O)	85.3 ($C_{carborane}$); 118.6, 119.5, 126.9, 127.7, 131.1, 132.9, 133.1, 133.4, 137.6, 144.1, 158.1, 160.6 (C_{Ar}); 195.1 ($C_{carbonyl}$)	92	96
11	3067 w, 3016 w (νCH); 2604 s (νBH); 1656 s (νC=O); 1593 s, 1499 s (νCC$_{Ar}$); 1243 s (νC–O)	78.2 ($C_{carborane}$); 118.4, 119.1, 119.8, 130.0, 130.1, 131.6, 132.8, 133.2, 133.8, 156.9, 160.2 (C_{Ar}); 194.5 ($C_{carbonyl}$)	93	97
12	3068 w, 3016 w (νCH); 2592 s (νBH); 1655 s (νC=O); 1592 s, 1499 s (νCC$_{Ar}$); 1243 s (νC–O)	85.3 ($C_{carborane}$); 118.6, 119.1, 119.4, 126.9, 132.8, 133.1, 133.5, 133.7, 158.1, 160.3 (C_{Ar}); 194.4 ($C_{carbonyl}$)	93	96
13	3065 w, 3018 w (νCH$_{Ar}$); 2927 m (νCH$_{aliph}$); 2605 s (νBH); 1680 s (νC=O); 1594 s, 1500 s (νCC$_{Ar}$); 1244 s (νC–O)	24.9, 29.8, 29.9, 30.1, 38.9 ($C_{aliphatic}$); 77.1 ($C_{carborane}$); 118.5, 119.7, 130.1, 130.8, 131.4, 132.9, 156.1, 160.7 (C_{Ar}); 194.1 ($C_{carbonyl}$)	43	72
14	3066 w (νCH$_{Ar}$); 2924 s (νCH$_{aliph}$); 2610 s (νBH); 1681 s (νC=O); 1593 s, 1499 s (νCC$_{Ar}$); 1244 s (νC–O)	24.4, 29.4, 29.5, 29.6, 38.5 ($C_{aliphatic}$); 84.8 ($C_{carborane}$); 118.2, 118.7, 126.2, 130.3, 132.4, 132.7, 157.5, 159.9 (C_{Ar}); 198.8 ($C_{carbonyl}$)	51	74
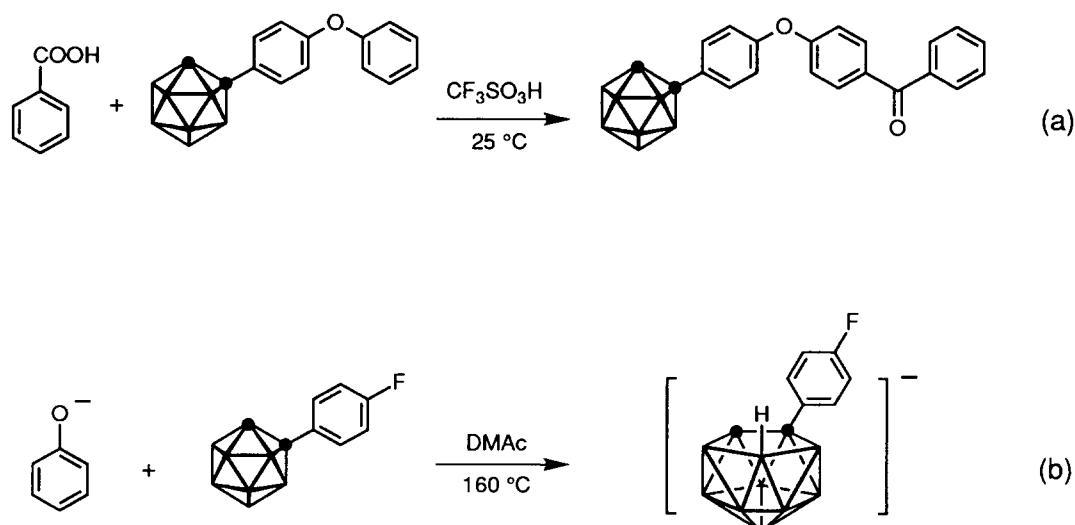
Figure 2 Model reactions for possible electrophilic and nucleophilic syntheses of poly(arylethercarborane)s

(the polyether synthesis)[8] or electrophilic condensation of a carboxylic acid or acid chloride with an aromatic either (the polyketone synthesis), a reaction promoted by superacids such as HF/BF_3 or trifluoromethanesulfonic acid[9]. Both possible approaches to the synthesis of carborane-based polyetherketones have been evaluated using model compounds[10]. Thus, electrophilic condensation of benzoic acid with a phenoxyphenyl derivative of *ortho*-carborane in anhydrous trifluoromethanesulfonic acid as solvent and catalyst (*Figure 2a*) at room temperature proceeded in high yield, with no evidence of cage degradation and with very high regioselectivity (>99% *para*-substitution by ^1H n.m.r.). In contrast, attempts to use the known electron-withdrawing power of the carborane cage to activate nucleophilic displacement of fluoride from an adjacent aromatic ring (*Figure 2b*) led only to cage-deboronation by the

phenoxide nucleophile[10], strongly suggesting that aromatic etherification is unlikely to provide a viable approach to *o*-carborane-based polyetherketones.

On the basis of the above model reactions, the bis(4-phenoxyphenyl)carborane derivatives **4** and **5**, the aromatic dicarboxylic acids **6** and **7**, and the aliphatic (C_{12}) diacid **8** (*Figure 3*) were chosen as potential monomers for electrophilic polycondensation in trifluoromethanesulfonic acid.

Preliminary studies of the reaction between **5** and **6** (*Figure 4*) confirmed that the polycondensation proceeded as anticipated from model reactions, but also demonstrated that the purity of the trifluoromethanesulfonic acid was a critical factor governing the molecular weight achieved. Acid which was freshly distilled under nitrogen yielded a polymer of inherent viscosity (η_{inh}) $0.66\,dl\,g^{-1}$, whereas reactions using undistilled acid gave polymers with η_{inh} no higher than $0.24\,dl\,g^{-1}$, and often a good deal lower. This result may well indicate the presence of a relatively high concentration of water in commercial 'anhydrous' trifluoromethanesulfonic acid.

High molecular weight polymers were subsequently obtained from all six combinations of the three diacids (**6–8**) and two diethers (**4** and **5**) using distilled trifluoromethanesulfonic acid as solvent and catalyst. Full characterization data for these new materials are given in *Tables 1* and *2*.

Structure

All the polymers shown in *Table 1* were essentially amorphous by d.s.c., and proved readily soluble in polar organic solvents such as chloroform, THF and NMP. Inherent viscosities (0.1% in NMP) were in the range $0.40–0.90\,dl\,g^{-1}$, and analysis by g.p.c. (in THF) suggested molecular weights (M_w) in the range 50 000–170 000 Daltons relative to polystyrene, with dispersity indices of 1.5–2.1. The general validity of the g.p.c. results was checked by an independent measurement of M_w for polymer **12**, based on a laser light scattering study. In the event, the light-scattering value for M_w of 59 000 Daltons differed by only some 10% from the g.p.c. result (*Table 1*). Tough, transparent films of all six polymers were readily obtained by evaporation of chloroform or dichloromethane solutions, and i.r. spectra of such films (*Figure 5*) confirmed the presence of aromatic or
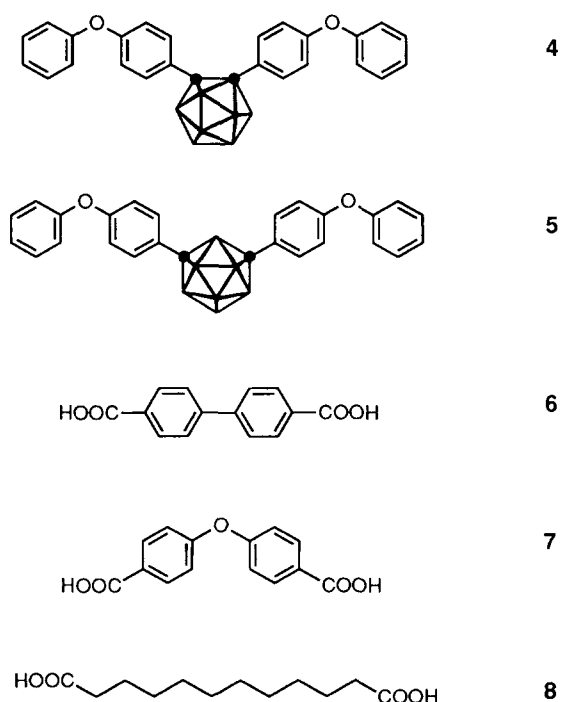

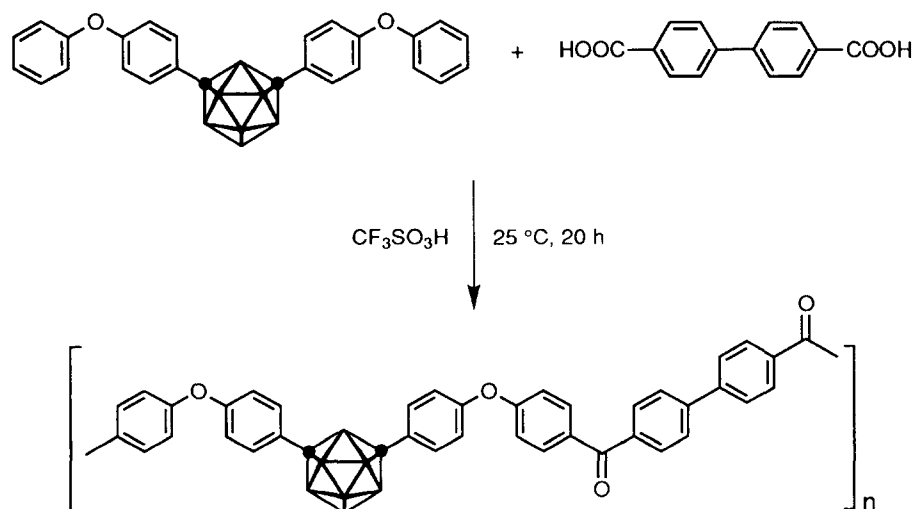**Figure 3** Monomers used for synthesis of poly(arylethercarborane)s

Figure 4 Polycondensation of 1,7-bis(4-phenoxyphenyl)-1,7-dicarbadodecaborane with biphenyl-4,4'-dicarboxylic acid

aliphatic/aromatic ketone groups (νC=O at 1655 or 1680 cm^{-1}, respectively), aromatic ether (νC–O at 1245 cm^{-1}), aromatic hydrogen (νC–H at 3050 cm^{-1}), and icosahedral carborane units (νB–H at 2605 cm^{-1}) units.

Polyacylation of bis(4-phenoxyphenyl)carboranes in trifluoromethanesulfonic acid was found to proceed with very high *para*-selectivity. Thus, the ^{13}C n.m.r. spectrum of polymer 9 (*Figure 6*) displays no resonances other than those assignable to an all-*para* aromatic substitution pattern; the signal-to-noise ratio of this spectrum demonstrates that the selectivity ratio for *para*- over *ortho*-acylation in the present polycondensation must exceed 200 : 1.

Thermochemical characteristics

Introduction of the rigid, bulky diarylcarborane unit into the backbone of an aromatic polyetherketone results in a significant increase in glass transition temperature. Polymer 11, for example, can be derived formally from the prototypical polyetherketone PEK (2)[11] by replacing every third ketone group with a *meta*-carborane unit. This results in an increase of some 30°C in T_g, but only at the expense of complete loss of crystallinity. There appears to be little difference between *ortho*- and *meta*-carborane residues in terms of their effect on T_g, the isomeric polymers 9 and 10, for example, having almost identical T_gs (212 and 210°C, respectively). Glass transition data for polymers 9–14 are given in *Table 1*.

For all polymers studied in this work, d.s.c. measurements indicated the onset of an exothermic process above *ca* 420°C. Thermogravimetric analysis (t.g.a.) under nitrogen showed evolution of volatile decomposition products

from approximately the same temperature and, for polymer 9, evolved-gas analysis in the temperature range 300–850°C showed the decomposition process to be associated mainly with evolution of carbon monoxide, hydrogen, water, and traces of benzene. The polymers (9–12) derived from aromatic diacids afforded extremely high 'ceramic yields' on pyrolysis in nitrogen (90–93% at 850°C), much higher than the semi-aliphatic polymers 13 and 14 based on dodecanedioic acid (*Table 2*). The very high mass-retention values observed for the former polymers are especially noteworthy, suggesting that these air-stable and readily-soluble materials may hold promise as precursor polymers for graphitic boron carbide[12]. Extended pyrolysis of polymer 10 at 1600°C under argon led to further evolution of carbon monoxide and produced a final ceramic yield of 79%, corresponding reasonably well to the value (80.5%) expected from equation (1):

$$2[C_{40}H_{34}B_{10}O_4]_n \rightarrow 5B_4C + 69C + 6CO$$
$$+ 2H_2O + 32H_2 \qquad (1)$$
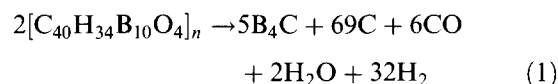
Thermolysis (t.g.a.) in air at up to 850°C led to mass-retention values for polymers 9–12 of around 97%. In contrast, it should be noted that conventional, all-aromatic polyetherketones such as $[-ArOArOArCOArArCO]_n$ (Ar = 1,4-C$_6$H$_4$, polymer 15)[9] retain less than 5% of their mass under these conditions (*Figure 7*). Since the mass-retention value calculated for complete combustion of polymer 9 to B$_2$O$_3$ is only 50%, our result suggests that superficial oxidation of the carborane-based materials must lead to formation of a surface-coating of inert, involatile boron(III) oxide, B$_2$O$_3$, which drastically limits further oxidative degradation.
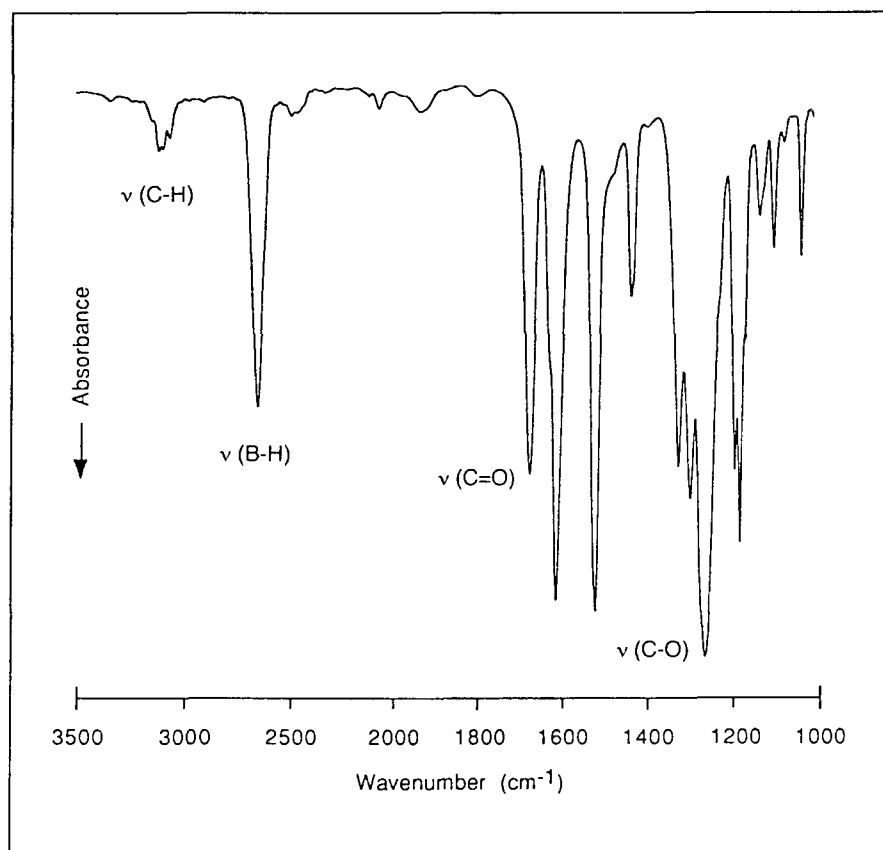

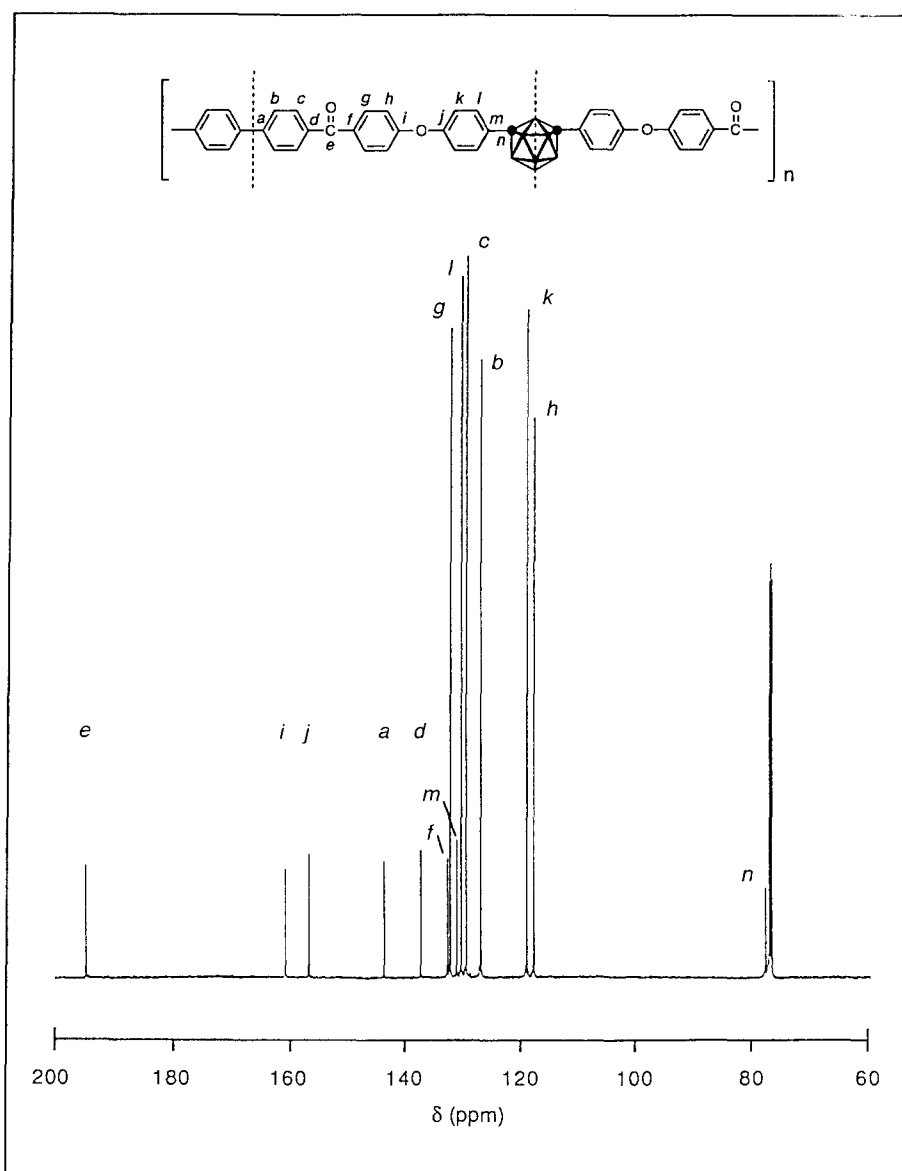**Figure 5** Infra-red spectrum of polymer 11 (film from chloroform)

Figure 6 The ^{13}C n.m.r. spectrum of polymer **9** (CDCl$_3$). Positions of individual resonances are shown in *Table 2*

It thus appears that the introduction of even a small proportion of icosahedral carborane units into an aromatic polyetherketone chain greatly enhances the already significant fire-retardant character of this type of polymer. In keeping with such extreme combustion-resistance, attempts to obtain elemental analyses of the poly(ether-ketonecarborane)s described here proved unsuccessful.

Polymer deboronation

In view of the hydrolytic stability of aromatic ether-ketone units and of the arene-carborane bond[10], it seemed possible that a new type of ionomer might be accessible by deboronation of poly(etherketonecarborane)s under strongly basic conditions (*Figure 8*). This type of reaction is known to be reasonably facile and essentially quantitative for many derivatives of *ortho*-carborane, and indeed the deboronation of polymer (**10**) was achieved by reaction with 0.5 M potassium hydroxide in methanol at reflux.

The resulting methanol-soluble polymer was precipitated as its tetra-*n*-butyl ammonium salt (**16**). I.r. spectra confirmed the presence of aromatic carbonyl groups

(νCO = 1647 cm^{-1}) and of *nido*-carborane residues (νBH = 2527 cm^{-1}), and ^{13}C n.m.r. (see Experimental section) indicated that the all-*para* aromatic substitution pattern was retained. In keeping with formation of an ionomer, solution viscometry in NMP showed a substantial increase in inherent viscosity, from 0.66 for polymer **10** to 1.61 dl g^{-1} for polymer **16**.

The anionic, *nido*-carborane residues present in ionomer **16** clearly provide scope for further derivatization. Formation of transition metal 'sandwich' complexes by such residues is for example particularly well established, leading in the present situation to the possible establishment of a novel metallo-cross-linking chemistry.

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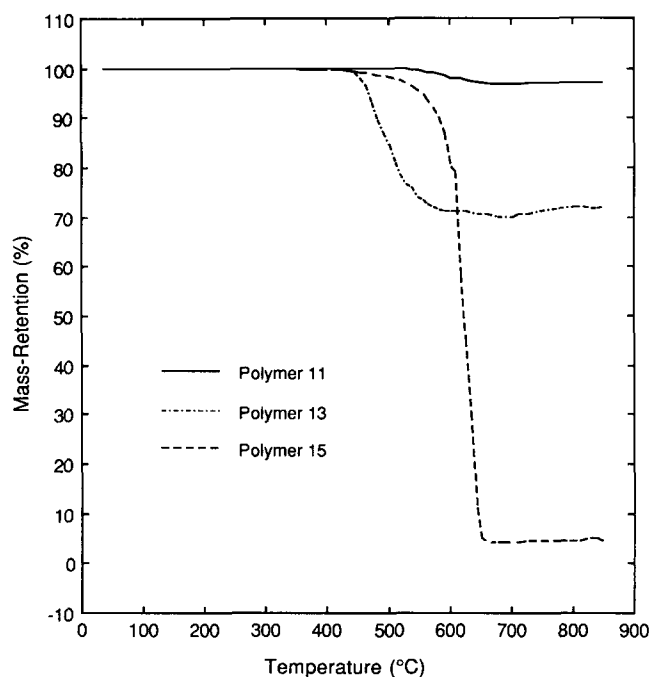
Figure 7 Thermogravimetric analyses (in air) of carborane-based and all-organic polyetherketones

Figure 8 Deboronation of polymer **10** to give the ionomer **16**

access to light-scattering instrumentation, and Miss R. K. Pinfield for experimental assistance.

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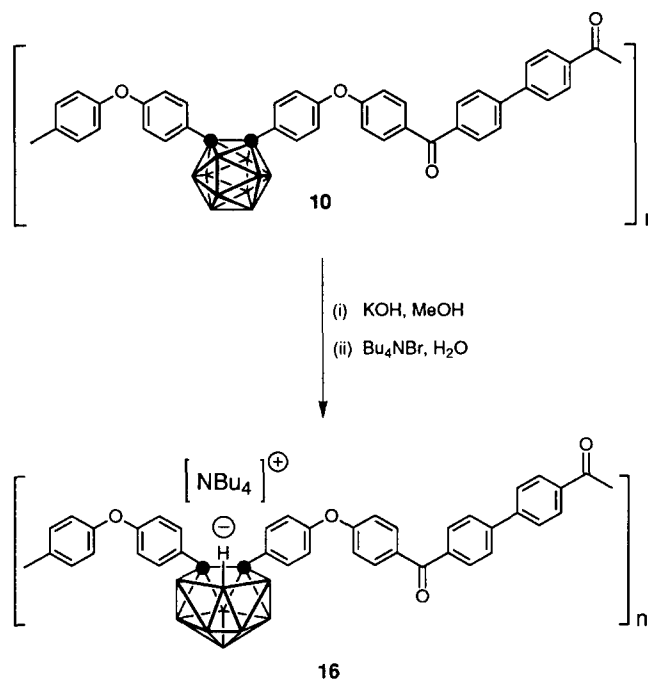5. Colquhoun, H. M., Daniels, J. A., Stephenson, I. R. and Wade, K. *Polym. Commun.* 1991, **32**, 9.
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