PII: S0032-3861(96)01016-6

# Polyetherketones based on *para*-carborane: synthesis, sulfonation, and membrane-forming characteristics

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Polycondensation of bis(4-phenoxyphenyl)-1,12-dicarbadodecaborane with aromatic and aliphatic dicarboxylic acids in trifluoromethanesulfonic acid affords a new family of high-MW poly(aryletherketone-carborane)s. The polymers derived from 4,4'-biphenyldicarboxylic acid and 4,4'-oxydibenzoic acid are both essentially amorphous when isolated, but the former undergoes an unusual cold-crystallization process beginning at, rather than above, its glass-transition temperature (267°C), and melts at 386°C. Solutions of the polycarborane derived from 4,4'-oxydibenzoic acid afford high-performance ultrafiltration membranes when gelled in water, with molecular weight cut-off values in the range 9000–16000 daltons. Poly(aryletherketone-carborane)s undergo quantitative, structure-defined sulfonation in 98% sulfuric acid, resulting in the controlled introduction of two sulfonic acid groups per repeat unit. The resulting ionomers are insoluble in water but readily soluble in the lower alcohols, to give solutions from which thin-film composite nanofiltration membranes may be fabricated. Such membranes exhibit water-fluxes and ion-selectivities which compare favourably to those of many commercial nanofiltration membranes. © 1997 Elsevier Science Ltd.

(Keywords: polyaryletherketone; *p*-carborane; sulfonation; membrane)

## INTRODUCTION

The conformational rigidity and extreme stability of icosahedral carboranes have led, in the past, to considerable interest in the development of carborane-based polymers for high-performance applications[1]. However, of such materials only the elastomeric poly-(carborane-siloxane)s (for example polymer **1**, *Figure 1*) are manufactured on a commercial scale[2]. This situation seems to reflect not only the high cost of carborane-containing monomers, but also the difficulty of connecting carborane cages in such a way that the stability of the carborane fragment is not compromised by the chemical characteristics of the linking group[3].

It is well-established that *aromatic* sub-units connected either directly, or by thermally- and chemically-stable linking groups such as ether, sulfone, and ketone[4], provide polymers (e.g. **2** and **3**, *Figure 1*) with excellent thermo-mechanical performance, and with the very high mechanical strength and chemical stability required for thin-film separation-membranes[5]. As part of a more general programme to develop new polymeric materials for membrane technology, we have investigated the synthesis, physical properties and substitution-chemistry of *para*-carborane-based polymers containing similar types of linking group (diarylether, ketone, and

biphenyl), and we now report on the potential of such polymers as membrane-forming materials.

## EXPERIMENTAL

Analytical techniques and instrumentation were as described in a previous paper[6]. Starting materials were sourced from Katchem Ltd, Czech Republic (*para*-carborane), Fluorochem Ltd, Glossop, UK (trifluoromethanesulfonic acid), Fluka, Gillingham, UK (polyethyleneglycols PEG 1000 and 10000) and the Aldrich Chemical Co. Ltd, Gillingham, UK. Unless otherwise indicated, reagents were used as received.

### Monomers

Biphenyl-4,4'-dicarboxylic acid and 4,4'-oxydibenzoic acid were purified as previously described, by recrystallization of the corresponding aroyl chlorides and subsequent hydrolysis in boiling water[6]. Terephthalic acid, azelaic acid, dodecanedioic acid, and hexadecanedioic acid were dried at 60°C under vacuum and used without further purification.

The diether monomer 1,12-bis(4-phenoxyphenyl)-1,12-dicarbadodecaborane was obtained as follows. To a solution of 1,12-dicarbadocaborane (1.44 g, 10 mmol) in dry 1,2-dimethoxyethane (50 cm³), under nitrogen, was added *n*-butyl lithium (13.2 cm³ of a 1.6 M solution in hexane, 22 mmol) followed by pyridine (6 cm³) and copper(I) chloride (2.02 g, 20 mmol). The solution was cooled to −20°C and 5.96 g (23 mmol) of freshly

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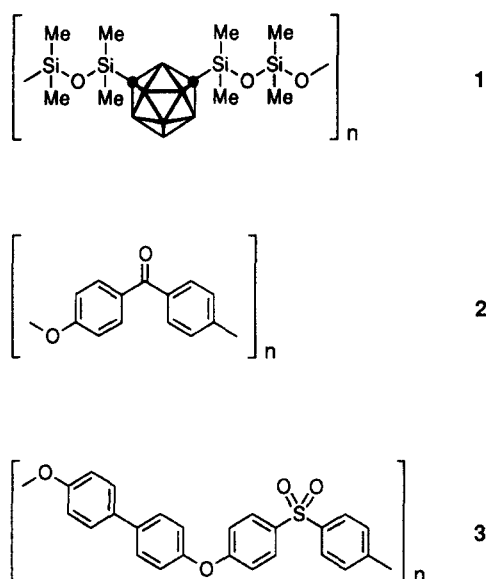
Figure 1 Structures of a poly(carboranesiloxane) (**1**), a poly-(aryletherketone) (**2**), and a poly(biarylethersulfone) (**3**)

sublimed 4-iodophenyl (phenyl)ether was added with stirring. The reaction mixture was allowed to warm to room temperature and was refluxed for 48 h before diluting with diethyl ether (100 cm$^3$). The solution was filtered and the filtrate was extracted with 2 M hydrochloric acid (4 × 25 cm$^3$) and water (4 × 50 cm$^3$) before drying over magnesium sulfate, filtering, and evaporating to ca. 25 cm$^3$, affording an orange solution containing suspended white crystals. This solid was filtered off and recrystallized from hexane to afford 2.48 g of the desired product. The original supernatant and the

mother-liquor from the recrystallization were combined, evaporated to dryness, and chromatographed on silica with pentane as eluent to afford a further 1.24 g of product, identified as *1,12-bis(4-phenoxyphenyl)-1,12-dicarbadodecaborane*, m.p. 206–207°C. Total yield 78%. Found: C, 65.13; H, 6.02%. Calculated for $C_{26}B_{10}H_{28}O_2$: C, 64.98, H, 5.87%. The mass spectrum showed M$^+$ ($B_{10}$ isotope pattern) in the range 476–484 daltons. Purity by d.s.c. was > 99%.

The diacid monomer 1,12-bis(4-carboxyphenyl)-1,12-dicarbadodecaborane was synthesized as follows. To a solution of 1,12-dicarbadocaborane (1.44 g, 10 mmol) in dry 1,2-dimethoxyethane (50 cm$^3$), under nitrogen, was added *n*-butyl lithium (13.2 cm$^3$ of a 1.6 M solution in hexane, 22 mmol) followed by pyridine (6 cm$^3$) and copper(I) chloride (2.02 g, 20 mmol). The solution was cooled to −20°C and 4.36 g (20 mmol) of 4-iodotoluene (freshly sublimed) was added with stirring. The reaction mixture was allowed to warm to room temperature and was refluxed for 48 h before diluting with diethylether (100 cm$^3$). The solution was filtered and the filtrate was extracted with 2 M hydrochloric acid (4 × 25 cm$^3$) and water (4 × 50 cm$^3$) before drying over magnesium sulfate, filtering, and evaporating to afford an orange solid. This was purified by column chromatography with cyclohexane/ethyl acetate (95/5) as eluent to give white, crystalline *1,12-bis(4-methylphenyl)-1,12-dicarbadodecaborane*, m.p. 232–233°C, in 84% yield. Found: C, 59.23; H, 7.46%. Calculated for $C_{16}B_{10}H_{24}$: C, 59.08; H, 7.43%. This compound (0.30 g, 0.78 mmol) was suspended in a mixture of glacial acetic acid (13 cm$^3$) and acetic anhydride (5 cm$^3$), and chromium trioxide (0.78 g, 7.8 mmol) was added with stirring. After 2 h the initially red-brown solution had become dark green, and this was then poured into water (80 cm$^3$). The resulting solid was

Table 1 Characterization data for poly(etherketone-*para*-carborane)s

| Polymer Structure | Code | $\eta_{inh}$ (dl g$^{-1}$) | $T_g^{onset}/T_m^{peak}$ (°C) | $M_n/M_w$ (g.p.c.) |
|---|---|---|---|---|
|  | 4 | 1.09 | 236/− | 53 800/111 400 |
|  | 5 | 1.21 | 267/386 | 155 000/254 200 |
|  | 6 | 0.86 | 267/317$^c$ | — |
|  | 7 | 0.85 | 140/− | 53 700/ 81 200 |
|  | 8 | 1.28 | 120/− | — |
|  | 9 | 0.85$^a$ | 91/122$^b$ | 20 100/ 66 900 |

$^a$ In chloroform (others in NMP)
$^b$ After solvent-induced crystallization in NMP
$^c$ Weak and irreversible endotherm

filtered off, washed with water, and dried. This solid was dissolved in saturated aqueous sodium hydrogen carbonate, the solution filtered, and then acidified with 2 M hydrochloric acid to reprecipitate the product, identified after filtering off and drying at 60°C under vacuum as *1,12-bis(4-carboxyphenyl)-1,12-dicarbadodecaborane*, 0.28 g, 94%. Found: C, 49.35; H, 5.22%. Calculated for $C_{16}B_{10}H_{20}O_4$: C, 50.85; H, 5.25%. m.p. > 350°C. The mass spectrum showed $M^+$ ($B_{10}$ isotope pattern) in the range 379–387 daltons.

*Polymerization procedure 1—synthesis of polymer 4* (Table 1)

In a typical polycondensation, 4,4'-oxydibenzoic acid (0.26 g, 1.00 mmol) and 1,12-bis(4-phenoxyphenyl)-1,12-dicarbadodecaborane (0.49 g, 1.02 mmol) were dissolved in anhydrous trifluoromethanesulfonic acid (9 cm³) 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 cm³), 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 1/2 h before filtering and drying under vacuum at 70°C. The resulting white polymer (4) was obtained in 95% yield and was characterized by d.s.c. ($T_g^{onset}$ at 236°C), solution viscometry in NMP ($\eta_{inh} = 1.09 \, dl \, g^{-1}$), and g.p.c. in THF ($M_n = 54000$; $M_w = 111000$). Polymers 5 and 7–9 were also prepared and isolated using this procedure. Full characterization data are given in *Tables 1* and 2.

*Polymerization procedure 2—synthesis of polymer 6* (Table 1)

Terephthalic acid (0.166 g, 1.00 mmol) and 1,12-bis(4-

phenoxyphenyl)-1,12-dicarbadodecaborane (0.49 g, 1.02 mmol) were stirred at room temperature in a mixture of anhydrous trifluoromethanesulfonic acid (9 cm³) and trifluoromethanesulfonic anhydride (1 cm³) under nitrogen for 20 h, giving an orange solution containing a small amount of undissolved solid. The reaction mixture was then heated to 80°C for 16 h, affording a clear, viscous, orange–brown solution which was cooled and worked up as in Procedure 1. The resulting cream-coloured polymer (6) was obtained in 91% yield and was characterized by d.s.c. ($T_g^{onset}$ at 267°C) and solution viscometry in NMP ($\eta_{inh} = 0.86 \, dl \, g^{-1}$). Further characterization data are given in *Tables 1* and 2.

*Synthesis of polymer 11 by sulfonation of polymer 5*

Beads of polymer 5 (0.40 g) were stirred vigorously in 98% sulfuric acid (20 cm³) at room temperature until dissolution was complete (12 h), and the dark yellow solution was allowed to stand for a further 8 days. It was then added dropwise with stirring to deionized water (200 cm³) and the resulting pale pink beads were filtered off, suspended in 200 cm³ of water and stirred at 40°C for 3 h. They were then washed with water (5 × 100 cm³) and dried in a vacuum desiccator for 48 h. The yield of dark red sulfonated polymer 11 ($\eta_{inh} = 4.54 \, dl \, g^{-1}$) was essentially quantitative. The $^{13}C$ n.m.r. spectrum (DMSO-$d_6$) showed resonances at $\delta = 82.4$, 117.9, 121.3, 127.1, 127.6, 129.1, 130.3, 130.7, 131.2, 132.0, 137.0, 139.5, 142.6, 152.6, 161.3, and 184.1 ppm. Polymer 10 was obtained by sulfonation of 4, using the same procedure, and its $^{13}C$ n.m.r. spectrum is shown, with assignments, in *Figure 6*.

*Membrane fabrication, characterization, and testing*

Ultrafiltration membranes were obtained from

**Table 2** Spectroscopic and thermogravimetric data for poly(etherketone-*para*-carborane)s

| Polymer | I.r. (cast film, cm⁻¹) | ¹³C n.m.r. (CDCl₃, δ) | Mass (%) retained at 850°C | |
|---|---|---|---|---|
| | | | In nitrogen | In air |
| 4 | 3056 w (νCH); 2609 s (νBH); 1656 s (νC=O); 1594 s, 1499 s (νCC_Ar); 1244 s (νC–O) | 82.0 (C_carborane); 117.8, 118.6, 119.0, 128.9, 132.3, 132.5, 133.4, 156.1, 159.7, 161.1 (C_Ar); 194.1 (C_carbonyl) | 90 | 88 |
| 5 | 3070 w, 3034 w (νCH); 2607 s (νBH); 1655 s (νC=O); 1593 s, 1500 s (νCC_Ar); 1242 s (νC–O) | 81.2 (C_carborane); 118.4, 119.1, 119.8, 130.0, 131.6, 132.8, 133.2, 133.8, 156.9, 160.2 (C_Ar); 194.5 (C_carbonyl) | 91 | 83 |
| 6 | 3070 m, 3050 m (νCH); 2604 s (νBH); 1668 s, 1648 s (νC=O); 1592 s, 1455 s (νCC_Ar); 1307 s, 1172 s, (νC–O) | 81.1 (C_carborane); 117.8, 119.2, 128.9, 129.5.0, 131.8, 132.6, 140.8, 161.1 (C_Ar); 195.3 (C_carbonyl) | 97 | 110 |
| 7 | 3070 w, 3026 w, 2930 m, 2854 m (νCH); 2610 s (νBH); 1681 s (νC=O); 1593 s 1499 s (νCC_Ar); 1244 s (νC–O) | 24.4, 29.2, 29.3, 38.4 (C_aliphatic); 82.0 (C_carborane); 117.9, 118.9, 128.8, 130.3, 132.1, 132.3, 156.1, 160.7, (C_Ar); 199.0 (C_carbonyl) | 78 | 75 |
| 8 | 3074 w, 3026 w, 2924 s, 2852 s (νCH); 2610 s (νBH); 1681 s (νC=O); 1593 s, 1499 s (νCC_Ar); 1244 s (νC–O) | 24.5, 29.4, 38.5 (C_aliphatic); 82.0 (C_carborane); 117.9, 119.0, 128.8, 130.3, 132.2, 132.3, 156.1, 160.8 (C_Ar); 199.2 (C_carbonyl) | 62 | 75 |
| 9 | 3054 w, 2922 s, 2852 s (νCH); 2609 s (νBH); 1681 s (νC=O); 1593 s, 1499 s (νCC_Ar); 1243 s (νC–O) | 24.4, 24.5, 29.2, 29.3, 29.5, 29.6 38.5 (C_aliphatic); 82.3 (C_carborane); 117.9, 119.0, 128.8, 130.3, 132.2, 132.3, 156.1, 160.8 (C_Ar); 199.0 (C_carbonyl) | 49 | 70 |

solutions of polymer **4** (7%, 10%, and 13% w/v) in N-methylpyrrolidone by casting 5 cm$^3$ of each polymer solution onto a 25 × 15 cm sheet of non-woven, polyester paper (*Awa-10* from Sanko Ltd, Japan; 100 μm in thickness) taped flat to a glass plate, and drawing down the film using a doctor-blade set at a height of 150 μm above the surface of the paper. The membrane was gelled by immersion in water at 20°C and soaked in running water for 30 min. It was then removed from the plate, soaked in water at 60°C for 5 min, immersed in 15% aqueous glycerol for a further hour, and finally allowed to dry in air at ambient temperature for 24 h. Duplicate sample discs (5.5 cm$^2$ in diameter) were cut from the sheet and were checked on a lightbox to ensure the absence of flaws or pinholes before testing.

Composite nanofiltration membranes were obtained by coating a solution of the sulfonated polymer **11** in methanol (1% w/v) onto 10 × 30 cm strips of polysulfone support-membrane (nominal MWCO 40 000) supplied by NWW Acumem Ltd (Widnes, UK). The strip of wet membrane passed directly from the bead-coating head into a forced-air oven where it was dried at 60°C for 3 min.

Membrane testing was carried out in crossflow mode using a series-connected pair of stainless steel test cells containing duplicate membrane sample discs. Crossflow velocity at the membrane surface was 1 m s$^{-1}$ and the transmembrane pressure was set at 2 bar for ultrafiltration and 5 bar for nanofiltration. Molecular weight cut-off determinations were based on rejection values, determined by g.p.c., for a mixed feed comprising three polyethyleneglycol fractions (1 K, 10 K, and 100 K), each at 0.1% concentration in water. Salt rejection values were determined conductimetrically, using 500 ppm feed solutions of NaCl, Na$_2$SO$_4$, CaCl$_2$, and MgSO$_4$. Membrane structures were examined using chromium-coated samples on a Hitachi S-900 field-emission scanning electron microscope, at an accelerating voltage of 5 kV.

## RESULTS AND DISCUSSION

### Polymer synthesis

The stability of icosahedral carboranes under super-acid conditions allows electrophilic polycondensation



Ar(COOH)$_2$ | CF$_3$SO$_3$H (solvent)
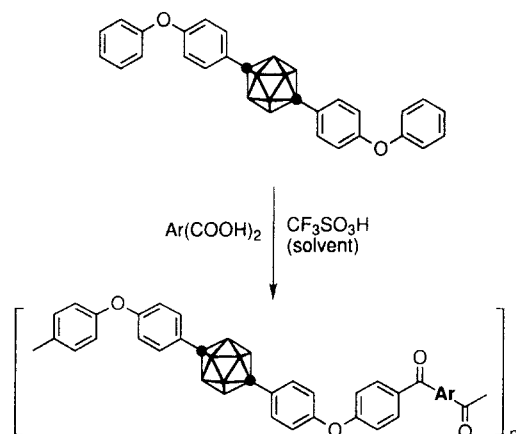
**4** (Ar = 4,4'-C$_6$H$_4$OC$_6$H$_4$); **5** (Ar = 4,4'-C$_6$H$_4$-C$_6$H$_4$)

**Figure 2** Synthesis of poly(aryletherketone-*para*-carborane)s

between carborane-based aromatic ethers and dicarboxylic acids in trifluoromethanesulfonic acid to be achieved without degradation of the carborane cage[7]. Previous work has shown that polymers in which aromatic etherketone segments alternate with diphenyl-1,2- or diphenyl-1,7-C$_2$B$_{10}$H$_{10}$ units can achieve relatively high glass transition temperatures (up to 220°C), but that such polymers, unlike their all-aromatic analogues, fail to crystallize under thermal (or indeed any other) conditions[6,7]. It seems likely that the non-crystalline nature of such polymers is due, at least in part, to the enforced angularity of the 1,2- and 1,7-carborane linkages, which prevent the polymer chain achieving an extended and therefore readily-recrystallizable conformation. In an attempt to produce *crystalline* poly(etherketone-carborane)s, with the potential advantages of increased modulus, greater temperature resistance, and enhanced ability to withstand solvent attack, we sought to develop a new type of polyetherketone which incorporates the geometrically linear diphenyl-1,12-C$_2$B$_{10}$H$_{10}$ (*para*-carborane) residue[8].

The key monomer for the present work, 1,12-bis-(4-phenoxyphenyl)-*para*-carborane, was obtained in 78% yield and > 99% purity by reaction of excess 4-iodophenyl(phenyl)ether with the di-copper(I) derivative of *para*-carborane. Polycondensations of this monomer with 4,4'-oxydibenzoic acid and with biphenyl-4,4'-dicarboxylic acid (*Figure 2*) proceeded rapidly at room temperature in dry, distilled trifluoromethanesulfonic acid (5 wt% total monomers) to give, after 3–4 h, viscous red solutions of poly(etherketone-carborane)s. The resulting high-MW polymers (**4** and **5** respectively) were isolated quantitatively by precipitation in water.

Residual acid was removed from the resulting beads of polymer by extraction, first with sodium hydroxide in refluxing 50% aqueous ethanol, then with refluxing ethanol, and the beads were finally dried under vacuum. Polyketones **7**, **8**, and **9** (*Tables 1* and *2*) were obtained from aliphatic diacids under very similar conditions. However, polyetherketone synthesis from terephthalic acid, where formation of the intermediate acylium ion is inhibited by the presence of two carboxyl groups on the same aromatic ring[9], requires addition of trifluoromethanesulfonic anhydride to the superacid medium[10]. In the present work this approach led to formation of a high molecular weight polyetherketone (**6**) from terephthalic acid and 1,12-bis(4-phenoxyphenyl)-*p*-carborane although, in comparison with the other polycondensations described here, much higher temperatures (80°C) and more extended polymerization times (*ca.* 16 h) were necessary. Even under these relatively forcing conditions however, the polymerization proceeded cleanly and without cage-degradation.

Attempted polycondensations between the carborane-based dicarboxylic acid 1,12-bis(4-carboxyphenyl)-1,12-dicarbadodecaborane and the diether monomers 1,4-diphenoxybenzene or 1,12-bis(4-phenoxyphenyl)-*p*-carborane unexpectedly led to rapid gelation (*ca.* 1 h) of the reaction mixtures. The products were isolated as intractable, dark yellow powders, which failed to redissolve even in trifluoromethanesulfonic acid. Some form of cross-linking is clearly occurring here, but the nature of this reaction has yet to be established.

Characterization of the new polymers **4**, **5** and **6** by d.s.c. (10°C min$^{-1}$ heating rate) showed that, whereas 4,4'-oxydibenzoic acid gave a purely amorphous material

(4) with a glass transition (onset) at 236°C, the polyketone (6) from terephthalic acid showed not only a sharply-defined $T_g$ at 267°C but also a weak and irreversible endotherm at 317°C ($\Delta H = 3\,\text{J}\,\text{g}^{-1}$), possibly the first hint of crystallinity in a poly(etherketone-carborane). More emphatic evidence of crystallinity was however obtained for polymer 5, derived from 4,4'-biphenyldicarboxylic acid. On the initial heating scan (*Figure 3*, solid line), no $T_g$ was evident, but a strong cold-crystallization exotherm ($\Delta H = 16.0\,\text{J}\,\text{g}^{-1}$) appeared as a double-peak centred at 286°C, followed by a melting endotherm ($\Delta H = 16.1\,\text{J}\,\text{g}^{-1}$) at 386°C. The relative magnitudes of these transitions suggest that polymer 5 is essentially non-crystalline in its 'as-made' state.

A second sample of polymer 5 which had been pre-crystallized at 300°C showed $T_m = 389°C$ and $\Delta H = 22.0\,\text{J}\,\text{g}^{-1}$. A possible $T_g$ was evident in the latter thermogram, with an onset temperature (*ca.* 270°C) close to that anticipated from the more clearly-defined glass transition of polymers 4 and 6. These results suggest anomalous phase-behaviour for polymer 5 in that the phenomenon of 'cold-crystallization' is generally observed only at temperatures well above the glass transition[11], whereas in the 'as-made' sample of polymer 5 this process begins at *ca.* 265°C, slightly below the apparent $T_g$. The two thermograms are however mutually consistent, in that no $T_g$ *is evident below the onset of cold-crystallization in the thermogram of the 'as-made' material.* Moreover, as the $T_g$ of a semi-crystalline polymer is normally higher than that of the wholly amorphous material, there is no inconsistency in cold-crystallization (of the amorphous polymer) beginning a few degrees below the $T_g$ of the pre-crystallized material.

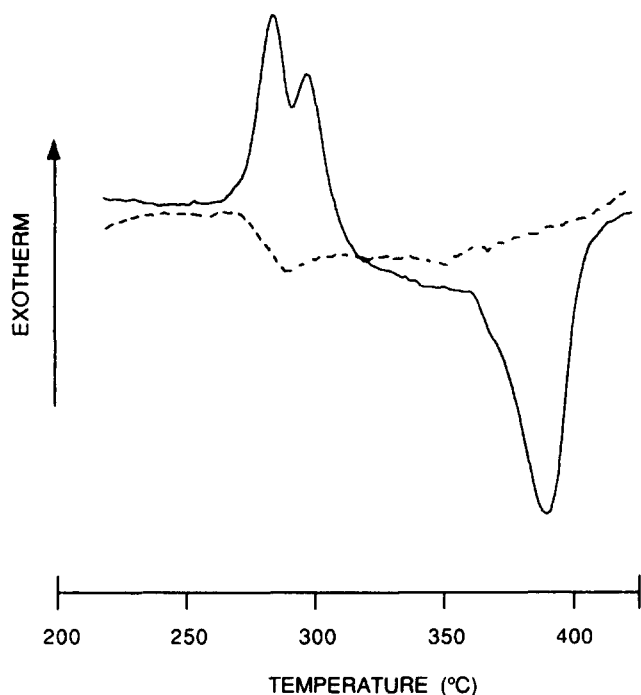The 'as-made' polymer 5 is readily soluble in chloroform to give solutions from which strong, transparent films can be cast, in keeping with the view that the polymer is essentially amorphous at this stage. Moreover, the d.s.c. thermogram of a sample of polymer 5 prepared by evaporation of a filtered chloroform solution showed neither the cold-crystallization exotherm observed for the original material nor a melting process, but definitely established the position of the $T_g^{\text{onset}}$ at 267°C (*Figure 3*, dashed line). The coincidence of the glass transition and the cold crystallization process seen in *Figure 3* suggests that the double-exotherm observed during the latter process may result from a step-change in crystallization rate as the polymer passes through its glass transition.

These observations also indicate that trace levels of pre-existing crystal nuclei are required to initiate cold-crystallization at the $T_g$, and that such nuclei are removed (during the dissolution or filtration stages) during film-casting. Dilute (0.1% w/v), filtered solutions of polymer 5 in chloroform are in fact stable for several days, allowing viscosity and g.p.c. data to be obtained, but at high concentrations (around 10% w/v) crystallization of the polymer is evident after only a few hours.

Inherent viscosities of 4 (in NMP), 5 (in chloroform), and 6 (in NMP) were 1.28, 1.09, and 0.87 dl g⁻¹ respectively, indicating that high molecular weight had been achieved in all three systems. This was confirmed by g.p.c. and by laser light-scattering, both carried out in THF solution. A sample of polymer 4 for example showed $M_w$ at 133 000 by g.p.c. (relative to polystyrene) and at 134 000 daltons by light-scattering. Full characterization data for 4, 5, and 6 are given in *Tables 1* and *2*.

The semi-aliphatic polymers 7, 8, and 9 all proved essentially amorphous in the 'as-made' state (by d.s.c.), the glass transition temperatures (*Table 1*) falling steadily with increasing aliphatic chain-length. Although 7 and 8 dissolved readily in NMP, polymer 9 proved surprisingly insoluble. Recovery of the sample which had been in contact with NMP and subsequent d.s.c. analysis showed that the $T_g$ was no longer evident, and that instead a strong melting endotherm was present ($T_m = 122°C$, $\Delta H = 22.5\,\text{J}\,\text{g}^{-1}$); clear evidence that solvent-induced crystallization had occurred. A second scan of this sample showed only the previously-seen glass transition.

Thermogravimetric analysis (10°C min⁻¹, to 850°C, under nitrogen) of polymers 4-6 gave mass retention values of between 90 and 97% (*Table 2*). For polymers 7-9 the mass retention in nitrogen decreased progressively from *ca.* 80% to 50% as the length of the aliphatic chain increased. Thermolysis in air led in one case to an *increase* in mass (*Table 2*), presumably reflecting conversion of the carborane cage to oxides of boron.

*Membrane fabrication and ultrafiltration performance*

The ready solubility of polymer 4 and its ability to form high-strength films suggested that this type of polymer, like the amorphous aromatic polysulfones[12], should have significant membrane-forming capabilities. Casting solutions of 4 were prepared in NMP at 7, 10, and 13% concentrations (w/v) and were coated onto non-woven polyester paper. The resulting films of polymer solution were gelled to form asymmetric membranes by immersion and consequent phase-inversion in deionized water, and after impregnation with aqueous glycerol to maintain pore-wettability, were allowed to dry in air.

Cross-flow ultrafiltration experiments using both pure water and an aqueous solution containing a mixture of
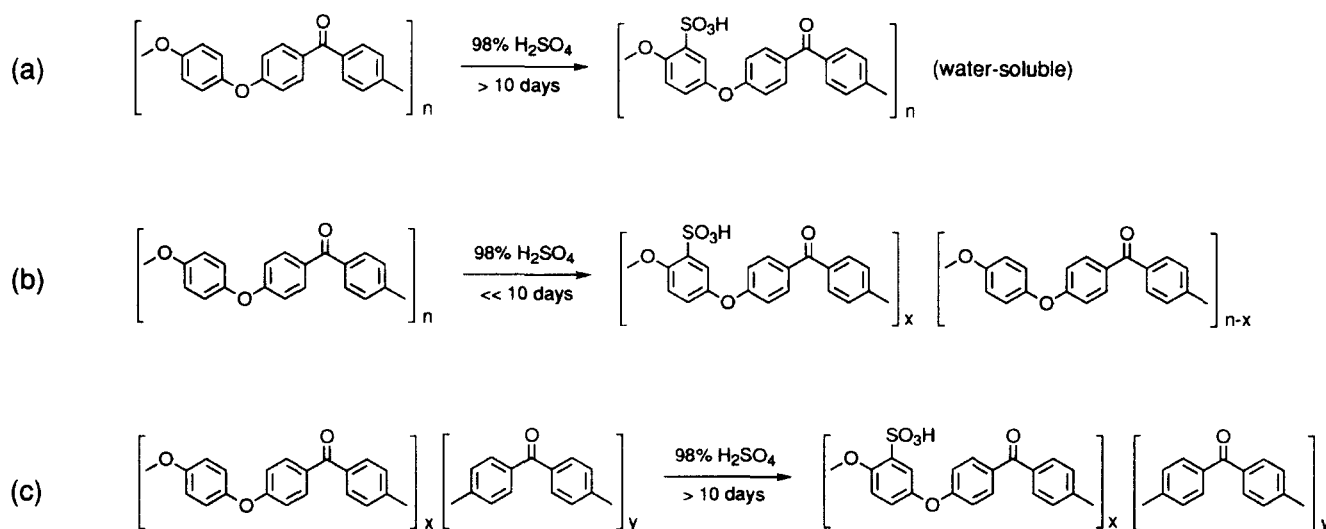


**Figure 3** D.s.c. traces for polymer 5 in the as-made state (solid line) and as a film formed by evaporation of a filtered chloroform solution (dashed line)

**Figure 4** Previous approaches to the controlled sulfonation of aromatic polyetherketones

standard-MW polyethylene glycols (*Table 3*) demonstrated that all three types of membrane were highly permeable, the pure-water permeability decreasing with increasing polymer concentration in the original casting solution. Despite the relatively primitive fabrication process used here, all three types of membrane proved capable of fractionating polymeric solutes according to molecular weight. The '13%' membrane in particular gave a very sharp molecular-weight cut-off (90% rejection) at around 9000 daltons, confirming the potential value of this type of polymer in membrane technology.

Scanning electron micrographs of membranes cast from polymer solutions at the three different concentrations showed, in cross-section, heavily macrovoided, skinned-asymmetric structures, the proportion of macrovoided to sponge-pore morphology decreasing progressively with increasing polymer concentration. High-resolution, field-emission SEM of a membrane cast from 10% polymer solution and coated with *ca.* 2 nm of chromium showed a uniformly nodular surface-structure with a mean nodule diameter of approximately 30 nm. From SEM it appears that the membranes' surface pores are located at internodule junctions, and indeed the size-scale of this porosity is quite consistent with the ultrafiltration results described above, which suggest a pore-size distribution in the range 3–7 nm[13].

**Table 3** Ultrafiltration characteristics of membranes cast from solutions of polymer 4 in NMP. Measurements at 2 bar transmembrane pressure and 1 m s$^{-1}$ crossflow velocity

| Polymer concn. (%) in casting solution | Rejn. values (%) for PEG-1000 PEG-10000 PEO-100000 | Molecular weight cut-off (daltons) | Pure water flux (l m$^{-2}$ h$^{-1}$) | U.F. flux (l m$^{-2}$ h$^{-1}$) |
|---|---|---|---|---|
| 7 | 9 78 96 | 16000 | 674 | 75 |
| 10 | 12 90 99 | 10000 | 491 | 61 |
| 13 | 12 95 100 | 9000 | 206 | 68 |

*Structure-defined sulfonation of poly(etherketone-carborane)s*

Sulfonation has been extensively investigated as a means of converting hydrophobic aromatic polyethers into hydrophilic polymers[14], especially for application as ultrafiltration and nanofiltration membranes. Very high levels of sulfonation should be avoided in such reactions, as this can lead (*Figure 4a*) to the polymer becoming water-soluble. Thus, to obtain a useful membrane-material the level of sulfonation must be restricted. This has been achieved in the past either by control of reaction conditions (*Figure 4b*)[15], or by using a copolymer in which only a specified, randomly distributed, number of aromatic rings are susceptible to sulfonation (*Figure 4c*)[16].

Interestingly, the carborane-based polyethers 4 and 5 seem to offer a third approach to the problem of achieving a specified level of polymer sulfonation. Only two of the six aromatic rings in their repeat units are activated towards electrophilic substitution (i.e. those arylether units attached directly to the carborane cage)
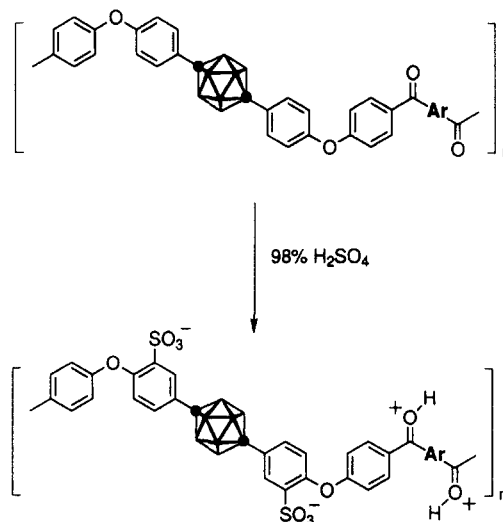


**10** (Ar = 4,4'-C$_6$H$_4$OC$_6$H$_4$); **11** (Ar = 4,4'-C$_6$H$_4$-C$_6$H$_4$)

**Figure 5** Sulfonation of poly(etherketonecarborane)s

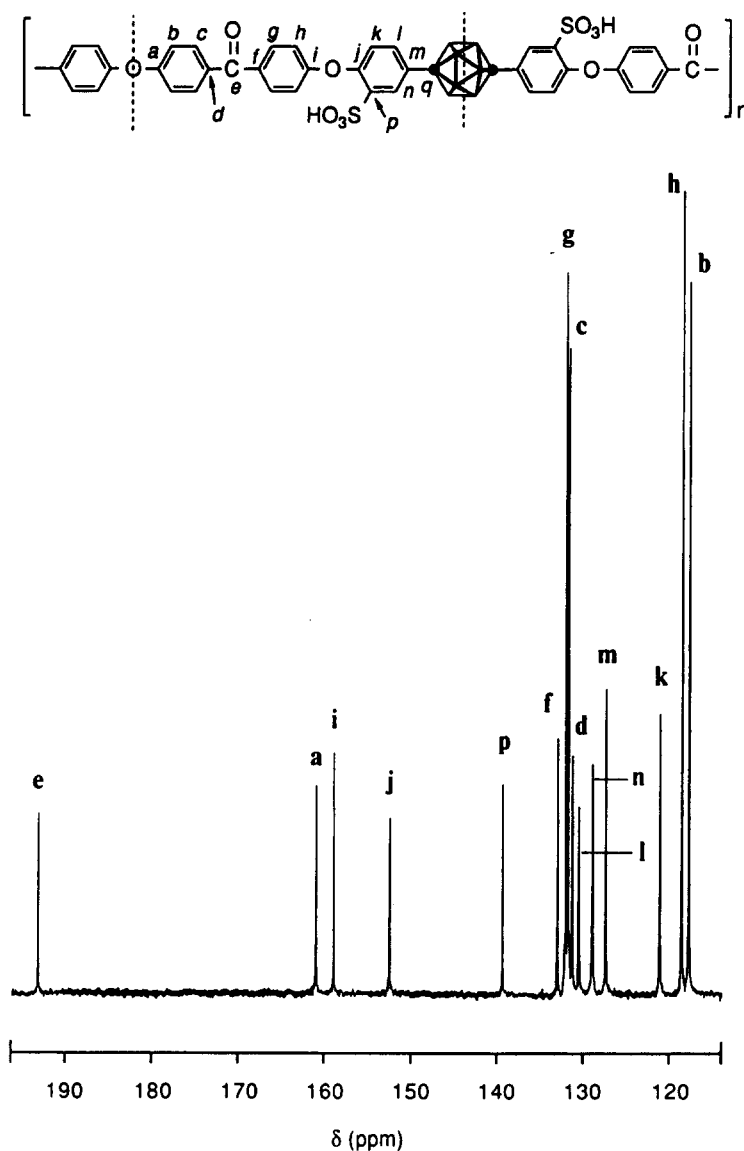**Figure 6** $^{13}$C n.m.r. spectrum (DMSO-$d_6$) of the sulfonated ionomer **10**, with assignments

and, since the *para*-carborane unit is itself unreactive to 98% sulfuric acid, it seemed possible that sulfonation of these polymers would lead to hydrophilic but water-insoluble polyethers. Here, for the first time, the sequence-distribution of sulfonic acid groups in a membrane polymer would be completely defined.

Polymers **4** and **5** were found to dissolve slowly on stirring vigorously in 98% sulfuric acid to give dark yellow solutions which, after several days, were added dropwise into water to give pale pink, translucent polymer beads. After washing and drying these shrank and became deep orange–red. This suggested that sulfonation had indeed occurred, as such colours are often characteristic of sulfonated polyetherketones, being associated with a zwitterionic polymeric structure involving protonated aromatic carbonyl groups (*Figure 5*)[17].

Quantitative sulfonation according to *Figure 5* was demonstrated for both polymers (giving ionomers **10** and **11**) by $^1$H and $^{13}$C n.m.r. (*Figure 6*). Viscosity measurements for **11** gave $\eta_{inh} = 4.54 \, dl \, g^{-1}$ (NMP). This very high value (cf. $\eta_{inh} = 1.21 \, dl \, g^{-1}$ for its precursor **5**) is consistent with formation of a polymer containing a high proportion of arenesulfonate ($ArSO_3^-$) groups, since the hydrodynamic radius of an ionomer is greatly expanded

relative to a neutral polymer of similar type and molecular weight.

Although insoluble in water, the ionomers **10** and **11** proved readily soluble in alcohols such as ethanol and methanol to give solutions from which tough, elastic films were formed on evaporation. Such ionomer solutions appeared to be ideal for the fabrication of composite membranes by solution-coating onto the surface of an ultrafiltration support-membrane, a process in which the solvent is absorbed by the porous support, and subsequently removed by evaporation[18]. Ionomers are particularly suited to this type of membrane fabrication process, as their expanded chain-conformations (resulting from charge–charge repulsions) limit the possibility of individual polymer molecules entering and blocking the surface-pores of the support-membrane. Ionomer molecules thus tend to remain on the surface of the support and ultimately coalesce, as the solvent is removed, to form a coherent supported film which may be no more than a few tens of nanometres in thickness. Such films may reject both dissolved ions (on the basis of both size and charge-effects) and molecules with MW's greater than a few hundred daltons, while transmitting water under

**Table 4** Nanofiltration characteristics of a composite membrane produced from ionomer **11**. Measurements at 5 bar transmembrane pressure and 1 m s$^{-1}$ crossflow velocity

| Feed solution (500 ppm) | Flux (1 m$^{-2}$ h$^{-1}$) | Rejection (%) |
|---|---|---|
| CaCl$_2$ | 50 | 10 |
| MgSO$_4$ | 46 | 26 |
| NaCl | 54 | 64 |
| Na$_2$SO$_4$ | 47 | 96 |

pressure, in a process generally referred to as *nanofiltration*[19].

In the present work, composite membranes were fabricated from a 1% solution of ionomer **11** in methanol, which was applied as a thin film to the surface of a polysulfone support-membrane [molecular weight cut-off at 90% rejection (MWCO) *ca.* 40 000] and were dried at 60°C in air. Cross-flow nanofiltration experiments at 5 bar transmembrane pressure, using solutions of different salts demonstrated a consistently high water flux (*ca.* 50 l m$^{-2}$ h$^{-1}$) through the membrane, comparable to or exceeding that of many commercial nanofiltration membranes[19]. The present membrane however showed more dramatic variations in salt rejection as a function of ionic charge (*Table 4*) than do most commercial membranes of this type[19].

Thus, sulfate (2−) is rejected much more strongly than chloride (1−), a result consistent with 'Donnan' exclusion by the high, fixed negative charge on the polymer[20]. Conversely, salts of divalent cations (Mg$^{2+}$ or Ca$^{2+}$) are rejected less strongly than analogous salts of sodium (1+), an effect resulting from more efficient shielding of the membrane's fixed charge by the more strongly bound divalent cations. For the present membrane, these effects lead to an order of magnitude increase in rejection between calcium chloride and sodium sulfate. Ion-selectivity of this type allows the use of membranes for the softening of drinking water, and has also been exploited in the de-sulfation of seawater, to avoid precipitation of barium sulfate during oil-recovery operations.

The ease of fabrication, high water-flux, and selective ion-rejection characteristics of composite nanofiltration membranes based on sulfonated polyarylcarboranes (combined with their chemical stability and mechanical strength) could thus prove to be of significant value in water-treatment, not only in membranes for water-softening[21] but also perhaps more generally in the demineralization and decontamination of potable and process waters.

## CONCLUSIONS

Introduction of icosahedral carborane cages into a normally-crystallizable aromatic polyetherketone chain-structure generally results in formation of an amorphous material, suggesting that icosahedral C$_2$B$_{10}$ cages are essentially incompatible with the polyetherketone crystal lattice. A few such polymers based on *p*-carborane can be induced to crystallize, but even here crystallization is unpredictable and requires either pre-nucleation or plasticization by solvent-contact. Most poly(aryletherketone-carborane)s resemble amorphous polyethersulfones, in that their $T_g$s are relatively high

(200–300°C), they exhibit very good mechanical strength and toughness, and are readily soluble in a range of dipolar aprotic solvents. They are thus amenable to membrane fabrication by the phase-inversion process, and afford asymmetric ultrafiltration membranes with high fluxes and sharp molecular weight cut-offs when cast from solution in NMP.

Sulfonation of poly(etherketone-carborane)s in 98% sulfuric acid occurs without polymer degradation and with very high regiospecificity, to give hydrophilic ionomers in which the distribution of sulfonic acid groups is fully defined. The solubility of these ionomers in solvents such as methanol and ethanol allows them to be coated from solution onto the surface of polysulfone support-membranes, giving thin-film-composite nanofiltration membranes possessing good permeability and ion-selectivity.

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