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Synthesis and characterization of fluorinated polyetherketones prepared from decafluorobenzophenone

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A series of fluorinated polyetherketones containing perfluoroaryl moieties was prepared by solution condensation polymerization. The synthesis involves the condensation of a dialkali metal salt of a bisphenol with decafluorobenzophenone. The reaction is rapid, free of side reactions, and yields polymers with high glass transition temperatures (T_gs) and excellent thermal stability. The T_gs of the polymers ranged from 155 to 223°C as measured by differential scanning calorimetry (d.s.c.). The dynamic mechanical thermal analysis of the polymers is also described. The dielectric constants of the polymers were characterized as a function of percent relative humidity. All of the fluorinated aromatic polyetherketones were processable from solution, to yield transparent, flexible films. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Considerable attention has been devoted to the preparation of fluorine-containing polymers because of their unique properties and high temperature performance. Among the high performance fluorinated polymers being studied for use in aerospace and electronic applications are the fluorinated aromatic polyethers prepared containing hexafluoroisopropylidene (HFIP) units[1]. Polymers containing HFIP units have been studied for applications as films, coatings for optical and microelectronics devices, gas separation membranes, and as a matrix resin in fibre-reinforced composites. Frequently the incorporation of HFIP units into the polymer backbone leads to polymers with increased solubility, flame resistance, thermal stability, and glass transition temperature (T_g), while also leading to decreased colour, crystallinity, dielectric constant, and moisture absorption.

Recently we reported on the synthesis and characterization of novel fluorinated poly(aryl ether)s containing perfluorophenylene moieties[2]. These fluorinated polyethers were prepared by reaction of decafluorobiphenyl with bisphenols. These polymers exhibit low dielectric constants, low moisture absorption, and excellent thermal and mechanical properties. Tough, transparent films of the polymers were prepared by solution casting or compression moulding. The fluorinated poly(aryl ether)s containing perfluorophenylene moieties are good candidates for use as coatings in microelectronics applications[3].

Poly(ether ketone)s[4-7] are also desirable because they are economically accessible by both nucleophilic and electrophilic routes, and can be easily processed because of the flexibilizing ether and ketone groups present in the polymer backbone.

On the basis of the above studies reported thus far, we have designed and synthesized a series of novel fluorinated polyetherketones (PEKs) by reaction of a bisphenol with decafluorobenzophenone in a polar aprotic solvent and in the presence of potassium carbonate as an acid acceptor. We found these new fluorinated polyetherketones to have good solubility, high T_gs, low dielectric constants, and excellent thermal stability.

EXPERIMENTAL

Reagents

All reagents were reagent-grade and were used without purification. Decafluorobenzophenone, phenolphthalein, dimethylacetamide (DMAc), and potassium carbonate were obtained from Aldrich Chemical. 4,4-(HFIP) diphenol (bisphenol AF), 1,1-bis(4-hydroxyphenyl)-1-phenylethane (bisphenol AP) and 9,9-bis(4-hydroxyphenyl)fluorene (HPF) were obtained from Kennedy and Klim.

Polymer synthesis

A typical synthesis of the fluorinated polyetherketone was conducted in a 100-ml round bottom flask equipped with a condenser, magnetic stirrer, and nitrogen inlet. A detailed synthetic method designed to prepared PEK **2** from decafluorobenzophenone and HPF was carried out using the following general procedure. To a 100-ml round bottom flask was added 5.57 g (0.015 mol) of decafluorobiphenyl, 5.19 g (0.015 mol) of HPF, and 45 g DMAc. The mixture was stirred until all the solids

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dissolved, then 6.2 g (0.045 mol) of potassium carbonate was added. The mixture was then heated to 160°C and stirred at this temperature under nitrogen for 3 h. The mixture was allowed to cool to room temperature and poured into rapidly stirred (blender) deionized water containing 1 wt% acetic acid to precipitate the polymer. The polymer was isolated by filtration, washed twice with deionized water and dried to yield the fluorinated PEK **2** as a white powder.

Polymer films

Solutions of the polymers (15–25 wt% solids) in a 1/1 mixture of *N*-methyl-2-pyrrolidinone (NMP) and cyclohexanone were spin-coated onto glass substrates. The coatings were dried for 45 min at 100°C, 45 min at 170°C, and 15 min at 250°C. The films, about 15 μm in thickness, were released from the glass substrates by placing the substrate in deionized water after drying. PEKs **1** and **2** were compression moulded at 240 and 300°C respectively, to yield transparent, colourless films.

Measurements

Dielectric constants were measured on polymer films of 20–30 μm thickness using the previously described fluid displacement method[8]. The capacitance of the films was measured using circular gold electrodes (diameter 1 inch) mounted in a brass dielectric cell held at a constant 25°C. Capacitance was measured at 10 kHz using a GenRad Precision LC Digibridge (Model 1688). Relative humidity was measured by a General Eastman dew point hygrometer (System 1100DP).

T_gs were determined using a Seiko 220C differential scanning calorimeter at a heating rate of 10°C min^{-1}. Thermal stability studies by thermal gravimetric analysis (t.g.a.) for the polymers were performed on a Seiko TGA/DTA 320 at a heating rate of 20°C min^{-1} in air under a flow rate of 350 ml min^{-1}.

PEK **1** and its model compounds were analysed by ^{13}C solution-state nuclear magnetic resonance (n.m.r.) on a Varian XL-300 operating at 75.4 MHz for ^{13}C and ^{19}F solution-state n.m.r. on a Bruker DMX-400 operating at 376.3 MHz for ^{19}F. Solution-state analysis of bisphenol AF was carried out in deuterated acetone and analysis of PEK **1** and decafluorobenzophenone was carried out in deuterated chloroform. ^{13}C chemical shifts were referenced to deuterated chloroform (77.0 ppm) or deuterated acetone (29.8 ppm) and ^{19}F chemical shifts were referenced to α,α,α-trifluorotoluene (−63.7 ppm). The sample concentrations were about 0.3% (w/v) and enough transients were collected to obtain an adequate signal-to-noise ratio for the peaks. In addition, 2D COSY (homonuclear shift correlation through *J*-coupling) n.m.r. was performed for PEK **1** to confirm the structure by correlating the *J*-couplings of the fluorines present in the synthesized polymer.

The dynamic mechanical response of the samples was monitored using a Rheometric Scientific DMTA MKII in the bending mode, with dual cantilever geometry. Rectangular samples, measuring 30 mm × 10 mm × 0.2 mm, were scanned isochronally at 2°C min^{-1} between −110°C and 300°C, and isothermally around the glass transition. Loss modulus (E''), storage modulus (E') and tanδ were recorded over the frequency range 0.03–200 Hz. All experiments were carried out in an inert atmosphere on the as-received samples.

RESULTS AND DISCUSSION

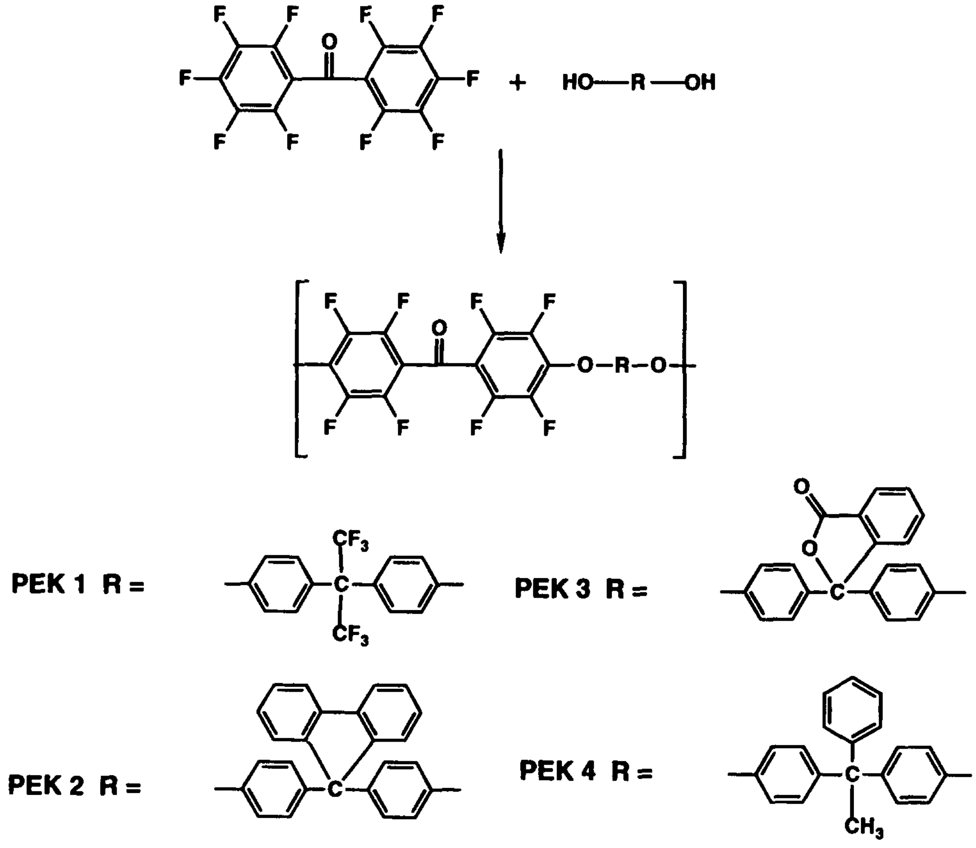
As depicted in *Scheme 1*, a series of fluorinated polyether ketones were prepared by the reaction of the dialkali metal salt of bisphenols with decafluorobenzophenone in a polar aprotic solvent. The reaction was rapid, free of side reactions, and yielded polymers with little colour. The dialkali metal salts of bisphenols were generated using potassium carbonate at 160°C. Aryl halides, when activated by an electron-withdrawing substituent, such as ketone, are readily susceptible to nucleophilic aromatic substitution polymerizations. As evidenced by ^{13}C and ^{19}F n.m.r., only the fluorines *para* to the ketone were displaced during the polymerization reaction.

Judging by the viscosity increase, the polymerization reactions were near completion in less than 2 h. The reaction of decafluorobenzophenone with bisphenol AF, HPF, phenolphthalein, and bisphenol AP resulted in the generation of PEKs **1–4**, respectively. The rate-determining step in this nucleophilic aromatic substitution polymerization reaction is the formation of an intermediate Meisenheimer complex[9]. Aryl halides *para* to an activating electron withdrawing group, such as ketone or sulfone, which can accept the negative charge developed through formation of an intermediate Meisenheimer complex, become susceptible to nucleophilic aromatic substitution. The rapid polymerization reaction of decafluorobenzophenone with bisphenols indicates that the presence of the electron-withdrawing aryl fluorines also help to stabilize the intermediate Meisenheimer complex.

Structure determination

The molecular structure of PEK **1** was confirmed by analysing the ^{19}F and ^{13}C n.m.r. spectra and Fourier transform infra-red (*FT*i.r.) spectra of PEK **1**. ^{19}F and ^{13}C n.m.r. spectra were compared with model compounds and ^{13}C and ^{19}F chemical shifts calculated. The ^{13}C spectrum for PEK **1** is dominated by signals ranging from 63.3 to 176.3 ppm corresponding to the aromatic and aliphatic carbons in the polymer. The ketone carbon centred at 176.3 ppm, aromatic ring carbons, and the isopropylidene carbons centred at 63.7 and 124 ppm are readily identifiable. The ^{13}C chemical shift assignments were made based on comparisons with the model compounds decafluorobenzophenone and bisphenol AF and from calculations based on substituted benzenes[10,11]. The ^{19}F spectrum of PEK **1** displays three signals. The two aromatic fluorines are at −152.4 and −142.1 ppm and the isopropylidene fluorines are at −65.0 ppm. Analysis of the 2D ^{19}F COSY n.m.r. (contour plot) of PEK **1** showed the normal 1D spectrum is along the diagonal. Off the diagonal, cross peaks were observed between nuclei that experience *J*-coupling to each other[12]. The 1D projection ^{19}F spectra were also on the side and the top of the 2D data set. The following conclusions were derived from the 2D ^{19}F COSY spectrum: (a) Cross peaks were observed for F2 (−152.4 ppm) *J*-coupled to F3 (−142.1 ppm), and (b) F3 was isolated and not *J*-coupled to any other fluorines. The observed chemical shifts for the ^{13}C and ^{19}F spectra of PEK **1** are listed in *Table 1*.

The key structural features of PEK **1** can be identified by *FT*i.r. spectroscopy. Key features in the *FT*i.r. spectrum of PEK **1** include the following absorptions: aromatic CH, 3049 cm^{-1}; ketone C=O, 1696 cm^{-1}; aromatic C=C, 1500 cm^{-1}; aromatic ether Ar–O–Ar, 1230 cm^{-1}; and CF_3 group, 1180 cm^{-1}.

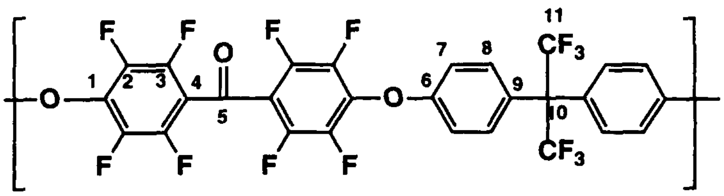


Scheme 1 Synthesis of fluorinated polyetherketones from decafluorobenzophenone

Table 1 The chemical shifts for the ^{13}C and ^{19}F spectra of PEK 1

^{13}C Chemical shifts (ppm)
C1 = 136.8
C2 = 143.2, 139.8
C3 = 147.0, 143.6
C4 = 115.4
C5 = 176.3
C6 = 156.6
C7 = 115.6
C8 = 132.0
C9 = 129.1
C10 = 64.0, 63.7, 63.3
C11 = 122.5, 125.8

^{19}F Chemical shifts (ppm)
F2 = −152.4
F3 = −142.1
F11 = −65.0



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Thermal characterization

The T_gs for the PEKs prepared from decafluorobenzophenone and bisphenol AF, HPF, phenolphthalein, and bisphenol AP as measured by d.s.c. were 155, 223, 215, and 175°C, respectively. The PEKs prepared with HPF and phenolphthalein, PEKs **2** and **3**, respectively, exhibit significantly higher T_gs than PEKs **1** and **4**, prepared from bisphenol AF and bisphenol AP, respectively. The higher T_gs in PEKs **2** and **3** are attributed to the presence of the large, cyclic side groups in the polymers. This is consistent with the work of Korshak *et al.*[13], who showed that the preparation of polyarylates containing rigid, cyclic side groups led to polymers with increased T_gs.

The thermal stabilities of the present polymers were studied by t.g.a. The t.g.a.s were performed in air at a heating rate of 20°C min^{-1}. The 5% weight loss in air for PEKs **1**–**4** are 425, 436, 359, and 442°C, respectively, by t.g.a.

As shown in *Figure 1*, PEK **3** shows a weight loss of 18% at 436°C. This theoretically corresponds to the weight fraction of the entire cyclic ester moiety. Although both PEK **2** and PEK **3** contain cyclic side groups, the lower thermal stability of PEK **3** compared to PEK **2** is attributed to the presence of the cyclic ester. It is postulated that the cyclic ester present in PEK **3** is the more thermally labile group present in the polymer. We have also found that other polyarylates prepared using phenolphthalein have lower thermal stability than do polymers

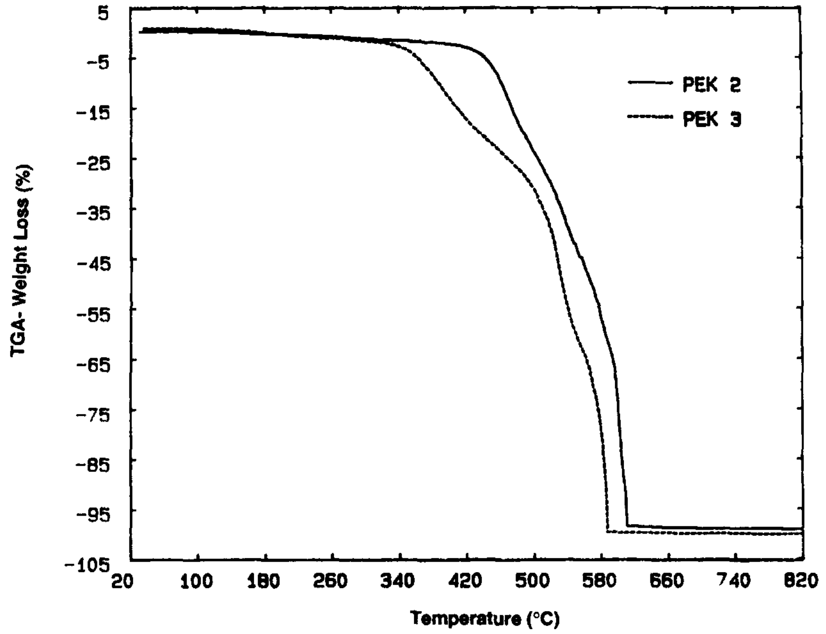

Figure 1 T.g.a. thermograms of PEK **2** and PEK **3**

prepared having similar structures but free of cyclic esters. For example, the fluorinated polyarylether prepared from decafluorobiphenyl and phenolphthalein has a t.g.a. onset of decomposition temperature in air about 50°C lower that the fluorinated polyarylether prepared from decafluorobiphenyl and HPF[14]. *Table 2* presents the d.s.c. and t.g.a. characterization data of PEKs **1–4**.

Table 2 Properties of fluorinated PEKs **1–4**

			Dielectric constant	
PEK	T_g (d.s.c.)	t.g.a.[a]	0% RH[b]	68% RH
1	155	425	2.68	2.79
2	223	436	2.80	3.00
3	215	359	2.75	2.95
4	175	442	2.98	3.19

[a] Onset of decomposition in air

[b] Relative humidity

Dynamic mechanical thermal analysis

Figure 2 shows an isochronal dynamic mechanical scan at 1 Hz for PEK **1** and **2**. Both polymers exhibit strong α-relaxation peaks at higher temperatures, which are associated with the glass transition, and broad and very weak secondary relaxations around −100°C. Similar, yet more intense, secondary relaxations previously observed in poly(aryl ether ether ketone) (PEEK) have been attributed to localized motions involving phenyl ring flips[15]. The relative weakness of these processes in PEKs **1** and **2** may result from the aromatic fluorine and biphenyl groups restricting the mobility of the phenyl rings. In addition, the fluorine groups may reduce chain interactions with water molecules, since water contributes to the β-relaxation in aromatic polymers[16]. The higher dynamic mechanical T_g of PEK **2** (236°C, compared with 160°C for PEK **1**) can be attributed to the bulky biphenyl side group. PEK **2** also exhibits a broad relaxation beginning around −50°C and continuing to the T_g. This is probably associated with restricted motions of the biphenyl side group since an equivalent relaxation is much less apparent in the PEK **1** scan.

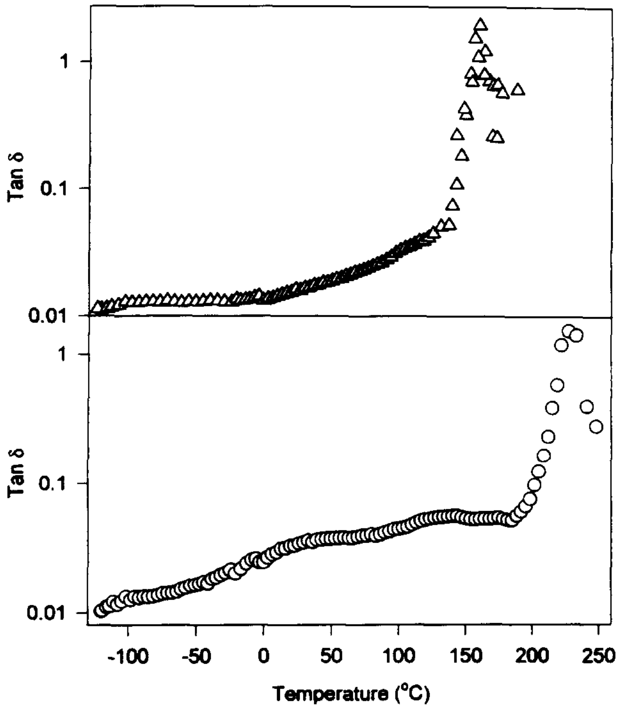

Figure 2 Dynamic mechanical scan for PEK **1** (△) and PEK **2** (○) at 1 Hz and a heating rate of 2°C min^{-1}

The shift in tanδ peak temperature with impressed frequency is plotted in *Figure 3*. The observed dependence can be described by the empirical Vogel–Fulcher (VF) expression[17]

$$\log f^* = \log f_0 - \frac{E}{2.303R(T - T_0)} \qquad (1)$$

where f^* is the frequency corresponding to temperature T from the mechanical loss peak, f_0 is the primitive frequency at the Vogel temperature T_0 (the relaxation time τ is defined as $\frac{1}{2}\pi f$) where the entropy of the system approaches 0 and E is an energy term related to bond rotational barriers. This expression is widely used to describe the relaxation times of polymers. The parameters derived from the fits in *Figure 3* are listed in *Table 3*. Although PEK **1** has the lower T_0 value it shows a slightly larger Vogel energy compared with PEK **2**, which suggests larger bond rotational barriers around the main chain for PEK **1**. A fit of the data in *Figure 3* to the Arrhenius equation showed the same trend and gave activation energies of $812 \pm 19\,\mathrm{kJ\,mol^{-1}}$ and $723 \pm 30\,\mathrm{kJ\,mol^{-1}}$ for PEKs **1** and **2**, respectively.

An alternative and much used empirical equation describing the temperature dependence of relaxation times is the Williams–Landel–Ferry (WLF) expression[18]

$$\log a_T = \log\left(\frac{\tau^*}{\tau^*_R}\right) = \frac{-C_1(T - T_R)}{C_2 + T - T_R} \qquad (2)$$

Where a_T is a shift factor, τ^* and τ^*_R are the relaxation times at temperatures T and T_R, respectively, and C_1 and C_2 are constants. The temperature dependence of the WLF shift factors, calculated from isothermal experiments, and the corresponding fits to the WLF equation are plotted in *Figure 4* for PEKs **1** and **2**. The WLF parameters are listed in *Table 2*. The effect of polymer structure on the temperature dependence of relaxation times is not apparent from *Figure 4*. It has been proposed, in the coupling model of Ngai *et al.*[19], that there is a correlation between chemical structure and the temperature dependence of relaxation times or shift factors. According to this model, segmental motions are, in part, governed by the extent of *inter*-molecular cooperativity between neighbouring segments. Specifically, polymers with smoother, less polar and more flexible polymer backbones will experience fewer constraints as chain segments relax[20].

To investigate this further for PEK **1** and **2** it is necessary to normalize the data in *Figure 4* using an arbitrary temperature, which can be taken from within or outside the measuring range. Often the d.s.c. T_g, or the temperature at which the relaxation time is equal to 1 s, is chosen. In this case we have used the temperature at which $\log a_T$ is equal to 4. The resulting plot, commonly referred to as a cooperativity plot, is shown in *Figure 5*. According to the coupling model materials which display the greatest temperature sensitivity in relaxation or shift factor (i.e. plots with greater '*steepness*') will be more intermolecularly coupled, and will require greater cooperation for large scale chain motions to occur. Applying this concept to *Figure 5*, the indication is that PEK **2** requires a greater degree of intermolecular cooperative motion, when compared with PEK **1**, since it produces the steeper cooperativity plot. Considering the significantly larger size of the biphenyl side group in PEK **2**, compared with the CF_3 groups in PEK **1**, it would be expected that PEK **2** would require a greater degree of cooperation for large scale chain motions to occur.

Dielectric constant

At 0% relative humidity (RH), PEKs **1–4** display dielectric constants (measured at 10 kHz) of 2.68, 2.80,

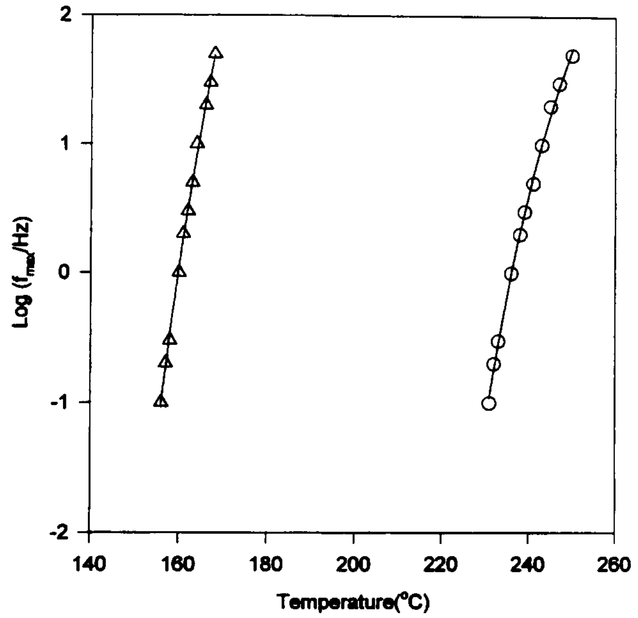

Figure 3 Temperature dependence of $\log(f_{\max})$ taken from dynamic mechanical scans: PEK **1** (△); PEK **2** (O)

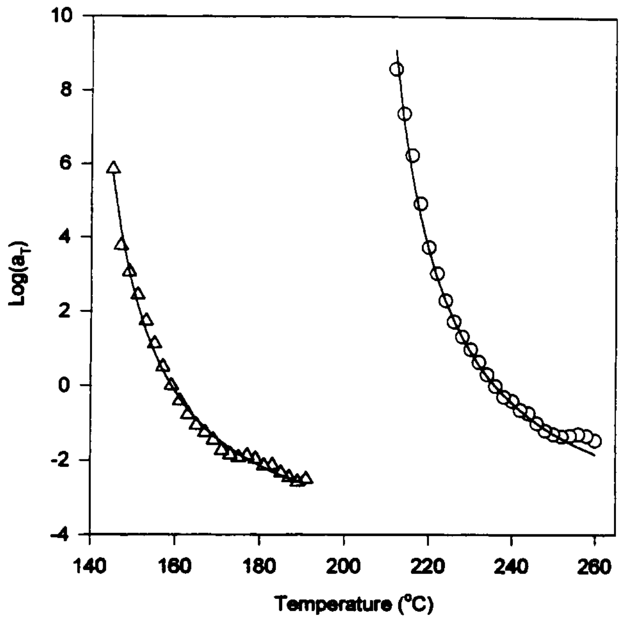

Figure 4 WLF shifts factors for PEK **1** (△) and PEK **2** (O). Solid lines are fits to WLF equation

Table 3 VF and WLF parameters for PEKs **1** and **2**

Sample	$\log f_0$ ($\mathrm{s^{-1}}$)[a]	E ($\mathrm{kJ\,mol^{-1}}$)[a]	T_0 (°C)[a]	C_1[b]	C_2 (K)[b]	T_R (°C)[b]
PEK **1**	12.2 ± 2.6	11.8 ± 5.3	109 ± 12	4.8 ± 0.2	25.7 ± 0.5	160
PEK **2**	6.58 ± 0.74	4.9 ± 1.2	197 ± 5	4.6 ± 0.3	36.1 ± 0.8	236

[a] From fits to VF equation
[b] From fits to WLF equation

2.75, and 2.98, respectively. At about 60% RH, the dielectric constants of PEKs **1–4** increased to 2.79, 3.00, 2.95, and 3.19, respectively. The relationships of dielectric constant to relative humidity for PEKs **1–4** are depicted graphically in *Figure 6*. For comparison the fluorinated poly(aryl ether) **5** (*Figure 7*), made by reaction of bisphenol AF and decafluorobiphenyl, displayed a dielectric constant of 2.50 at 0% RH and increased to 2.60 at 60% RH.

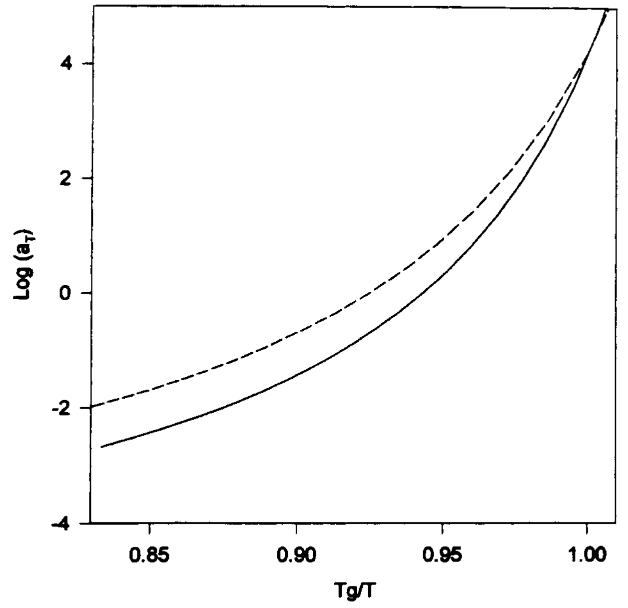

Figure 5 Cooperativity plots for PEK **1** (- - - - -) and PEK **2** (——) with T_g defined as temperature at which $\log a_T = 4$

The fluorinated PEKs display higher dielectric constants than the fluorinated poly(aryl ether) **5**. It was previously reported that the dielectric constant of a polymer is a function of the polymer's total polarizability, αT[21,22]. Therefore, the increased dielectric constants of the fluorinated PEKs **1–4** compared to the fluorinated poly(aryl ether) **5** are attributed to the polar nature of the ketone groups present in these polymers.

We have previously reported that polymers exhibiting high moisture absorption also show greater increases in dielectric constant with increasing relative humidity[2,8,23] compared to polymers having lower moisture absorption. The relationship of moisture absorption in polyimides vs relative humidity has also been reported by others[24–26]. It then follows that the larger increases in the dielectric constants of fluorinated PEKs **1–4** compared to the fluorinated poly(aryl ether) **5** are attributed to higher levels of moisture absorption facilitated by hydrogen bonding of water to the ketone groups in PEKs **1–4**.

CONCLUSION

We have demonstrated that the fluoro groups in the *para* position of decafluorobenzophenone are preferentially displaced by the dialkali metal salt of a bisphenol to yield fluorinated polyetherketones containing perfluoroaryl moieties. All four fluorinated polyetherketones were soluble in polar aprotic solvents and were cast into flexible, creasable films. This method provides general synthetic

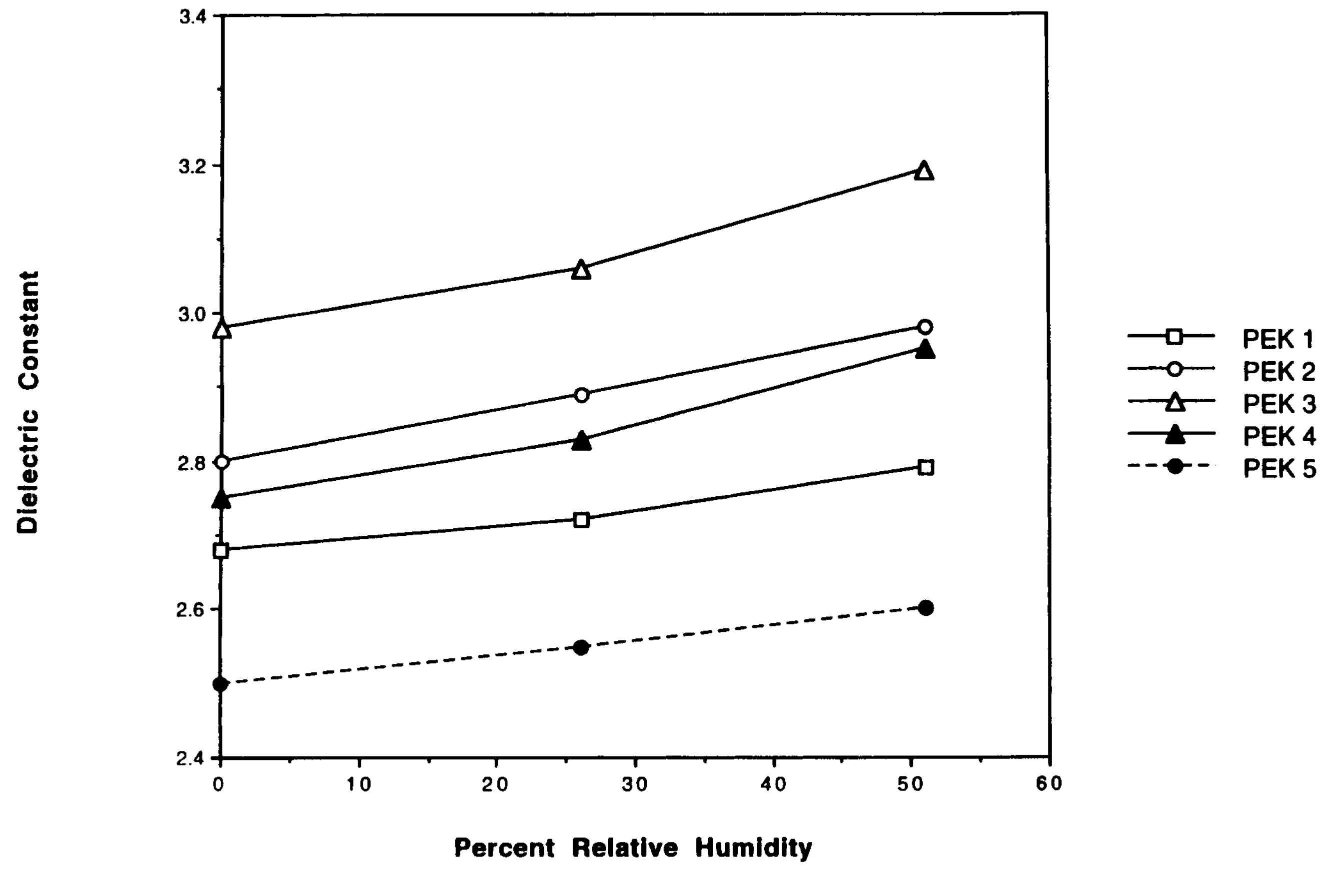

Figure 6 Relationship of dielectric constant to percent relative humidity for polymers **1–5**

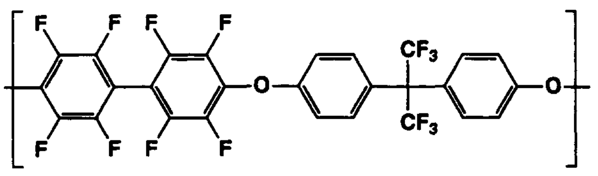

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Figure 7 Polyetherketone **5**

methodology for the preparation of low dielectric constant, high-temperature resistant, high T_g fluorinated aromatic polyetherketones.

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