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Synthesis and properties of new alternating poly(aryl ether) copolymers containing cyano groups

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A general method for the preparation of poly(aryl ether) alternating copolymers containing pendent cyano groups has been developed. We found that the activated aryl fluorides in 2-chloro-7-fluorobenzonitrile are selectively displaced by phenoxides to yield 3-chloro-2-cyanophenyl ethers as the exclusive products. Utilizing this selectivity, several new, high molecular weight, soluble poly(aryl ether amide) and poly(aryl ether ketone) alternating copolymers containing pendent cyano groups were prepared. The T_gs of the copolymers ranged from 160 to 262°C. The dielectric constants of the copolymers were characterized as a function of percent relative humidity. All of the copolymers were processable from solution to yield transparent, flexible films. At elevated temperatures the cyano groups undergo crosslinking reactions yielding films with high solvent resistance. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

High temperature resistant aromatic polymers have long been known for their usefulness in meeting the high performance requirements for polymer films, moulding resins and coating materials required by the aerospace and electronics industries. Aromatic polymers containing sulfone, carbonyl or ether linkages are desirable because they are more economically accessible by both nucleophilic and electrophilic routes than the fully aromatic polyarylenes. Tractability is also increased by introducing flexiblizing groups such as ethers into the polymer chain. Commercially available poly(ether ketone)s[1] and poly(ether sulfone)s[2] are widely used in high performance applications because of their unique combination of chemical, physical and mechanical properties.

Another class of poly(aryl ether)s which has been investigated for high performance applications comprises the poly(arylene ether)s containing heterocyclic moieties. The synthetic approach to these poly(aryl ether)s involves the nucleophilic displacement of activated aromatic dihalides by alkali metal bisphenoxides in a polar aprotic medium. Heterocycles such as benzoxazoles[3,4], imidazoles[5], benzimidazoles[6], oxadiazoles[7,8] and pyridazines[9,10] have been incorporated within poly(arylene ether)s utilizing this synthetic

procedure. These synthetic approaches have been developed such that the heterocyclic units are incorporated into poly(arylene ether)s using both heterocyclic containing bisphenol monomers and heterocyclic containing activated dihalide monomers.

The synthesis of aromatic poly(ether amide)s[11] by nucleophilic displacement of activated aryl fluorides has been reported. In addition, work has also appeared describing the synthesis of poly(ether ketone amide)s and poly(ether ketone imide)s using Friedel–Crafts syntheses[12].

Aromatic polyethers containing pendent cyano groups (poly(ether nitrile)s) have also been studied. For example, Kricheldorf *et al.* described the preparation of aromatic polyethers containing pendent cyano groups by the condensation of silylated diphenols with difluorobenzonitriles[13]. A series of fluorinated polyimides and fluorinated poly(imide amide)s containing pendent cyano groups were also prepared and characterized to determine their dielectric constants as a function of relative humidity (r.h.) and their thermal characteristics. The fluorinated polyimides and fluorinated poly(imide amide)s containing pendent cyano groups were prepared by reaction of bis(4-aminophenoxy)benzonitriles with a fluorinated dianhydride and with a fluorinated diacid chloride containing preformed imide rings[14].

The objective of this work was to develop new synthetic

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methodology which would allow for the preparation of a series of new alternating copoly(aryl ether)s containing pendent cyano groups. The major advantage of this synthetic approach is that greater structural variety can be introduced in the polymer backbone.

EXPERIMENTAL

Materials

N,N-Dimethylacetamide (DMAc), N-methyl-2-pyrrolidinone (NMP), cyclohexanone, 4-cyanophenol, 4-methoxyphenol, 4-phenoxyphenol, 4-aminophenol, 2-chloro-6-fluorobenzonitrile, terephthaloyl chloride, isophthaloyl chloride and potassium carbonate were obtained from Aldrich and used without purification. 4,4-(Hexafluoroisopropylidene)diphenol (bisphenol AF), 9,9-bis(4-hydroxyphenyl)-fluorene (HPF), and 1,1-bis(4-hydroxyphenyl)-1-phenylethane (bisphenol AP) were obtained from Kennedy and Klim and used without purification.

Model reactions

2-(p-Methoxyphenoxy)-6-(p-cyanophenoxy)benzonitrile (1). Potassium carbonate (1.4 g) was added to a solution of 1.20 g (0.0077 mol) of 2-chloro-6-fluorobenzonitrile and 0.95 g (0.0077 mol) of 4-methoxyphenol in 25 ml of DMAc. The mixture was heated at 150°C with stirring under nitrogen for 16 h, and was then allowed to cool to room temperature. G.c./mass spectral analysis of the mixture showed 3-chloro-2-cyano-4'-methoxydiphenyl ether (CME) (M+/e = 259) to be the only product of the reaction, no evidence of the 3-fluoro-2-cyano-4'-methoxydiphenyl ether being observed. An additional 1.4 g of potassium carbonate and 0.916 g (0.0077 mol) of 4-cyanophenol were added to the reaction mixture. The mixture was heated a second time at 150°C with stirring under nitrogen for 16 h, and was then allowed to cool to room temperature. An aliquot of the reaction mixture was examined by g.c./mass spectrometry; the only product observed was 2-(*p*-methoxyphenoxy)-6-(*p*-cyanophenoxy)benzonitrile (1) (M+/e = 342). The reaction mixture was decanted from the insoluble potassium halides and residual potassium carbonate. A 1 : 1 mixture of water and methanol was added until the solution became slightly cloudy. The mixture was allowed to stand at room temperature for several hours and the resulting solid was isolated by filtration, washed with methanol, and dried. The solid was recrystallized from ethanol to yield 1.77 g (67% yield) of MCB as a white crystalline solid (m.p. = 123–125°C). Elemental analysis calculated for $C_{21}H_{14}N_2O$: C, 73.68; H, 4.12; N, 8.18. Found: C, 73.48; H, 4.2; N, 8.06.

Monomer synthesis

N,N-Bis[4-(3-chloro-2-cyanophenoxy)phenyl] terephthalamide (2a). Anhydrous potassium carbonate (3.5 g, 0.025 mol) was added to a stirred solution of 3.14 g (0.022 mol) of 2-chloro-6-fluorobenzonitrile, 2.40 g (0.022 mol) of 4-aminophenol and 50 ml of DMAc. The mixture was heated to 150°C for 17 h with stirring under nitrogen and was then allowed to cool to room temperature, upon which 25 ml of DMAc and 10 ml of pyridine were added. The mixture was cooled in an ice bath and 2.23 g (0.011 mol) of terephthaloyl chloride was added while stirring. The mixture was then removed from the

ice bath and stirred for an additional 1 h at room temperature. Water was added to the mixture to precipitate the product. The crude product was recrystallized from DMAc to afford **2a** as white crystals (m.p. = 319–321°C, 78% yield). Elemental analysis calculated for $C_{34}H_{20}N_4O_4Cl_2$: C, 65.92; H, 3.25; N, 9.04; Cl, 11.45. Found: C, 66.10; H, 3.55; N, 8.78; Cl, 11.68.

N,N-Bis[4-(3-chloro-2-cyanophenoxy)phenyl)]isophthalamide (2b). Using conditions described for the preparation of **2a**, but with isophthaloyl chloride used in place of terephthaloyl chloride, **2b** was prepared. Yield = 71%; m.p. = 248–250°C. Elemental analysis calculated for $C_{34}H_{20}N_4O_4Cl_2$: C, 65.92; H, 3.25; N, 9.04; Cl, 11.45. Found: C, 66.02; H, 3.14; N, 8.86; Cl, 11.42.

3-Chloro-2-cyano-4'-phenoxydiphenyl ether (CCPE). Anhydrous potassium carbonate (5.0 g, 0.036 mol) was added to a stirred solution of 5.25 g (0.034 mol) of 2-chloro-6-fluorobenzonitrile, 6.32 g (0.034 mol) of 4-phenoxyphenol and 100 ml of DMAc. The mixture was heated at 160°C for 17 h with stirring under nitrogen, allowed to cool to room temperature, and 200 ml of methylene chloride was then added. The solution was washed three times with about 100 ml of water, dried over $MgSO_4$, and concentrated under vacuum. The diether was filtered, washed with water and dried, affording a white solid. The crude product was recrystallized from hexane/toluene to afford CCPE as white crystals (m.p. = 97–99°C, 81% yield). Elemental analysis calculated for $C_{19}H_{12}NO_2Cl$: C, 70.92; H, 3.76; N, 4.35; Cl, 11.02. Found: C, 70.62; H, 3.68; N, 4.59; Cl, 11.33.

1,3-Bis[(4-(3-chloro-2-cyanophenoxy))-4-phenoxybenzoyl]-benzene (3). To a 250 ml round-bottom flask was added 10.00 g (0.031 mol) of CCPE, 3.16 g (0.0155 mol) of isophthaloyl chloride, 2.3 g (0.0246 mol) of dimethyl sulfone and 122 g of dichloromethane. The mixture was stirred under nitrogen until the solids dissolved, was cooled in an ice bath, and 14.5 g (0.109 mol) of aluminium chloride was added. The mixture was stirred for 1 h at ice bath temperature, 2 h at room temperature, and 1 h at reflux. The mixture was allowed to cool to room temperature and poured into methanol. The resulting solid was filtered, washed with methanol and water, dried, and recrystallized from DMAc. M.p. = 190–192°C. Calculated for $C_{46}H_{26}N_2O_6Cl_2$: C, 71.42; H, 3.39; N, 3.62; Cl, 9.17. Found: C, 71.74; H, 3.63; N, 3.42; Cl, 9.04.

Polymerization

Aromatic polyethers were prepared by the reaction of a bisphenol and **2** or **3** in the presence of potassium carbonate in DMAc at 160°C as depicted in *Schemes 4 and 5*. A typical polymerization was carried out as follows. To a 100 ml round-bottom flask was added 3.09 g (0.005 mol) of **3a**, 1.68 g (0.005 mol) of 4,4'-(hexafluoroisopropylidene)diphenol, 25.2 g of DMAc and 2.1 g (0.016 mol) of potassium carbonate. The mixture was heated to 160°C with stirring under nitrogen for 17 h, and was then allowed to cool to room temperature. The polymer was precipitated by pouring the reaction mixture into a blender containing about 100 ml of water, filtered, washed three times with water and dried to yield 4.6 g (92% yield) of a white powder.

Polymer films

Solutions of the polymers (15–25 wt% solids) in a 1/1 mixture of DMAc 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 thick, were released from the glass substrates by placing the substrate in deionized water after drying.

Measurements

Dielectric constants were measured using the fluid displacement method described previously[15]. The capacitance of the films was measured using circular gold electrodes (1 in. diameter) 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 Eastern dew point hygrometer (System 1100DP). Thermal gravimetric analysis (t.g.a.) was determined, using a heating rate of $20°C min^{-1}$, on a Seiko DSC 220C. Infrared spectral analysis was performed on a Bio-Rad FTS-60A *FT*i.r.

Dynamic mechanical thermal analysis (d.m.t.a.) was performed using a Rheometrics DMTA, Mk III, in the tensile mode, at a frequency of 1 Hz and applied force 0.5 N (for sample **4d**). For samples **4b** and **4c** it was necessary to increase the applied force to 4 N to prevent buckling of the sample. Samples were in the form of cast films roughly 10×10 mm in dimension and about 0.2 mm thick, and were maintained in an atmosphere of dry, oxygen-free nitrogen during the scans, which were done at a heating rate of $3°C min^{-1}$.

The *FT*i.r. spectra were recorded on a Digilab FTS-60 spectrometer at a resolution of $8 cm^{-1}$. They are the result of 32 scans. The data were acquired in the transmission mode using a KBr substrate. The samples were solvent cast and dried prior to examination.

Molecular weight distributions were determined using a Waters 6000A GPC with one Polymer Laboratories 500A and two Jordi 25 cm mixed bed columns. Narrow molecular weight polystyrene standards were used for calibration. The measurement utilized a u.v. detector operating at 254 nm. The polymer samples were dissolved in THF at a concentration of 1 mg in 10 ml and injected in 100 μl aliquots. The inherent viscosity of the polymers was determined at 20°C for solutions with a concentration of 0.5 g polymer (100 ml)$^{-1}$ of N-methyl-2-pyrrolidinone (NMP), using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

The synthetic routes to poly(aryl ether)s include both electrophilic aromatic substitution and oxidative coupling. However, the nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to high performance, high temperature resistant polyarylethers. Aryl halides, when activated by an electron-withdrawing substituent such as ketone, sulfone or cyano, are readily susceptible to nucleophilic aromatic substitution polymerizations. The rate-determining step in nucleophilic aromatic substitution is the formation of an intermediate Meisenheimer complex[16].

The nature of the aryl halide can have a significant effect on the rate of Meisenheimer complex formation[17]. When the halide is Cl, Br or I the relative rate of aryl halide displacement varies by a factor of about 5. However, when the aryl halide is F the relative rate is

3300 (compared with $I = 1$). The fact that the fluoro group is the best leaving group among the halogens in most aromatic nucleophilic substitutions is due to the greater electron-withdrawing character of the fluorine. The carbon of the C–F bond is more positive and thus more susceptible to nucleophilic attack.

Since the reactivities of aryl halides can vary greatly, it was our desire to utilize the different reactivities of the activated aromatic halogens to prepare alternating copolymers. The idea was to use activated dihalo aromatic monomers containing two different halogens having markedly different reaction rates to prepare polyarylether alternating copolymers. Since fluoro groups have much faster reaction rates, they would be expected to be displaced preferentially over other halogens. Therefore, an activated aryl monomer containing both a fluoro group and another halo group would be expected to react with phenoxides first at the C–F position, followed by reaction at the other carbon–halo position. A useful monomer to investigate this idea is 2-chloro-6-fluorobenzonitrile. In this monomer, both halogens are activated by the cyano group and are in similar steric environments.

To demonstrate the feasibility of using 2-chloro-6-fluorobenzonitrile in the preparation of alternating copolyethers, the model reaction of a monophenoxide with 2-chloro-6-fluorobenzonitrile was investigated. Our first reaction involved the reaction of 4-methoxyphenol with 2-chloro-6-fluorobenzonitrile in N,N-dimethylacetamide (DMAc) in the presence of K_2CO_3. G.c./mass spectral analysis of the reaction showed that 2-chloro-6-(*p*-methoxyphenoxy)benzonitrile was formed preferentially ($> 99\%$) over 2-fluoro-6-(*p*-methoxyphenoxy) benzonitrile. Reaction of 2-chloro-6-(*p*-methoxy phenoxy) benzonitrile with 4-cyanophenol in DMAc in the presence of K_2CO_3 yielded 2-(*p*-methoxyphenoxy)-6-(*p*-cyanophenoxy)benzonitrile (**1**) (*Scheme 1*). The model reactions demonstrated that the fluoro- and chloro-substituents were cleanly displaced by the phenoxides in the order predicted. The high selectivity and yield
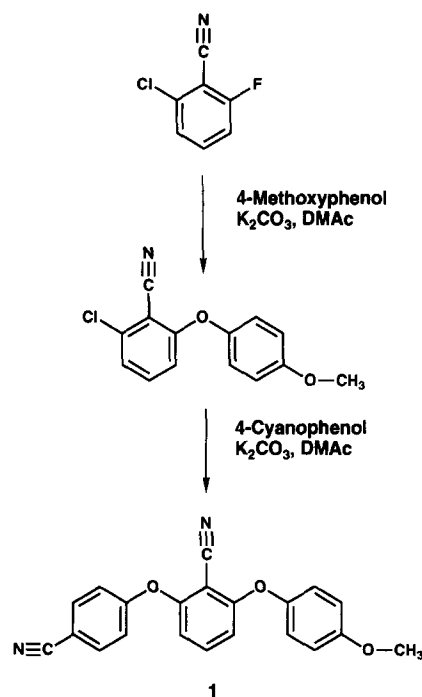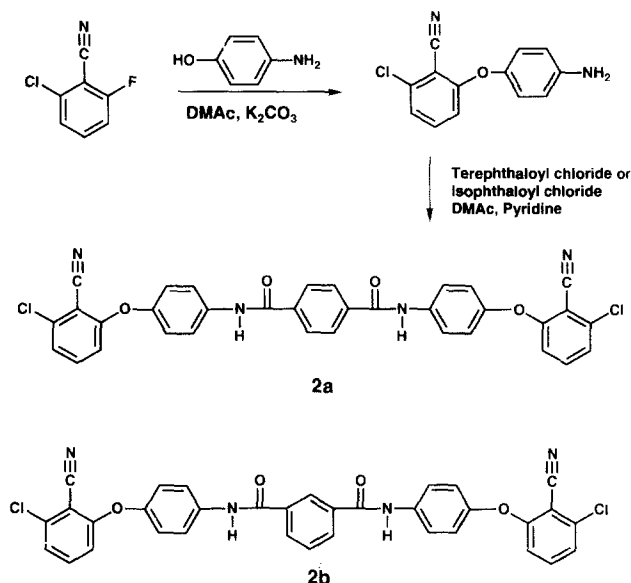

Scheme 1 Reaction of 2-chloro-6-fluorobenzonitrile with phenols
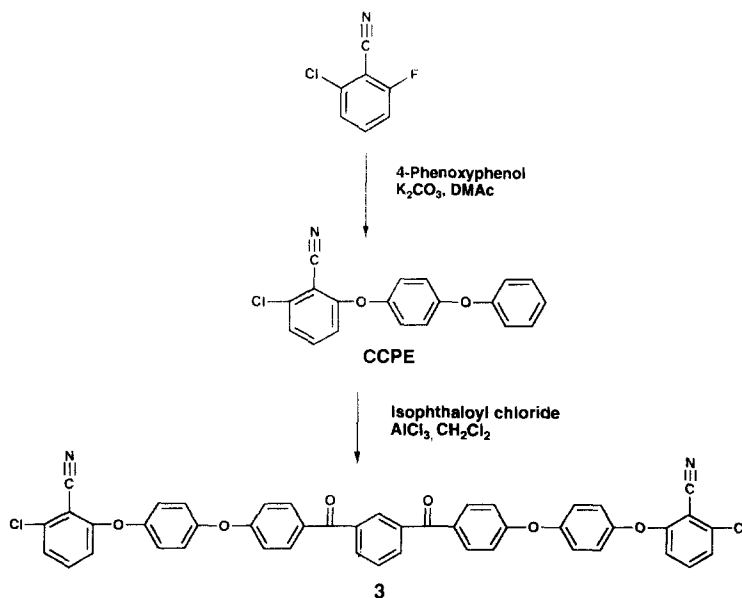
observed in each of the displacements demonstrated that these reactions are suitable for polymer-forming reactions.

To demonstrate the utility of using monomers containing halogens having different rates of halo displacement in the preparation of alternating copolyethers, 2-chloro-6-fluorobenzonitrile was used to prepare a series of bis(2-chloro-1-cyanophenyl)ethers containing amide and ketone moieties. Monomers **2** and **3** were readily prepared from 2-chloro-6-fluorobenzonitrile and 4-aminophenol or 4-phenoxyphenol, respectively, in high yield by electrophilic aromatic substitution in DMAc with potassium carbonate. 4-Aminophenoxide and 4-phenoxyphenoxide generated under the reaction conditions selectively displaced the fluoro groups in 2-chloro-6-fluorobenzonitrile to yield **2** and **3** respectively. *Schemes 2* and *3* depict the preparation of monomers **2** and **3** containing the amide and ketone functionalities, respectively. The resulting products were isolated, dried and recrystallized to yield white, crystalline solids.

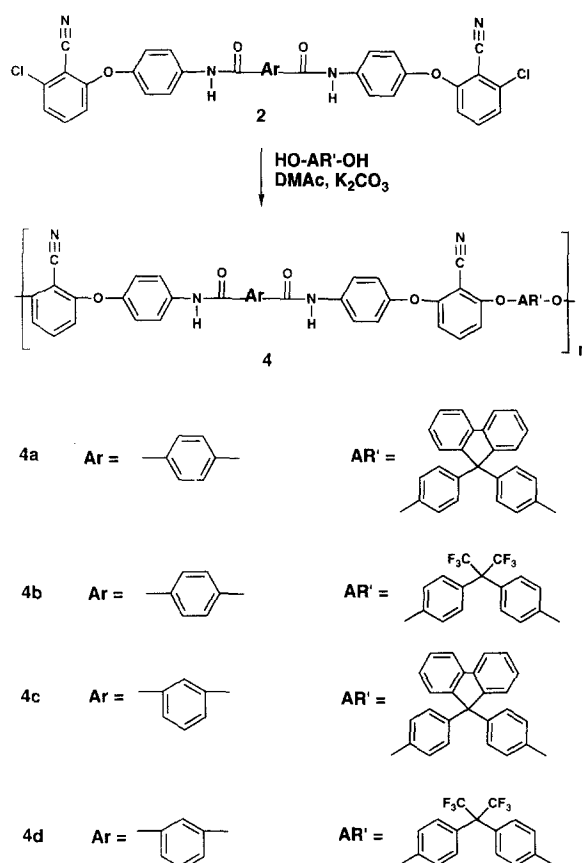Polymerization of the bis(2-chloro-1-cyanophenyl)-

ethers **2** and **3** was carried out with various bisphenols in DMAc in the presence of an excess of K_2CO_3 (*Schemes 4* and *5*). Polymerization reactions were run under nitrogen at 160°C for 16 h at about 20 wt% solids. Judging by the viscosity increase, the polymerization reactions were near completion after only about 8 h at 160°C. After cooling to room temperature, the polymers were then coagulated in water, washed with water, and dried to yield white powders. In each case the yield was essentially quantitative. This general procedure was applied to various diphenols, yielding polymers **4a–d** and **5a–c**.

Scheme 4 Synthesis of poly(aryl ether amide)s **4**

Scheme 2 Synthesis of aryl ether amide monomers **2a** and **2b**

Scheme 3 Synthesis of aryl ether ketone monomer **3**
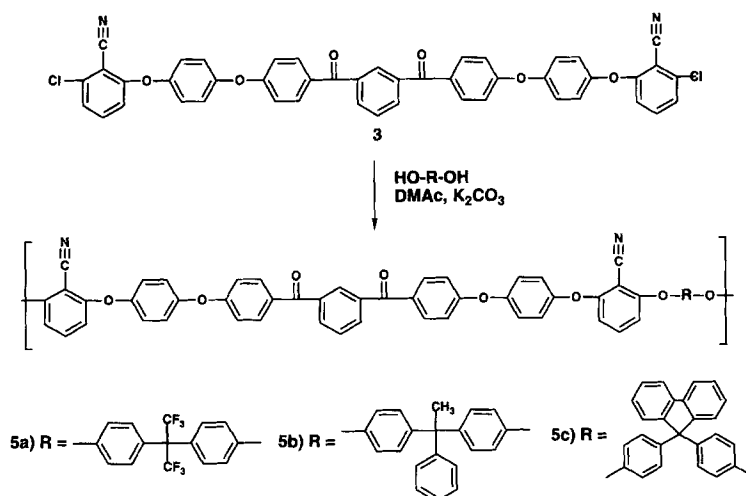
Scheme 5 Synthesis of poly(aryl ether ketone)s **5**

Size exclusion chromatography of **4a–b** and **5a–c** showed that the polymers were of high molecular weight and displayed very high polydispersity. A low molecular weight fraction, which we attribute to cyclic oligomers, was observed for all five polymers tested. However, the presence of the oligomeric species did not have an especially negative effect on the polymer properties since all the polymers yielded flexible, creasable films showing good mechanical integrity. Characterization of the inherent viscosity (i.v.) of polymers **4a–d** also showed them to be of high molecular weight, with the polymers having i.v.s ranging from 0.38 to 0.95 dl g^{-1}. Molecular weight characterization results for **4a–d** and **5a–c** are tabulated in *Table 1*.

The poly(aryl ether) copolymer powders **4a–d** and **5a–c** were soluble in DMAc, NMP, tetrahydrofuran, and mixtures of DMAc and cyclohexanone. Solutions of the polymers (15–25 wt% solids) in a 1/1 mixture of DMAc and cyclohexanone were spin-coated onto glass substrates and dried to yield transparent, flexible films. The poly(aryl ether) copolymer powders **4a–d** and **5a–c** could also be compression moulded at 200–280°C to yield transparent, flexible films.

The first heating of all samples during the d.s.c. thermal analysis showed a number of transitions caused by processing history which were not repeatable on cooling or on a second heating. We therefore only report the T_gs observed on the second heating. The T_gs reported below may be higher than those for polymers which have not seen thermal treatment. However, we were unable to obtain good d.s.c. thermograms for the unheated samples because of process history related transitions. In an effort to obtain useful d.s.c. thermograms we carried out the d.s.c. experiments on both polymer powders and polymer films. Both forms showed numerous non-repeatable transitions during their first heating. The poly(aryl ether amide)s **4a–d** displayed T_gs ranging from 216 to 265°C. Polymers **4a** and **4b**, which contain the *para*-substituted phenylene rings, have higher T_gs, 265 and 234°C, than do the analogous polymers, **4c** and **4d**, prepared with the *meta*-substituted phenylene rings whose T_gs are 262 and 216°C respectively. The poly(aryl ether ketone)s **5a–c** have lower T_gs than the poly(aryl ether amide)s **4a–d**. The T_gs for **5a–c** range from 160 to 202°C. The increased T_gs of poly(aryl ether amide)s **4a–d** can be explained by the strong hydrogen bonding interactions between the amide

groups in the polymer main chain. The T_gs for the polymers **4a–d** and **5a–c**, measured during the second heating cycles, are listed in *Table 1*.

Hergenrother[18] has previously reported that aromatic polymers containing pendent cyano groups undergo crosslinking upon heating to elevated temperatures. In addition, Bruma[19] has described the thermal crosslinking of fluorinated poly(amide imide)s containing pendent cyano groups. The crosslinking reaction was described as the thermally induced trimerization of the cyano groups to the *sym*-triazines. It was also reported that repeated thermal cycling to 350 or 400°C caused the glass transition temperature (T_g) of these polymers to increase as a result of crosslinking.

Although no exotherm peaks are detected in the d.s.c. thermograms, we found that thermal treatment of films of polymers **4a–d** and **5a–c** at 350°C for 2 h yielded insoluble, crosslinked products. The failure to detect an exotherm in the d.s.c. thermograms would be expected if the thermal crosslinking reactions of the cyano groups are slow and/ or the heat of reaction is small. The crosslinking reactions of the cyano groups may also be sterically inhibited by the two ether linkages, both of which are *meta* to the cyano group. This steric interference would cause slow crosslinking reactions and could explain the high temperatures needed for the crosslinking reactions to proceed.

Thermal gravimetric analysis of **4a–d** reveals that the polymers exhibit initial weight loss in air (scan rate = 20°C min^{-1}) at 452, 459, 426 and 456°C respectively. Thermal gravimetric analysis of **5a–c** reveals that these polymers exhibit initial weight loss in air (scan rate = 20°C min^{-1}) at 478, 468 and 516°C respectively.

Table 1 Properties of polymers **4a–d** and **5a–c**

Polymer	ν_{inh} (dl g^{-1})	Molecular weight		T.g.a. in air, onset (°C)	T_g (d.s.c.) (°C)
		M_n	M_w		
4a	0.38	8300	27 000	426	265
4b	0.54	12 800	123 000	456	234
4c	0.55	–	–	452	262
4d	0.95	–	–	459	216
5a	–	13 700	75 400	478	160
5b	–	14 000	80 000	468	172
5c	–	14 500	129 100	516	202

The results of d.s.c. and t.g.a. thermal analysis of polymers **4a–d** and **5a–c** are summarized in *Table 1*.

The tan δ vs temperature plots for all three polymers exhibited an α transition (the glass transition), and weak β and γ transitions. In addition, **4b** and **4c** showed an α' transition at a higher temperature than that of the α transition, the latter appearing as a shoulder on the α' transition, so that the α transition temperature could be estimated only approximately in these cases. For each polymer, the β transition temperature was 0.70–0.74 T_g. The results of the d.m.t.a. scans are shown in *Table 2*.

The precision of measurement of the transition temperatures is estimated to be ± 1 K except for the α transition temperatures for polymers **4b** and **4c**, for which the precision is of the order ± 2–3 K. Included in

Table 2 is the onset temperature, $T_{E'}$, for the reduction in storage modulus associated with the α transition.

As shown by Cassel and Twombly[20] for an epoxy composite reference material, the storage modulus onset temperature agrees well with the glass transition temperature determined by d.s.c. (*Table 1*) for polymer **4d**, whereas the temperature corresponding to the tan δ maximum is significantly higher. For polymer **4b**, T_g from d.s.c. is close to $T_{\alpha'}$, and for **4c**, T_g from d.s.c. has the same value, within experimental uncertainty, as T_α.

The observed γ relaxations may be attributable to the motion of pendent CN groups, and the origin of the β relaxations is possibly oscillation of main chain segments. However, in the absence of further evidence these interpretations are speculative. The source of the α' relaxation is at present not known.

The key structural features of the polymers can be identified by *FT* i.r. spectroscopy. Key features in the *FT* i.r. spectrum of **4b** include the following absorptions: amide NH, $3312\,\mathrm{cm}^{-1}$, aromatic CH, $3049\,\mathrm{cm}^{-1}$, cyano CN, $2202\,\mathrm{cm}^{-1}$; amide C=O, $1596\,\mathrm{cm}^{-1}$; aromatic C=C, $1502\,\mathrm{cm}^{-1}$; and aromatic ether Ar–O–Ar, $1253\,\mathrm{cm}^{-1}$. The key features in the *FT* i.r. spectrum of **5b** include the following absorptions: aromatic C–H, $3069\,\mathrm{cm}^{-1}$, aliphatic C–H, $2971\,\mathrm{cm}^{-1}$; ketone C=O, $1659\,\mathrm{cm}^{-1}$; cyano

Table 2 Results of d.m.t.a. scans for polymers **4b–d**

Polymer	T_α (°C)	$T_{E'}$ (°C)	$T_{\alpha'}$ (°C)	T_β (°C)	T_γ (°C)	T_g (d.s.c.) (°C)
4b	236	211	223	95	−100	234
4c	273	246	261	100	−102	262
4d		217	232	95	−103	216
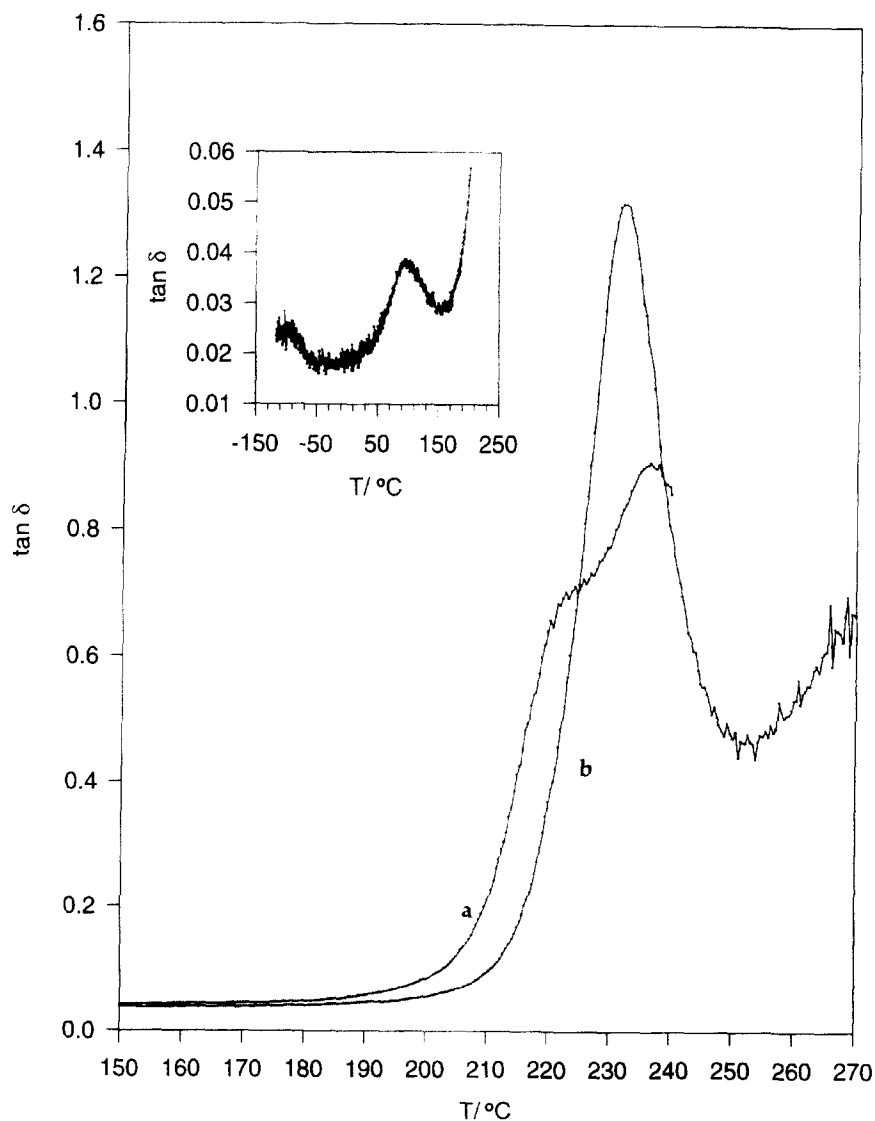
Figure 1 D.m.t.a. traces showing the temperature variation of tan δ for polymers **4b** (curve a and inset) and **4d** (curve b)
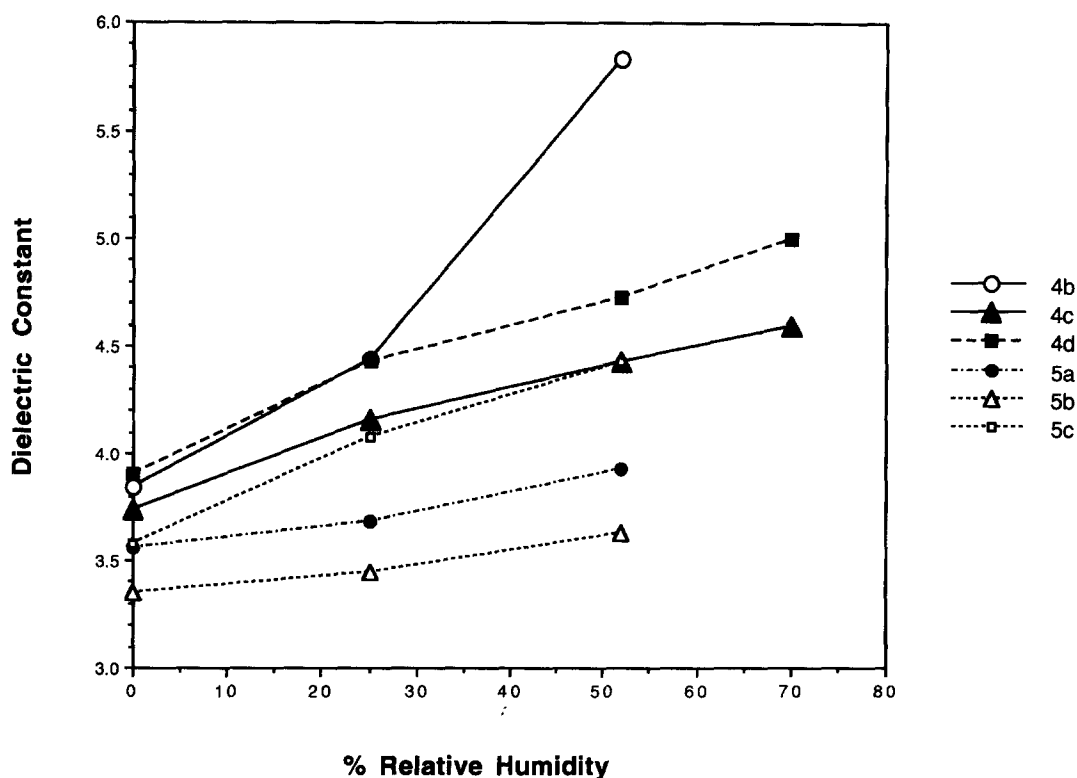
Figure 2 Effect of humidity on dielectric constants of polymers **4b–d** and **5a–c**

CN, $2202\,\mathrm{cm}^{-1}$; aromatic C=C, 1592 and $1491\,\mathrm{cm}^{-1}$, and aromatic ether Ar–O–Ar, $1245\,\mathrm{cm}^{-1}$.

At 0% relative humidity (r.h.), **4b–d** have dielectric constants (measured at 10 kHz) of 3.84, 3.74 and 3.90 respectively. At 52% r.h., the dielectric constants of **4b–d** increased to 5.83, 4.43 and 4.73 respectively. At 0% relative humidity (r.h.), **5a–c** have dielectric constants (measured at 10 kHz) of 3.56, 3.35 and 3.58 respectively. At 52% r.h., the dielectric constants of **5a–c** increased to 3.93, 3.63 and 4.43 respectively. Since the dielectric constant of a polymer is a function of the polymer's total polarizability, α_T, polymers displaying higher dielectric constants have higher polarizability[21,22]. The higher dielectric constants of polymers **4b–d** compared to polymers **5a–c** are attributed to the presence of the polarizable amide moieties in **4b–d**. The relationships of dielectric constant to relative humidity for polymers **4b–d** and **5a–c** are depicted graphically in *Figure 2*.

We have previously reported that polymers exhibiting high moisture absorption also show greater increases in dielectric constant with increasing relative humidity[14,15,23] compared to polymers having lower moisture absorption. This relationship of moisture absorption in polyimides vs relative humidity has also been reported by others[24,25]. It then follows that the large increases in the dielectric constants of the poly(aryl ether) copolymers **4b–d** with increasing relative humidity, compared to those of polymers **5a–c** prepared without amide groups, are attributed to higher levels of moisture absorption facilitated by hydrogen bonding of water to the amide groups in **4b–d**.

CONCLUSION

Poly(aryl ether amide) and poly(aryl ether ketone) alternating copolymers containing pendent cyano groups have been prepared by nucleophilic aromatic substitution. The generation of the aryl ether linkages was controlled by utilizing the differences in reactivities of the activated chloro and fluoro substituents in 2-chloro-6-fluorobenzonitrile. We have demonstrated that the fluoro group is preferentially displaced over the chloro group and that alternating copolyethers can be prepared using this methodology. This method provides a general synthetic methodology for the preparation of high-temperature resistant, high T_g poly(aryl ether) alternating copolymers. These copolymers can also be thermally crosslinked to yield solvent resistant films. The major advantage of this synthetic approach is that greater structural variety can be introduced in the polymer backbone and the molecular architecture of the polymers can be more completely controlled.

ACKNOWLEDGEMENTS

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