Synthesis and properties of new alternating copolyethers containing pendent cyano groups

Frank W. Mercer* and Martin T. McKenzie
Raychem Corporation, Corporate Research and Development, Mail Stop 123/6602, 300 Constitution Drive, Menlo Park, CA 94025, USA

and Allan Easteal and Simonne J. Moses
Chemistry Department, University of Auckland, Private Bag 92019, Auckland, New Zealand
(Received 28 February 1994)

A general method for the preparation of polyarylether alternating copolymers containing pendent cyano groups has been developed. We found that the activated aryl fluorides in 2-chloro-6-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 polyarylether alternating copolymers containing pendent cyano groups were prepared by sequential reaction of 2-chloro-6-fluorobenzonitrile with the potassium salts of two different diphenols. Reaction of two moles of 2-chloro-6-fluorobenzonitrile with one mole of a diphenoxide yields a bis(3-chloro-2-cyanophenyl)ether (bis-CCPE) as the only product. Subsequent reaction of a second bisphenoxide with the bis-CCPEs causes displacement of the activated chloro groups and formation of alternating copolymers. 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. The glass transition temperatures of the resulting crosslinked films ranged from 156 to 254°C depending on polymer structure and cure conditions.

(Keywords: polyarylether; alternating copolymer; cyano)

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 for the aerospace and electronics industry. 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 flexibilizing groups such as ethers into the polymer chain. Commercially available polyetherketones[1] and polyethersulfones[2] are widely used in high-performance applications because of their unique combination of chemical, physical and mechanical properties.

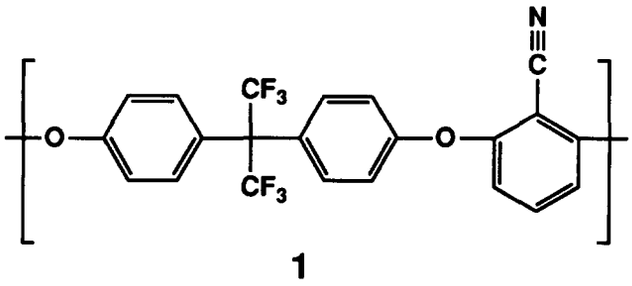
Another class of polyarylethers that has been investigated for high-performance applications are the poly(arylene ether)s containing heterocyclic moieties. The synthetic approach to these polyarylethers involves the nucleophilic displacement of activated aromatic dihalides by alkali metal bisphenoxides in a polar aprotic medium. Heterocycles such as benzoxazoles[3,4], imidazoles[5], benzimidazoles[6], phenylquinoxalines[7,8], 1,2,4-triazoles[9], oxadiazoles[10,11], and pyridazines[12,13] 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.

Aromatic polyethers containing pendent cyano groups are a class of high-temperature resistant polymer that have received only limited study. Aromatic polyethers containing pendent cyano groups can be prepared by the condensation of a dialkali metal salt of a diphenol with 2,6-dihalobenzonitrile or 2,4-dihalobenzonitrile in an anhydrous dipolar aprotic solvent. For example, polymer **1** (*Figure 1*) can be prepared by reaction of 4,4'-(hexafluoroisopropylidene)diphenol and 2,6-difluorobenzonitrile in the presence of K_2CO_3 in a polar aprotic solvent[14].

The objective of this work was to develop new synthetic methodology which would allow for the preparation of a series of new alternating copolyarylethers containing pendent cyano groups. The major advantage of this synthetic approach is that greater structural variety can be introduced in the polymer backbone.

*To whom correspondence should be addressed

0032-3861/94/24/5355–09



1

Figure 1 Polyarylether 1 (previously described)

EXPERIMENTAL

Materials

N,*N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), cyclohexanone, 4-cyanophenol, 4-methoxyphenol, resorcinol, 2-chloro-6-fluorobenzonitrile and potassium carbonate were obtained from Aldrich and used without purification. 4,4-(Hexafluoroisopropylidiene)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* (*3*). Potassium carbonate (1.4 g, 0.010 mol) 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 (g.c.–m.s.a.) of the mixture showed 3-chloro-2-cyano-4′-methoxydiphenyl ether (**2**) ($M + /e = 259$) to be the only product of the reaction. No evidence of 3-fluoro-2-cyano-4′-methoxydiphenyl ether was observed by g.c.–m.s.a. An additional 1.4 g (0.010 mol) of potassium carbonate and 0.916 g (0.0077 mol) of 4-cyanophenol was added to the above reaction mixture. The mixture was heated a second time at 150°C with stirring under nitrogen for 16 h. The reaction mixture was allowed to cool to room temperature. An aliquot of the reaction mixture was examined by g.c.–m.s.a. and the only product observed was 2-(*p*-methoxyphenoxy)-6-(*p*-cyanophenoxy)benzonitrile (**3**) ($M + /e = 342$). 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 of **3** as a white crystalline solid (melting point (MP) = 123–125°C, 67% yield). Elemental analysis calculated for $C_{21}H_{14}N_2O$: C, 73.68; H, 4.12; N, 8.18. Found: C, 73.48; H, 4.20; N, 8.06.

Monomer synthesis

1,3-Bis(2-cyano-3-chlorophenoxy)benzene (***4A***). 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, 1.21 g (0.011 mol) of resorcinol and 50 ml of DMAc. The mixture was heated at 150°C for 17 h with stirring under nitrogen. The mixture was allowed to cool to room temperature, 150 ml of dichloromethane was added and the mixture was poured into 150 ml of water. The organic layer was separated and washed twice more with 100 ml water. The organic phase was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product was recrystallized from toluene/hexane to afford 1,3-bis(2-cyano-3-chlorophenoxy)benzene (**4A**) as white crystals (MP = 139.5–141°C, 78% yield). G.c./m.s.a. showed only a single product ($M + /e = 379$). Elemental analysis calculated for $C_{20}H_{10}N_2O_2Cl_2$: C, 63.01%; H, 2.64%; N, 7.35%; Cl, 18.6%. Found: C, 63.10%; H, 2.55%; N, 7.28%; Cl, 18.8%.

4,4′-Bis(2-cyano-3-chlorophenoxy)biphenyl (***4B***). Anhydrous potassium carbonate (5.5 g, 0.040 mol) was added to a stirred solution of 5.44 g (0.035 mol) of 2-chloro-6-fluorobenzonitrile, 3.25 g (0.0175 mol) of 4,4′-dihydroxybiphenyl and 70 ml of DMAc. The mixture was heated at 150°C for 17 h with stirring under nitrogen, allowed to cool to room temperature, and water was added to precipitate the product. The diether was filtered, washed with water and dried, affording a white solid. The crude product was recrystallized from toluene to afford 1,3-bis(2-cyano-3-chlorophenoxy)biphenyl (**4B**) as white crystals (MP = 205–206°C, 82% yield). Elemental analysis calculated for $C_{26}H_{14}N_2O_2Cl_2$: C, 68.29%; H, 3.09%; N, 6.13%; Cl, 15.5%. Found: C, 68.39%; H, 2.98%; N, 6.21%; Cl, 15.61%.

9,9-Bis[4-(2-cyano-3-chlorophenoxy)phenyl]fluorene (***4C***). 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, 5.95 g (0.017 mol) of 9,9-bis(4-hydroxylphenyl)fluorene, 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 water was added to precipitate the product. The diether was filtered, washed with water and dried, affording a white solid. The crude product was recrystallized from xylene/cyclohexanone to afford 9,9-bis[4-(2-cyano-3-chlorophenoxy)phenyl]fluorene (**4C**) as white crystals (MP = 244–245°C, 81% yield). Elemental analysis calculated for $C_{39}H_{22}N_2O_2Cl_2$: C, 75.37%; H, 3.57%; N, 4.51%; Cl, 11.41%. Found: C, 75.22%; H, 3.68%; N, 4.59%; Cl, 11.33%.

Polymerization

Aromatic polyethers were prepared by the reaction of a bisphenol and **4** in the presence of potassium carbonate in DMAc at 160°C. A typical polymerization was carried out as follows: To a 100 ml round-bottomed flask was added 2.29 g (0.005 mol) of **4B**, 1.68 g (0.005 mol) of 4,4′-(hexafluoroisopropylidiene)diphenol, 20.2 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 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 3.3 g (92% yield) of **5B** as 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 mm in thickness, were released from the glass substrates by placing the substrate in deionized water after drying.

Measurements

Dielectric constants were measured using the previously described fluid displacement method[15]. The capacitance of the films was measured using circular gold electrodes (1 in (2.5 cm) 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 Eastman dewpoint hygrometer (System 1100DP). Thermal gravimetric analysis (t.g.a.) was determined using a heating rate of 20°C min^{-1}. T.g.a. was performed on a Seiko DSC 220C. Infra-red spectral analysis was performed on a Bio-Rad FTS-60A FT-IR.

The Fourier transform infra-red (*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.

The molecular weight distributions were measured using a Waters GPC in the dual-detection mode (differential refractive index (DRI) and u.v.). The u.v. detector was operated at 254 nm. The samples were prepared by dissolving 10 mg of polymer in 10 ml THF. The injection volume was 50 ml. Separations were effected using two Polymer Labs 10 m PL mixed-B columns. THF was used as the mobile phase. The molecular weight distributions were calculated relative to narrow polystyrene standards ranging in molecular weight from 10^2 to 4×10^6.

Samples were prepared for differential scanning calorimetry (d.s.c.) by punching 4 mm discs from films such that the ultimate sample weight was 4–5 mg. The discs were stacked in an aluminium pan with a crimped lid to optimize thermal contact. The samples were scanned in a PL 12000 DSC at 10°C min^{-1} from ambient to 400°C under a nitrogen atmosphere. The samples were then cooled at 10°C min^{-1} to about 25°C. The heat/cool/heat cycle was repeated three times thereafter. Glass transition temperatures were recorded during the second, third and fourth heating cycles.

The approximate intrinsic viscosities were measured at a concentration of 0.5 g/100 ml. The approximate intrinsic viscosity is defined as η_{sp}/c where η_{sp} is the specific viscosity and c is the concentration. A 125.0 ± 0.7 mg sample of each polymer was dissolved in 1:1 cyclohexanone/*N*-methyl-2-pyrrolidinone in a 25 ml volumetric flask. Flow times for solvent and each solution were measured at 298 ± 0.05 K using a factory-calibrated Cannon Instrument Co. Ubbelohde-type viscometer. Flow times were in the range 135–198 s, and were reproducible to a few tenths of a second. Specific viscosities were calculated as $t_{solution}/t_{solvent}$.

RESULTS AND DISCUSSION

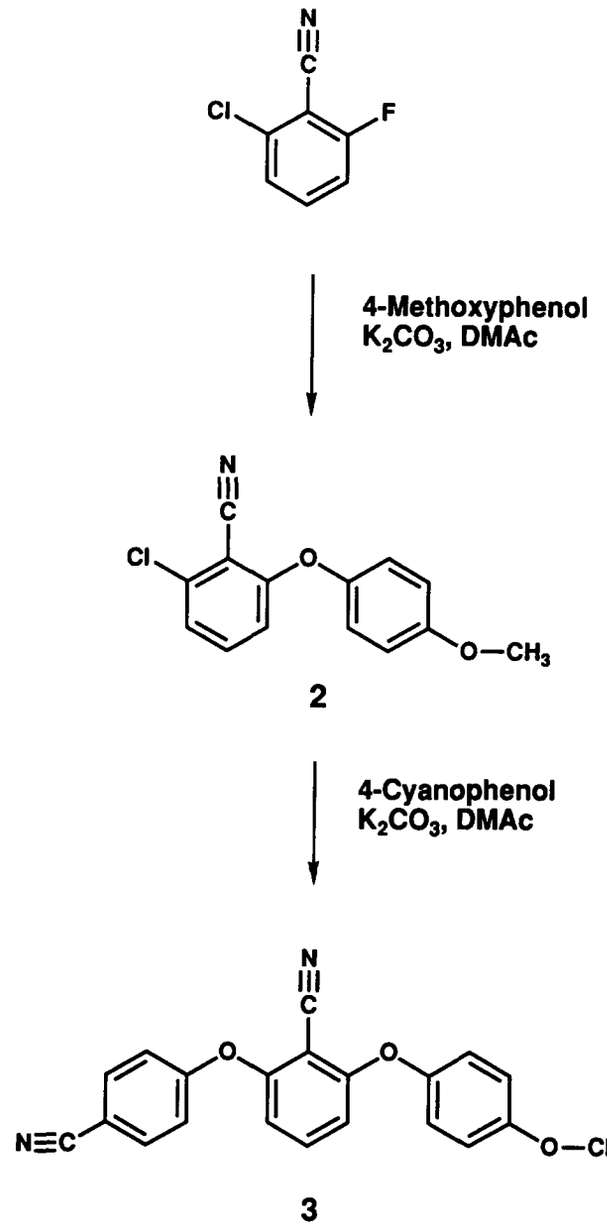
The synthetic routes to polyarylethers include electrophilic aromatic substitution and oxidative coupling. However, the nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to high-performance, high-temperature resistant polyarylethers. Aryl halides, when activated 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. When the halide is Cl, Br or I the relative rates of aryl halide displacement varies by a factor of about 5. However, when the aryl halide is F the relative rate was 3300 (compared with I = 1)[17]. 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.–m.s.a. of the reaction showed that 2-chloro-6-(*p*-methoxyphenoxy)benzonitrile (**2**) was formed preferentially (>99%) over 2-fluoro-6-(*p*-methoxyphenoxy)benzonitrile. Reaction of 2-chloro-6-(*p*-methoxyphenoxy)benzonitrile (**2**) with 4-cyanophenol in DMAc in the presence of K_2CO_3 yielded 2-(*p*-methoxyphenoxy)-6-(*p*-cyanophenoxy)benzonitrile (**3**) as the only product (*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 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 (**4**) (*Scheme 2*). Bis(2-chloro-1-cyanophenyl)ether preparation was carried out using a series of three diphenols to prepare the monomers **4A–C**. All reactions were run under nitrogen at 160°C for 9 h at about 20 wt% solids. After cooling to room temperature, the resulting products were

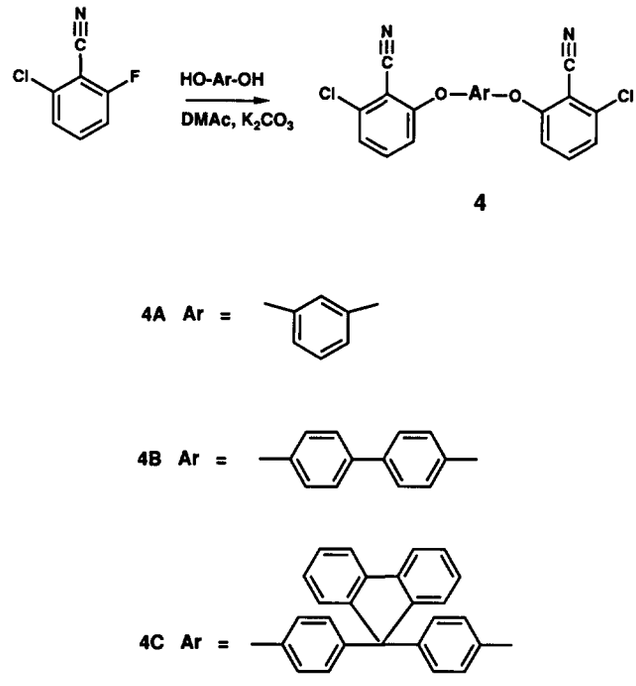


Scheme 1

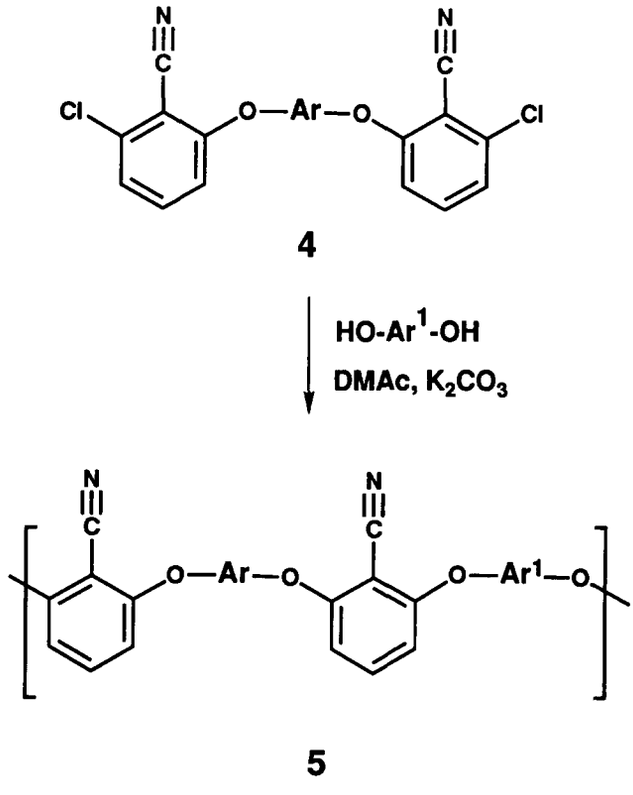
isolated in water, dried, and recrystallized to yield white, crystalline solids.

Polymerization of the bis(2-chloro-1-cyanophenyl)-ethers (**4**) was carried out with various bisphenols in DMAc in the presence of an excess of K_2CO_3 (*Scheme 3*). 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 **5A–F** depicted in *Figure 2*.

The poly(aryl ether) copolymer powders **5A–F** were soluble in DMAc, chloroform, cyclohexanone and tetrahydrofuran. 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



Scheme 2



Scheme 3

transparent, flexible films. The poly(aryl ether) copolymer powders **5A–F** could also be compression moulded at 200–280°C to yield transparent, flexible films.

The molecular weight distributions and average intrinsic viscosities of samples **5A–F** were measured. The results are tabulated in *Table 1*. In general, the molecular weights and viscosities trend similarly, as expected. Deviations can be explained by the error involved in the g.p.c. measurement. The synthetic conditions used result

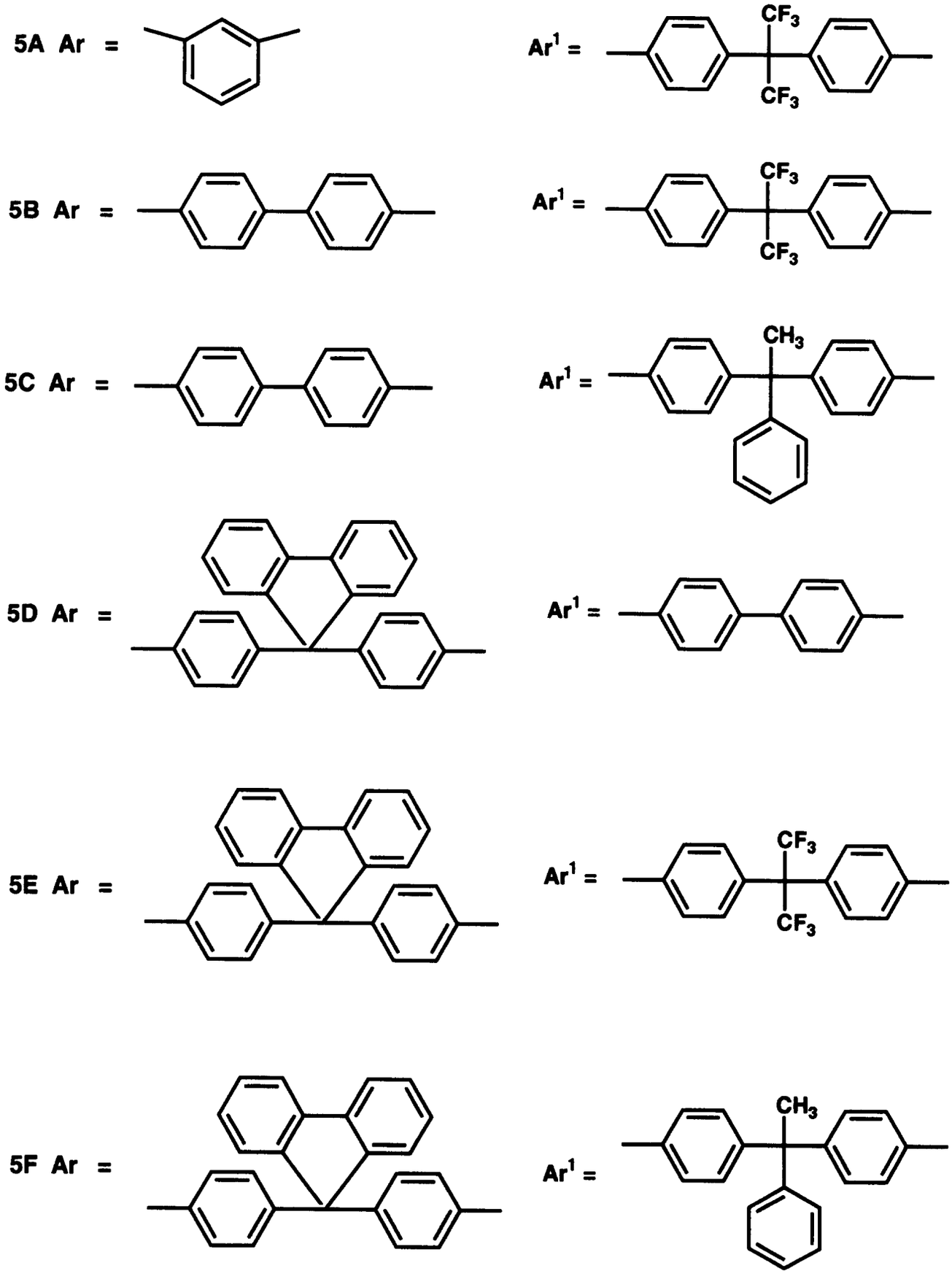


Figure 2 Structures of polyarylethers **5A–5F**

Table 1 Molecular weight characterization of polyarylethers **5A–5F**

Property	Polymer					
	5A	**5B**	**5C**	**5D**	**5E**	**5F**
M_n	11 500	19 500	26 000	17 100	11 800	11 500
M_w	66 300	96 900	109 300	98 600	44 300	38 800
Polydispersity	5.7	5.0	4.2	5.7	3.7	3.3
Specific viscosity[a]	0.42	0.79	0.91	0.75	0.33	0.37

[a]Calculated as $t_{solution}/t_{solvent}$

Table 2 Thermal characterization of polyarylethers **5A–5F**

Polymer	T_g (°C) after cycling to 300°C			T_g (°C) after cycling to 400°C
	2nd heating	3rd heating	4th heating	2nd heating
5A	160	162	162	177
5B	155	156	156	196
5C	175	189	194	194
5D	198	200	202	254
5E	153	196	209	208
5F	200	216	218	199

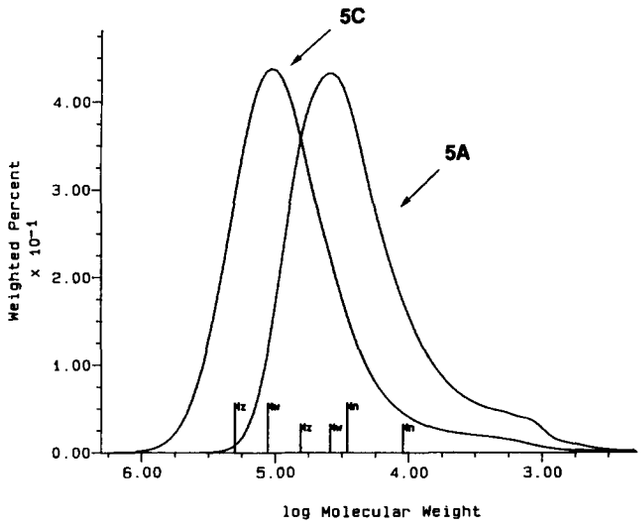


Figure 3 Molecular weight distributions for polyarylethers **5A** and **5C**

in a range of molecular weight distributions (and thus physical properties), and specific molecular weights can be achieved. Molecular weight distributions for **5A** and **5C** are depicted in *Figure 3*.

We have characterized the glass transition temperature (T_g) values for the poly(aryl ether) copolymers **5A–F** as a function of thermal cycling. T_g values were measured after two, three and four heating and cooling cycles in which the samples were heated at 10°C min^{-1} from room temperature to 300°C, followed by cooling back to room temperature, also at 10°C min^{-1}. T_g values were also measured after one heating–cooling–heating cycle under the following conditions: samples heated from room temperature to 400°C at 10°C min^{-1}, held at 400°C for 5 min, cooled to room temperature at 10°C min^{-1}, followed by a second heating to 400°C, also at 10°C min^{-1}. T_g values of **5A–F** were measured during the second heating during these cycles.

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. This was the case for both polymer powders and films. We report the T_g values observed on subsequent heatings in *Table 2*.

The T_g values of the polymers containing pendent cyano groups increase with thermal cycling. It is notable that for **5A**, **5B** and **5D** there is little change in T_g after heating cycles up to 300°C. The T_gs of these polymers increase significantly upon exposure to 400°C. On the other hand, polymers **5C**, **5E** and **5F** show an increase in T_g upon thermal cycling to 300°C. Hergenrother[18] has previously reported that aromatic polymers containing pendent cyano groups undergo crosslinking upon heating to elevated temperatures. The crosslinking reaction was described as the thermally induced trimerization of the cyano groups to the *sym*-triazines. *FT*i.r. experiments were performed to test this interpretation for our samples.

Samples **5C** and **5F** were examined by *FT*i.r. before and after thermal treatments. The results are shown in *Figures 4* and *5*, respectively. The *FT*i.r. spectras before heating are shown in *Figures 4* and *5*. Functional group analysis of the spectra is consistent with the proposed structures, that is, the materials demonstrate a high degree of aromaticity as seen in the 1600 cm^{-1} region. The appearance of the 3000 cm^{-1} region is also indicative of aromaticity. A band due to cyano functionality is observed in both spectra as expected. Strong features in the 1200–1300 cm^{-1} area can be attributed to the aryl ether moiety (aryl–O stretching mode). The bands in the 1400–1550 cm^{-1} region are consistent with the substitution of the aromatic functionality.

After heating to 350°C in air for 15 min, **5C** and **5F** showed slight discoloration, but the process did little to change the spectra of either material. However, after treatment at 400°C in air for 30 min, we observed a decrease in the relative intensity of the cyano band and a concomitant increase in intensities of bands at 1728, 1660, 1617, 1590 and 1479 cm^{-1}. The changes are highlighted in the difference spectrum shown in *Figure 6*. The observations shown for **5F** are essentially the same as for sample **5C**.

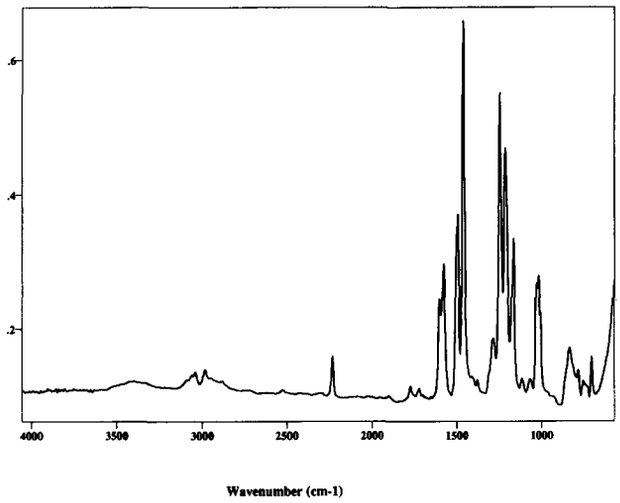


Figure 4 *FT* i.r. spectrum of polymer **5C**

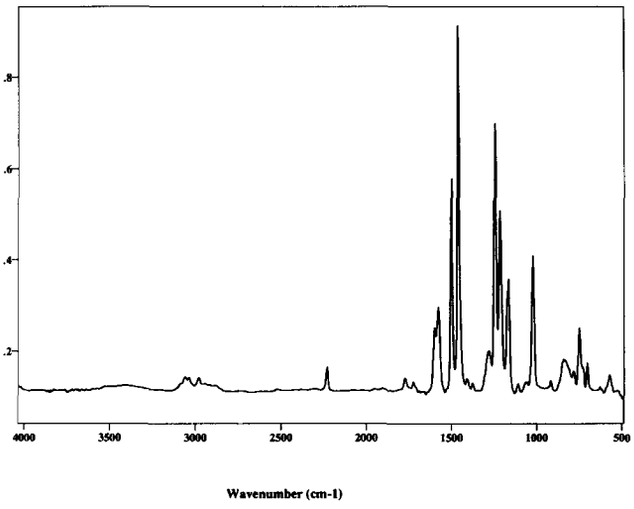


Figure 5 *FT* i.r. spectrum of polymer **5F**

These results suggest that the cyano group is reacting, which is consistent with prior work. However, it is difficult to assign any of the new bands to a triazine group. The reported position for a strong triazine band is 1550 cm^{-1}; such a band was not observed. The 1728 cm^{-1} band is probably due to the formation of carbonyls. The other bands suggest the formation of Ar–C=N groups, perhaps through the reaction of two cyano moieties. The data are not sufficient for an unambiguous assignment of structure. However, it appears that the d.s.c. results can be explained by the thermally induced reaction of the cyano groups to form a functionality containing C=N.

The d.s.c. results indicate that polymers **5A**, **5B** and **5D** undergo crosslinking at temperatures above 300°C. Samples **5C**, **5E** and **5F** appear to begin crosslinking at temperatures below 300°C. The temperatures for **5C**, **5E** and **5F** are lower than those required to observe changes by *FT*i.r. This may be due to the difference in heating control and effectiveness between a large oven and a d.s.c. cell. It may also be due to the degree of reaction required to observe an increase in glass transition, that is, it may be that the T_gs respond to small changes in chemistry that are hard to detect spectroscopically.

No peaks showing exotherms are detected in the d.s.c. thermograms. This 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 be sterically inhibited by the two ether linkages, both of which are *meta* to the cyano group. This steric interference would cause slow reaction. It would also explain the high temperatures needed for the crosslinking reactions to proceed.

Thermal gravimetric analysis of **5A–F** reveals that the polymers exhibit initial weight loss in air (scan rate = 20°C min^{-1}) at 405, 476, 465, 525, 464 and 441°C, respectively.

At 0% relative humidity (RH), **5A–F** have dielectric constants (measured at 10 kHz) of 3.49, 3.61, 3.64, 3.79, 3.76 and 3.47, respectively. At 52% RH, the dielectric constants of **5A–F** increased to 5.67, 4.84, 4.73, 4.20, 4.40 and 3.83, respectively. *Table 3* presents the characterization data of the poly(aryl ether) copolymers **5A–F**. The relationships of dielectric constant to relative humidity for polymers **5A–F** are depicted graphically in *Figure 7*.

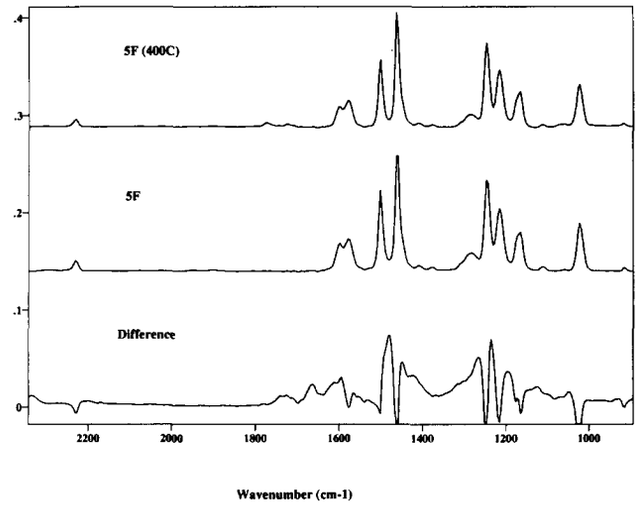


Figure 6 *FT* i.r. spectra **5F** – heat treatment results

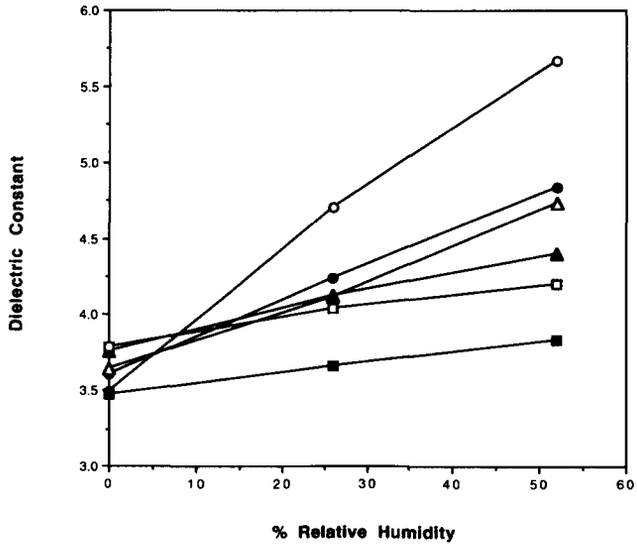


Figure 7 Relationship of dielectric constant *versus* percentage relative humidity for polyarylethers **5A–5F**. ○, **5A**; ●, **5B**; △, **5C**; □, **5D**; ▲, **5E**; ■, **5F**

Table 3 Thermal and dielectric characterization of alternating copolyethers containing pendent cyano groups

Property	Polymer					
	5A	**5B**	**5C**	**5D**	**5E**	**5F**
T.g.a. (°C) (onset in air)	405	476	465	525	464	441
Dielectric constant						
0% RH	3.49	3.61	3.64	3.79	3.76	3.47
52% RH	5.67	4.84	4.73	4.20	4.40	3.83

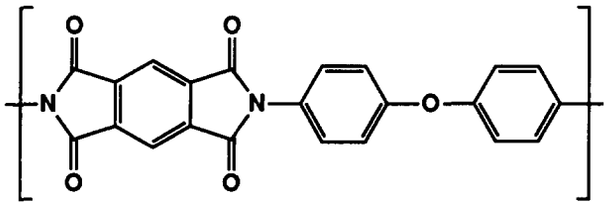
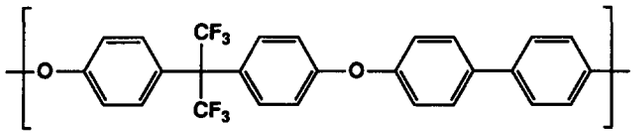


Figure 8 PMDA–ODA



6

Figure 9 Polyarylether **6** (previously described)

For comparison, one of the most common polyimides used as a dielectric in microelectronics applications is PMDA–ODA (*Figure 8*), made by reaction of pyrometallic dianhydride (PMDA) and 4,4′-diaminodiphenylether (ODA)[19]. For PMDA–ODA, the dielectric constant is 3.10 at 0% RH and 3.71 at 58% RH[15].

The previously reported[20] fluorinated poly(aryl ether) **6** has dielectric constants at 0% RH and 57% RH of 2.94 and 3.25, respectively. All of the poly(aryl ether)s, **5A–F**, described in this paper have dielectric constants significantly greater than that of **6**. Since the dielectric constant of a polymer is a function of the polymers total polarizability, a_T, polymers displaying higher dielectric constants have higher polarizability[21,22]. The high dielectric constants of the poly(aryl ether) copolymers **5A–F**, compared with that of **6**, are attributed to high polarizability of the cyano groups in the polyarylethers **5A–F**.

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 with polymers having lower moisture absorption. This relationship of moisture absorption in polyimides *versus* 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 **5A–F** with increasing relative humidity, compared with polymer **6** prepared without cyano groups, are attributed to higher levels of moisture absorption facilitated by hydrogen bonding of water to the cyano groups in **5A–F**. In a similar manner, we have previously shown that polyimides and poly(imide amide)s containing pendent cyano groups also have higher moisture absorptions and higher dielectric constants than do polyimides and poly(imide amide)s prepared without cyano groups[26].

CONCLUSION

Polyarylether 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. It is expected that the differences in reactivities of fluoro and chloro displacement could also be used to prepare other polyarylethers, such as polyethersulfones and polyetheroxadiazoles. This polymerization method should provide a general route for preparing polyarylether alternating copolymers where the structure of the polymer can be controlled by incorporation of two different diphenols into the polymer backbone in a selective manner. This method also provides for general synthetic methodology for the preparation of high-temperature resistant, high T_g polyarylether 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.

REFERENCES

1 Attwood, T. E., Davidson, P. C., Freeman, J. C., Hoy, J. C., Rose, J. B. and Staniland, P. A. *Polymer* 1981, **22**, 1096
2 Rose, J. B. *Polymer* 1974, **15**, 456
3 Hilborn, J. G., Labadie, J. W. and Hedrick, J. L. *Macromolecules* 1990, **23**, 2845
4 Smith, J. W. Jr., Connell, J. W. and Hergenrother, P. M. *Polymer* 1992, **33** (8), 1742
5 Harris, F. W., Ahn, B. H. and Cheng, S. Z. D. *Polymer* 1993, **34** (14), 3083
6 Connell, J. W. and Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 1667
7 Connell, J. W. and Hergenrother, P. M. *Polymer* 1992, **33** (17), 3739
8 Hedrick, J. L. and Labadie, J. W. *Macromolecules* 1988, **21**, 1883
9 Connell, J. W., Hergenrother, P. M. and Wolf, P. W. *Polymer* 1992, **33** (16), 3507
10 Mercer, F. W. *Polym. Mater. Sci. Eng. Proc.* 1992, **66**, 268
11 Hedrick, J. L. and Tweig, R. *Macromolecules* 1992, **25**, 2021
12 Johnson, R. N., Farnham, A. G., Clendinning, R. A., Hale, W. F. and Merriam, C. N. *J. Polym. Sci. (A-1)* 1967, **5**, 2375
13 Mercer, F. W. *High Perf. Polym.* 1994, **5**, 275
14 Mercer, F. W. and Goodman, T. D. *Polym. Prepr.* 1991, **32** (2), 189

15 Mercer, F. W. and Goodman, T. D. *High Perf. Polym.* 1991, **3** (4), 297
16 March, J. 'Advanced Organic Chemistry', J. Wiley, New York, 1985
17 Bunnett, J. F., Garbish, E. W. and Pruit, K. M. *J. Am. Chem. Soc.* 1957, **79**, 385
18 Hergenrother, P. M. *Macromolecules* 1974, **7**, 575
19 Economy, J. 'Contemporary Topics in Polymer Science', Vol. 5 (Ed. E. J. Vandenberg), Plenum Press, New York, 1984
20 Farnham, A. G. and Johnson, R. N. *US Patent 4 108 837*, 1978
21 Hougham, G., Tesoro, G. and Shaw, J. *Polym. Mater. Sci. Eng.* 1989, **61**, 369
22 Hougham, G., Tesoro, G., Viehbeck, A. and Chapple-Sokol, J. *Polym. Prepr.* 1993, **34** (1), 375
23 Mercer, F. W. and Goodman, T. D. '1990 International Electronics Packaging Society Conference Proceedings', International Electronics Packaging Society, Wheaton, IL, 1990, pp. 1042–1062
24 Sacher, E. and Susko, J. R. *J. Appl. Polym. Sci.* 1979, **23**, 2355
25 Moylan, C. R., Best, M. E. and Ree, M. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 87
26 Mercer, F. W., McKenzie, M. T., Bruma, M. and Schulz, B. *Polym. Int.* 1994, **33**, 399