Examination of the thermal and thermomechanical behaviour of novel cyanate ester homopolymers and blends with low coefficients of thermal expansion

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ABSTRACT

A new four-step synthetic method is presented and applied to the preparation of three novel dicyanate monomers that comprise aryl/alkylene ether backbones with high molecular flexibility in high purity. The multi-step route involves four individual high yielding steps (each greater than 70%), thus giving an overall reaction yields for all four steps between 42% and 50% depending on the length of the backbone. The products of all steps are characterised using Fourier transform infrared spectroscopy, ¹H nuclear magnetic resonance spectroscopy, elemental analysis and melting point determination. DSC and alysis of ‘uncatalysed’ samples (i.e. those polymerised thermally in absence of a specific catalyst) display relatively sharp melting endotherms ranging from 66°C to 125°C, depending on the length (and hence flexibility of the backbone). All monomers display broad polymerisation exotherms within close agreement (87 ± 2 kJ/mol. cyanate), although the polymerisations occur in different temperature regimes. When catalysed (aluminium(III) acetylacetonate/dodecylphenol), DSC reveals that the exothermic polymerisation peaks occur at significantly lower temperatures than the uncatalysed analogues and have much narrower profiles, but tend occur in a similar temperature regime (i.e. the peak maxima fall within 205°C - 216°C). The recorded polymerisation enthalpies for the catalysed monomers are ca. 93 ± 9.9 kJ/mol.

Assessment of the thermal stabilities of the cured polycyanurates using TGA shows that the polymers lose 5% of their masses by ca. 346-366°C, comparable with the commercial dicyanate AroCy B10, despite the greater aliphatic character. DMTA analysis is performed on the homopolymer of the commercial dicyanate AroCy B10 to validate the method and the results obtained are consistent with published data. The T_g values of the homopolymers of (4a), (4b) and
(4c) are determined from the peak maxima of the loss tangent, tan δ and are found to be 221°C (4a), 139°C (4b), and 121°C (4c) and fall in the expected order as the backbone chain length and hence flexibility is increased. The storage moduli at 25°C for the binary blends are significantly lower than the respective homopolymers, but the reduction in E’ over the temperature range 25°C to 200°C is significantly improved compared with AroCy B10. When combined with AroCy B10, binary blends showed a reduction in CTE of up to 12 ppm/°C while maintaining the same value of T_g.

**Keywords:** cyanate esters, polycyanurates, blends, synthesis, characterization, thermal analysis, thermogravimetric analysis, thermomechanical analysis.

**INTRODUCTION**

The commercial introduction of a prepolymer of bisphenol A dicyanate in 1975 [1] was initially targeted at the then new and growing market for substrates for advanced printed circuit boards (e.g. multichip modules or MCMs). The combination of exceptionally low dielectric constants, ε = 2.2-2.7 and dissipation factors, D_t = 0.003 at GHz frequencies, coupled with low loss behaviour has ensured the continuing application of cyanates in the fabrication of microelectronics components such as multichip modules [2] and latterly in stealthy coatings and structures [3]. Cured cyanates typically offer high performance characteristics somewhat intermediate between epoxy resins and BMIs [4] (e.g. glass transition temperatures, T_g, of between 200 and 300°C depending on structure and degree of cure) although very low moisture absorption (as low as 0.6-2.5 weight % depending on backbone structure, compared with figures of 4-4.5 weight % for bismaleimides or 3-6 weight % for commercial epoxies) can lead to good hot/wet properties. Cyanates may adhere to a variety of substrates, e.g. metals, glass and carbon fibres and cyanate adhesives have yielded values of 14-20 MPa (for lap shear strength) on 20224 T-3 aluminium alloy (some 50-100% higher than corresponding BADGE and TGDDM epoxy adhesives (cured with aromatic diamines), but it is their behaviour on silicon that is of particular interest in the microelectronics arena because of the ubiquity of this material in the formation of MCMs. Typically, the latter are formed from sequentially built layers of metallised conductors on ceramic or silicon substrates and unreinforced
polymer dielectric films. Despite (and partly owing to) the good adhesion observed on these substrates, there remains the strong possibility of disbonding and delamination of the layers as thermal processing takes place, given the large differences in the coefficients of thermal expansion (CTE) of the components used in MCMs. Inevitably, with a complex structure of this kind, the costs mount as the likelihood of scrapping a multilayer board increases with layer count. The aim of the present work was stimulated by the pressure to produce thermosetting polymers with relatively high $T_g$ and fracture toughness with lower values of CTE than those currently observed in commercial resin systems.

In common with epoxy resins and addition polyimides such as bismaleimides (BMIs), both more established in the commercial arena, polycyanurates (cyanate esters) are attractive for a variety of technological applications, for which cheaper commodity polymers (or even traditionally expensive thermosets) offer inferior performance. Cured cyanates typically offer high performance characteristics somewhat intermediate between epoxy resins and BMIs [5]. Thus, cyanates have been used as advanced structural composite matrices, due to their relatively high glass transition temperatures ($T_g$) of between 200 and 300$^\circ$C depending on structure and degree of cure and low moisture absorption (as low as 0.6-2.5 weight % depending on backbone structure, compared with figures of 4-4.5 weight % for bismaleimides or 3-6 weight % for commercial epoxies). This leads, in turn, to good hot/wet properties: when cured, the methylated commercial monomer AroCy M was found to retain 83% of its flexural modulus at 150$^\circ$C after immersion in boiling water, compared with 53% for a commercial aerospace epoxy (based on a tetruglycidyl amine) [6]. Furthermore, the composite materials may be formulated to achieved attractive levels fracture toughness (e.g. $G_{IC} = 454$ J/m$^2$ for Fiberite 954-3) for thermoset polymers after blending with engineering thermoplastics [7].

The exceptionally low dielectric constants, $\varepsilon = 2.2$-2.7 and dissipation factors, $D_t = 0.003$ at GHz frequencies, coupled with low loss behaviour has ensured the application of cyanates in the fabrication of microelectronics components such as multichip modules [8] and stealthy coatings and
structures [9]. In common with epoxy resins, cyanates may adhere to a variety of substrates, e.g. metals, glass and carbon fibres and cyanate adhesives have yielded values of 14-20 MPa (for lap shear strength) on 20224 T-3 aluminium alloy (some 50-100% higher than corresponding BADGE and TGDDM epoxy adhesives (cured with aromatic diamines). Moreover, these values are maintained to 200-232°C [10]. More recently, cyanate esters have stimulated increasing interest within the satellite industry where the combination of all of the aforementioned features and high specific strength as composites (resistance to microcracking, which can occur from thermal cycling.) have allowed them to supplant existing epoxy resins as materials of choice in space structures [11,12].

A number of synthetic routes to the preparation of cyanate monomers has been reported and reviewed comprehensively [13], although the most important commercial route, first reported by Grigat and Pütter some forty years ago [14,15] and involving the treatment of phenols with cyanogen chloride (or more typically cyanogen bromide in laboratory preparations such as the route reported in this work), still form the basis of modern methods, albeit in a modified form. Importantly, although the preparation involves the use of toxic reagents, the resulting monomers generally have low toxicities (e.g. LD₅₀ ≥ 3 g/kg for the dicyanate of bisphenol A). In previous unreported experiments [16] designed to produce the dicyanates examined within this paper, the use of a variety of protecting groups (e.g. tetrahydropyranyl, benzyl or methyl ethers, etc.) met with limited success. For example, having produced (bis-4-(4-methoxyphenoxy) phenylethoxyethane from dichloroethane in high yield and purity (with the intention of cleaving the methyl ether to yield the diphenol prior to cyanation), it was not possible to deprotect this group using e.g. recognised methods such as boron tribromide [17] without breaking the alkylene ether backbone. Consequently, it was decided that it would be better to find a new protecting group and use a suitable aldehyde as a protecting group to enable its removal easily whilst leaving the alkylene ether backbone intact and this led to the current study.
EXPERIMENTAL

Materials

The following regents were obtained from a range of sources (indicated in parentheses, along with the purity where noted) and were all used as received, unless otherwise noted in the experimental text. Dichloromethane (DCM), methanol, acetone, \textit{N,N}-dimethylformamide (DMF), anhydrous potassium carbonate and phosphorus pentoxide, sodium thiosulphate, sodium hydrogen carbonate, sodium sulphate, sodium hydroxide (all GPR grade and obtained from Fisher Scientific). \textit{N,N}-Dimethylacetamide (DMAc) (99%), triethylamine (99%), deuterio-chloroform (CDCl$_3$), deuterio-acetone (CD$_6$CO), deuterio-methanol (CD$_3$OD), dichloroethane, 2-chloroethylether, 1,2-bis-(2-chloroethoxy)ethane, 4-hydroxybenzaldehyde, 3-chloroperoxybenzoic acid (MCPBA) 70-75% (were all obtained from Aldrich Chemical Co.). 4-Methoxyphenol (99%) was obtained from Acros Organics and anhydrous sodium sulphate (GPR) from BDH. The commercial dicyanate monomer, AroCy B10, based on bisphenol A (shown in Figure 1) was obtained from Ciba Speciality Chemicals. Aluminum(III) acetylacetonate (99%) (Al(acac)$_3$) and 4-dodecylphenol (mixture of isomers) were obtained from Sigma Aldrich and were used without further purification.

Apparatus

Fourier transform infrared (FT-IR) spectra were recorded using a Perkin-Elmer (system 2000 FT-IR) spectrometer interfaced with a PC running PE-Spectrum v 2.00 software or a Nicolet Avatar 320 FT-IR spectrometer running Nicolet OMNIC ESP 5.1 software. The samples were presented on an ATR module, 16 scans, at a resolution of 4 cm$^{-1}$, were recorded and co-added to produce the final spectrum. $^1$H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC300 spectrometer operating at 300 MHz. Solutions of samples were prepared in CDCl$_3$, CD$_3$OD, D$_6$-acetone according to solubility and spectra were acquired at 298 K using tetramethylsilane (TMS) as an internal standard where applicable.

Elemental analysis was performed using a Leeman Labs., Inc. CE 440 elemental analyser using a weighed sample, typically 1-3 mg. Acetanilide was used to calibrate the instrument followed by a
set of standards (S-benzyl thiuronium chloride and phenylthioiurea) to check the calibration. The accuracy with standard organic compounds is +/-0.15 % absolute plus +/-0.15 % relative. Melting temperatures were determined using a Kopfler flat bed micro melting point (m.p.) apparatus and a heating rate of 4 K min\(^{-1}\).

Differential scanning calorimetry (DSC) experiments were performed on the catalysed and uncatalysed cyanate esters of the synthesised alkyl ether dicyanate monomers and blends was a TA instruments DSC Q100 series controlled by a Viglen computer, running TA Q series advantage software. Samples (ca. 4.5 ± 0.5 mg) were encapsulated in crimped aluminium pans. Samples were placed in the heating chamber at room temperature ca. 25°C and the ‘run’ program was set to heat to 40°C and held for one minute. Data recording began when the cell temperature was at the desired temperature using a variety of heating rates (5, 10, 15, and 20 K min\(^{-1}\)), at a temperature range of 35-350°C. All measurements were made under N\(_2\) with a continuous flow rate of 20 cm\(^3\) min\(^{-1}\). For glass transition temperature (T\(_g\)) measurements, following the initial 10 K min\(^{-1}\) scan, samples were quenched and cooled at the same rate prior to a second, re-scan, experiment at 10 K min\(^{-1}\). The T\(_g\) was determined by measuring the mid-point position of the discontinuity of the baseline.

Thermogravimetric (TG) analysis was performed using a ULVAC Sinku-Riko differential thermo-gravimetric analyzer TGD 7000. Prior to running the sample, the sample holder (platinum boat) was heated at a rate of 80 Kmin\(^{-1}\) to above 800°C to remove any residual material from any previous experiments and allowed to cool to room temperature. The shaved samples (ca. 8.7 ± 0.5 mg) of the cured neat resin were measured at a heating rate of 10 Kmin\(^{-1}\) between 25 and 800°C. Measurements were made under N\(_2\) (20 cm\(^3\) min\(^{-1}\)) using a platinum boat.

Dynamic mechanical thermal analysis (DMTA) measurements for the polymers were undertaken in dual cantilever bending mode on cured neat resin and blend samples of 10 x 30 x 1 mm\(^3\) using a Polymer Laboratories Dynamic Mechanical Thermal Analyser with a Polymer Laboratories environmental controller unit. Temperature scans were performed between -150 and 300°C at 5 K min\(^{-1}\) at a frequency of 1 Hz.
Thermomechanical analysis (TMA) measurements for the polymers were undertaken using a Seiko Instruments, Inc. EXSTAR6000 TMA/SS6000 and calibrated using quartz crystal with a known CTE, before performing measurements in penetration mode (probe weight 4.9 mN, analysis surface area 9.026 mm$^2$) on cured neat resin samples (ca. 0.7-1.1 x 5 x 5 mm$^3$) supported on quartz. Temperature scans were performed between 25 and 300°C at 5 K min$^{-1}$.

**Synthesis and characterization**

A series of general methods were employed to produce three different cyanate ester monomers, differing only in the bridging chain length (i.e. the value of $n$). Consequently, the entire preparative procedure is described for compounds 1a, 2a, 3a, and 4a ($n = 1$), but for the remaining compounds only the stoichiometries, the characterisation data, and variations in the method are given.

*X preparation of 4,4’-[ethane-1,2-diylbis(oxy)]dibenzaldehyde (1a, n = 1)*

A 3-neck round bottom flask, equipped with a magnetic stirrer bar, thermometer and condenser was charged with 4-hydroxybenzaldehyde (153.62 g, 1.26 mol.), dichloroethane (62.24 g, 0.63 mol.), potassium carbonate (347.72 g, 2.52 mol.) and DMF (500 cm$^3$). The mixture was stirred and heated to reflux (110°C) for at least 48 hours under these conditions and under a nitrogen blanket. The reaction mixture was left to cool to room temp before extracting into DCM and water added to dissolve any salts. The DCM product layer was removed and the aqueous layer washed with DCM. The DCM layers were combined and washed with water and dried over sodium sulphate (room temperature, overnight). The solvent was removed by rotary evaporation and under reduced pressure to obtain a crude product. A needle-like, off-white crystalline solid was obtained by recrystallisation in warm diethyl ether and the product collected by filtration and dried in a desiccator with P$_2$O$_5$ under reduced pressure (overnight) to yield 124.06 g (72.9 %), m.p. = 113–115°C. Elemental analysis calculated for C$_{16}$H$_{14}$O$_4$: %C (71.10), %H (5.22); found: %C 70.59, %H (4.75).
300 MHz $^1$H NMR $\delta_H$ (CDCl$_3$, ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum, 1a, 9.91 (1H, s, C-H due to aldehyde), 7.88-7.85 (4H, d, $J_H = 8.8$ Hz, Ar-H ortho to aldehyde link); 7.08-7.05 (4H, d, $J_H = 8.8$ Hz, Ar-H and meta to aldehyde link); 4.45 (4H, s, C-H between ether links para to aldehyde links).

Preparation of 4,4’-[ethane-1,2-diylbis(oxy-1,4-phenylene)]diformate (2a, n = 1)

A 3-neck round bottom flask, equipped with a magnetic stirrer bar, thermometer and condenser was charged with bis-(4,4’-formylphenoxy)ethane (120.71 g, 0.45 mol.), 3-chloroperoxybenzoic acid (MCPBA) (300.63 g, 1.74 mol.), and DCM (900 cm$^3$). The mixture was stirred at room temperature for 4 hours under these conditions and under a nitrogen blanket. A milky suspension was formed and the resultant reaction mixture was treated with saturated (aq) NaHCO$_3$ (600 cm$^3$). After ca. 2 hours, and when the mixture had stopped effervescing, the DCM layer was collected and the aqueous layer washed with DCM (3 x 50 cm$^3$). The organic layers were combined and washed with 10% Na$_2$S$_2$O$_3$ (aq) (3 x 50 cm$^3$), followed by water (3 x 50 cm$^3$), then brine (3 x 50 cm$^3$) and finally dried over sodium sulphate (overnight). The solvent was removed by rotary evaporation and under reduced pressure to obtain a crude product. A white crystalline solid was obtained by recrystallisation from warm methanol and the product collected by filtration and dried in a desiccator with P$_2$O$_5$ under reduced pressure to yield 109.39 g (81.0 %), m.p. = 133–135°C. Elemental analysis calculated for C$_{16}$H$_{14}$O$_6$: %C (63.57), %H (4.67); found: %C (63.41), %H (4.56).

300 MHz $^1$H NMR $\delta_H$ (CDCl$_3$, ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum, 8.28 (1H, s, C-H due to oxy aldehyde), 7.08-7.05 (4H, d, $J_H = 8.8$ Hz, Ar-H ortho to oxy aldehyde link); 6.97-6.94 (4H, d, $J_H = 9.3$ Hz, Ar-H and meta to oxy aldehyde links); 4.31 (4H, s, C-H between ether links para to oxy aldehyde links).

Preparation of 4,4’-[ethane-1,2-diylbis(oxy)]diphenol (3a, n = 1)
A 3-neck round bottom flask, equipped with a magnetic stirrer bar, thermometer and a round bottom flask, equipped with a magnetic stirrer bar, thermometer and condenser was charged with bis-(4,4’-formyloxyphenoxy)ethane (108.02 g, 0.36 mol.), sodium hydroxide (57.18 g, 1.43 mol.), ethanol (800 cm$^3$) and water (300 cm$^3$). The mixture was stirred and heated to reflux (130°C) for 24 hours under these conditions and under a nitrogen blanket. The reaction mixture was left to cool to room temperature before neutralising with hydrochloric acid (3 M) forming a solid, which was extracted into DCM. The DCM layers were combined and washed with water and dried over sodium sulphate; the solvent was removed by rotary evaporation and under reduced pressure to obtain a crude product. A solid was obtained by recrystallisation in warm ethanol and water and then the product collected by filtration and dried in a desiccator with P$_2$O$_5$ under reduced pressure to yield 70.25 g (79.8 %), m.p. = 213–215°C. Elemental analysis calculated for C$_{14}$H$_{14}$O$_4$: %C (68.28), %H (5.73); found: %C (67.90), %H (5.69).

300 MHz $^1$H NMR $\delta_{\text{H}}$ (CD$_3$OD, ppm from TMS assignments refer to structure shown in the accompanying NMR spectrum, 6.82-6.79 (4H, d, $J_H = 8.8$ Hz, Ar-H ortho to hydroxy link); 6.72-6.69 (4H, d, $J_H = 8.8$ Hz, Ar-H and meta to hydroxy links); 4.18 (4H, s, C-H between ether links para to hydroxy links).

Preparation of 4,4’-[ethane-1,2-diylbis(oxy-1,4-phenylene)]dicyanate (4a, n = 1)

A 3-neck round bottom flask, equipped with a magnetic stirrer bar, dropping funnel and a drying tube, was charged with bis-(4,4’-hydroxyphenoxy)ethane (69.82 g, 0.28 mol.) and cyanogen bromide (66.07 g, 0.62 mol.). The reactants were dissolved in acetone (800 cm$^3$) and the solution cooled to below -5°C in a methanol/cardice bath. Triethylamine (63.18 g, 0.62 mol.) was added dropwise via the dropping funnel to the stirring solution, at a rate such that the reaction mixture was maintained below –5°C. After the addition of triethylamine, the reaction mixture was left stirring for 30 minutes and then allowed to warm to room temperature. The mixture was washed, by fast stirring, with water to remove triethylamine hydrobromide (the principal by-product). The product was extracted with DCM and washed with water (3 x 50 cm$^3$). The organic product layer was dried
over sodium sulphate and the solvent removed by rotary evaporation to give the crude product. A light yellow solid was obtained by recrystallisation from a 50/50 mixture of ethanol and water to yield 79.02 g (94.1 %), m.p. = 118–120°C. Elemental analysis calculated for C_{16}H_{12}N_{2}O_{6}: %C (64.86), %H (4.08), %N (9.46); found: %C (64.49), %H (3.81), %N (9.27).

### 300 MHz \(^1\)H NMR \(\delta_{\text{H}}\) (CDCl\(_3\), ppm from TMS):

Assignments refer to structure shown in the accompanying NMR spectrum, 26-7.23 (4H, d, \(J_H = 9.3\) Hz, Ar-H ortho to cyanate link); 7.02-6.97 (4H, d, \(J_H = 9.3\) Hz, Ar-H and meta to cyanate links); 4.33 (4H, s, C-H between ether links para to cyanate links).

#### Preparation of 4,4'-[oxybis(ethane-1,2-diyl)oxy]dibenzaldehyde (1b, n = 2)

Using the previous method, the following quantities were used: 4-hydroxybenzaldehyde (77.70 g, 0.64 mol.), dichloroethane (45.5 g, 0.32 mol.), potassium carbonate (175.88 g, 1.27 mol.) and DMF (400 cm\(^3\)). A light yellow crystalline solid was obtained by recrystallisation from warm diethyl ether: yield 90.25 g (90.3 %), m.p. = 130–132°C. Elemental analysis calculated for C\(_{18}\)H\(_{18}\)O\(_5\): %C (68.78), %H (5.77); found: %C (67.64), %H (5.70).

### 300 MHz \(^1\)H NMR \(\delta_{\text{H}}\) (CDCl\(_3\), ppm from TMS):

Assignments refer to structure shown in the accompanying NMR spectrum, 9.89 (1H, s, C-H due to aldehyde), 7.84-7.81 (4H, d, \(J_H = 8.8\) Hz, Ar-H ortho to aldehyde link); 7.03-7.00 (4H, d, \(J_H = 8.8\) Hz, Ar-H and meta to aldehyde links); 4.26-4.23 (4H, t, \(J_H = 4.5\) Hz, C-H between ether links para to aldehyde links); 3.99-3.96 (4H, t, \(J_H = 4.5\) Hz, C-H between ether links in the centre of the molecule).

#### Preparation of 4,4'-[oxybis(ethane-1,2-diyl)oxy-1,4-phenylene)]diformate (2b, n = 2)

Using the previous method, the following quantities were used: bis-(4,4'-formylphenoxy)ethoxyethane (88.94 g, 0.28 mol.), 3-chloroperoxybenzoic acid (MCPBA) (190.47 g, 1.10 mol.) and DCM (800 cm\(^3\)), saturated (aq) NaHCO\(_3\) (500 cm\(^3\)). A light yellow crystalline solid was obtained by recrystallisation from warm methanol: yield 80.84 g (82.5 %), m.p. = 67–69
Elemental analysis calculated for C\textsubscript{16}H\textsubscript{18}O\textsubscript{5}: %C (66.19), %H (6.25); found: %C (65.78), %H (6.41).

**300 MHz \textsuperscript{1}H NMR \delta_{\text{H}} (CD\textsubscript{3}OD, ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum**, 6.80-6.77 (4H, d, \(J_{\text{H}} = 8.9\) Hz, Ar-H ortho to hydroxy link); 6.70-6.67 (4H, d, \(J_{\text{H}} = 8.9\) Hz, Ar-H and meta to hydroxy links); 4.07-4.04 (4H, t, \(J_{\text{H}} = 4.5\) Hz, C-H between ether links para to hydroxy links); 3.86-3.83 (4H, t, \(J_{\text{H}} = 4.5\) Hz, C-H between ether links in the centre of the molecule).

**Preparation of 4,4’-{oxybis(ethane-1,2-diyl)-1,4-phenylene}diphenol (3b, \(n = 2\))**

Using the previous method, the following quantities were used: bis-(4,4’-formyloxyphenoxy)ethoxyethane (79.93 g, 0.23 mol.), sodium hydroxide (36.92 g, 0.92 mol.), ethanol (600 cm\textsuperscript{3}) and water (200 cm\textsuperscript{3}). A light brown solid was obtained by recrystallisation in warm ethanol and water: yield 45.18 g (67.4 %), m.p. = 95–97\textdegree C. Elemental analysis calculated for C\textsubscript{16}H\textsubscript{18}O\textsubscript{5}: %C (66.19), %H (6.25); found: %C (65.78), %H (6.41).

**300 MHz \textsuperscript{1}H NMR \delta_{\text{H}} (CD\textsubscript{3}OD, ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum**, 6.06-6.03 (4H, d, \(J_{\text{H}} = 9.3\) Hz, Ar-H ortho to oxy aldehyde), 7.06-7.03 (4H, d, \(J_{\text{H}} = 9.3\) Hz, Ar-H and meta to oxy aldehyde links); 4.16-4.13 (4H, t, \(J_{\text{H}} = 4.5\) Hz, C-H between ether links para to oxy aldehyde links); 3.94-3.91 (4H, t, \(J_{\text{H}} = 4.5\) Hz, C-H between ether links in the centre of the molecule).

**Preparation of 4,4’-{oxybis(ethane-1,2-diyl)-1,4-phenylene}dicyanate (4b, \(n = 2\))**

Using the previous method, the following quantities were used: bis-(4,4’-hydroxyphenoxy)ethoxyethane (44.36 g, 0.16 mol.) and cyanogen bromide (36.98 g, 0.35 mol.), acetone (800 cm\textsuperscript{3}), triethylamine (35.44 g, 0.35 mol.). An off-white solid was obtained by recrystallisation from a 50/50 mixture of ethanol and water to yield 47.78 g (97.9 %), m.p. = 109–
111 °C. Elemental analysis calculated for C_{18}H_{16}N_{2}O_{5}: %C (63.52), %H (4.74), %N (8.23); found: %C (63.09), %H (4.63), %N (7.99).

**300 MHz ^1H NMR δ_{H} (CDCl₃, ppm from TMS):** assignments refer to structure shown in the accompanying NMR spectrum, 7.23-7.18 (4H, m, \( J_H = 9.3 \) Hz, Ar-H ortho to cyanate link); 6.98-6.93 (4H, m, \( J_H = 9.3 \) Hz, Ar-H and meta to cyanate links); 4.17-4.13 (4H, t, \( J_H = 4.5 \) Hz, C-H between ether links closest to Ar-O para to cyanate links); 3.94-3.91 (4H, t, \( J_H = 4.5 \) Hz, C-H between ether links in the centre of the molecule).

Preparation of 4,4'-[ethane-1,2-diylbis(oxyethane-1,2-diroyloxy-1,4-phenylene)]dibenzaldehyde (1c, \( n = 3 \))

Using the previous method, the following quantities were used: 4-hydroxybenzaldehyde (68.15 g, 0.56 mol.), dichloroethane (52.20 g, 0.28 mol.), potassium carbonate (154.26 g, 1.12 mol.) and DMF (400 cm³). A very light brown crystalline solid was obtained by recrystallisation in warm diethyl ether: yield 85.89 g (85.9 %), m.p. = 63–65 °C. Elemental analysis calculated for C_{20}H_{22}O_{6}: %C (67.03), %H (6.19); found: %C (65.87), %H (6.14).

**300 MHz ^1H NMR δ_{H} (CDCl₃, ppm from TMS):** assignments refer to structure shown in the accompanying NMR spectrum, 9.88 (1H, s, C-H due to aldehyde), 7.84-7.81 (4H, d, \( J_H = 8.8 \), Ar-H ortho to aldehyde link); 7.02-7.00 (4H, d, \( J_H = 8.2 \), Ar-H and meta to aldehyde link); 4.23-4.19 (4H, t, \( J_H = 4.5 \), C-H between ether links para to aldehyde links); 3.91-3.88 (4H, t, \( J_H = 4.5 \), C-H between ether links closest to Ar-O-CH₂); 3.76 (4H, s, C-H at centre of the molecule).

Preparation of 4,4'-[ethane-1,2-diylbis(oxyethane-1,2-diroyloxy-1,4-phenylene)]difomate (2c, \( n = 3 \))

Using the previous method, the following quantities were used: *bis*(4,4'-formylphenoxy)ethoxyethane (82.62 g, 0.23 mol.), 3-chloroperoxybenzoic acid (MCPBA) (155.19 g, 0.90 mol.) and DCM (800 cm³), saturated (aq) NaHCO₃ (500 cm³). An off-white solid was
obtained by recrystallisation from methanol: yield 70.09 g (77.9 %), m.p. = 34–36°C. Elemental analysis calculated for C_{20}H_{22}O_{8}: %C (61.53), %H (5.68); found: %C (60.72), %H (5.76).

300 MHz \(^1\)H NMR \(\delta_{H}\) (CDCl\(_3\), ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum, 8.27 (1H, s, C-H due to oxy aldehyde), 7.05-7.02 (4H, d, \(J_H = 9.3\), Ar-H ortho to oxy aldehyde link); 6.93-6.90 (4H, d, \(J_H = 8.8\), Ar-H and meta to oxy aldehyde links); 4.13-4.10 (4H, t, \(J_H = 4.5\), C-H between ether links para to oxy aldehyde link); 3.88-3.86 (4H, t, \(J_H = 4.5\), C-H between ether links closest to Ar-O-CH\(_2\)); 3.75 (4H, s, C-H at centre of the molecule).

**Preparation of 4,4’-[ethane-1,2-diylbis(oxyethane-1,2-diyl-oxy-1,4-phenylene)]diphenol (3c, \(n = 3\))**

Using the previous method, the following quantities were used: bis-(4,4’-formyloxyphenoxy)ethoxyethane (68.89 g, 0.18 mol.), sodium hydroxide (28.23 g, 0.71 mol.), ethanol (75 cm\(^3\)) and water (25 cm\(^3\)). A light yellow needle like crystalline solid was obtained by recrystallisation from warm ethanol and water: yield 50.27 g (85.2 %), m.p. = 108–110°C. Elemental analysis calculated for C\(_{18}\)H\(_{22}\)O\(_6\): %C (64.66), %H (6.63); found: %C (64.41), %H (6.84).

300 MHz \(^1\)H NMR \(\delta_{H}\) (CD\(_3\)OD, ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum, 6.79-6.76 (4H, d, \(J_H = 9.3\), Ar-H ortho to hydroxy link); 6.71-6.67 (4H, d, \(J_H = 8.8\), Ar-H and meta to hydroxy links); 4.04-4.00 (4H, t, \(J_H = 4.5\), C-H between ether links closest to Ar-O para to hydroxy link); 3.80-3.77 (4H, t, \(J_H = 4.5\), C-H between ether links closest to Ar-O-CH\(_2\)); 3.70 (4H, s, C-H at centre of the molecule).

**Preparation of 4,4’-[ethane-1,2-diylbis(oxyethane-1,2-diyl-oxy-1,4-phenylene)]dicyanate (4c, \(n = 3\))**

Using the previous method, the following quantities were used: bis-(4,4’-hydroxyphenoxy)ethoxyethane (49.58 g, 0.15 mol.) and cyanogen bromide (34.56 g, 0.33 mol.), acetone (500 cm\(^3\)), triethylamine (33.05 g, 0.33 mol.). An off-white solid was obtained by adding a 50/50 mixture of ethanol and water: yield 50.27 g (85.2 %), m.p. = 108–110°C. Elemental analysis
calculated for C_{20}H_{20}N_{2}O_{6}: \%C (62.49), \%H (5.24), \%N (7.28); found: \%C (62.41), \%H (5.15), \%N (7.18).

300 MHz $^1$H NMR δ$_{H}$ (CDCl$_3$, ppm from TMS): assignments refer to structure shown in the accompanying NMR spectrum, 7.22-7.19 (4H, m, $J_H = 9.3$, Ar-H ortho to cyanate link); 6.96-6.93 (4H, m, $J_H = 9.3$, Ar-H and meta to cyanate links); 4.14-4.11 (4H, t, $J_H = 4.5$, C-H between ether links closest to Ar-O para to cyanate link); 3.88-3.85 (4H, t, $J_H = 4.5$, C-H between ether links closest to Ar-O-CH$_2$); 3.75 (4H, s, C-H at centre of the molecule).

Formulation of monomer/co-catalyst blends

Prior to incorporation in the dicyanate, the co-catalyst package, comprising Al(acac)$_3$ and dodecylphenol in the molar ratio of 1:25, were first homogenised by heating to 80ºC (in a vial in a water bath) before cooling to room temperature. The co-catalysts were then introduced into the dicyanate monomers by mixing in a pestle and mortar at room temperature to a homogeneous mixture (see Error! Reference source not found. for molar ratios). The ensuing blends were used in the thermal analyses directly after incorporation of the co-catalysts. Storage of catalysed blends was undertaken in a refrigerator (+5 ºC) with care being taken to minimise the exposure of the blends to atmospheric moisture.

Insert Table 1 Catalyst and monomer molar ratios

Cure schedule for polymers

A glass side was placed and clipped over a glass slide-covered high temperature silicone adhesive slide with a pre-cut PTFE template of dimensions 35 x 10 x 1 mm$^3$, and heated in an oven to 230ºC to remove residual solvent in the adhesive. This ensured that the PTFE adhered to the glass. The prepared moulds were placed on a pre-heated hot plate at 90ºC for (4a), at 80ºC for (4b) and at 60ºC for (4c). Each blend was placed in one of these templates and allowed to become molten, sufficient sample was added to cover the entire volume of the template. The monomers and blends were heated as neat melts to ensure that voids did not occur during the cure process due to trapped air or
solvents released, as this can be harmful to the properties of the polymer. The molten monomers and blends were then transferred to a vented oven under air and cured at 180°C/1h and finally at 230°C/1h. The cure schedule is relatively mild to compensate for the presence of the alkylene ether dicyanates because in preliminary studies, using a common commercial cure schedule\(^1\), the homopolymers of (4a), (4b) and (4c) produced very dark polymers, suggesting charring. There is no suggestion that this cure schedule is optimised for either of the monomers.

**RESULTS AND DISCUSSION**

The original choice for an examination of the alkylene ether backbone moiety was prompted by previous work by one of the co-authors [18], albeit with another family of thermosetting polymers (bismaleimides) for which brittleness can also be a challenge. However, in this previous publication, the synthetic route employed for the preparation of BMIs via diamines followed by cyclodehydration of the corresponding bismaleamic acid, could not be employed directly with the present compounds, necessitating a different approach. During the current work, a series of three cyanate monomers, having similar alkylene ether backbone structures that differ in length and generically identified by \( n = 1, 2, 3 \) to denote the number of ethoxy segments in the chain [4a, b, c], was successfully prepared in good yields by the same four step reaction pathway (Scheme 1) using aldehydic protecting groups.

The first step was a modified combination of reported methods of ether synthesis of hydroxyaldehydes previously reported by different authors: for example, Jiang *et al.* [19] prepared the dialdehyde \( n = 1 \) [1a] by reacting dibromoethane and 4-hydroxybenzaldehyde with LiH as the reducing agent at -78°C in ethanol over 2.5 days. A similar reaction was carried out by Simion *et al.* [20] using a 2% NaOH solution as the reducing agent and refluxed in ethanol for 72 hours, then over ice for a further 24 hours. Similarly, the dialdehyde \( n = 3 \) [3a] was synthesised by Guilani *et al.* [21] using Na metal dissolved in ethanol and refluxed overnight. The second and third steps of the procedure were modified from that reported by Nagvekar *et al.* [22] involving the conversion of

\(^1\) A typical casting procedure for cyanate ester resins incorporating zinc naphthenate (60-150 ppm metal) and nonyl phenol (2 phr) involves a gelling step (104-150°C), followed by curing at 177°C (1 hr) + 210°C (1 hr) and a free-standing post cure at 250°C (2 hr).
terminal aldehyde to hydroxyl via oxyaldehydic functions. Reactions for the synthesis of the dicyanate monomers [4a,b,c] were subsequently scaled up first from 10 g to 40 g and then to 100 g preparations; all scale up reactions gave comparable results to those of the initial reactions. For the purpose of this study, the analyses of the final scale up preparations of the three dicyanates were used for the polymer preparations and are discussed below.

**Insert Scheme 1 synthetic route to the dicyanate monomers [4a, b, c]**

**Analysis of Step 1**

This preparation step was common for all three backbones differing only slightly in terms of reaction time and reaction work-up method and the infrared spectra are shown (Figure 1) for all dibenzoaldehydes [1a,b,c]. For characterization purposes, the principal peaks of interest in this first step are those produced by the aldehyde and ether backbone structures, e.g. the CH$_2$ stretching bands for the alkyl ether backbone appear at 2900 cm$^{-1}$, along with the aryl-alkyl ether stretching at around 1200 cm$^{-1}$ (asymmetric stretch) and 1100 cm$^{-1}$ (symmetric stretch) respectively. This is an indication that the backbone structure was successfully created in this reaction. The two aldehydic C-H stretching bands are around 2800 cm$^{-1}$, producing the first overtone at around 1390 cm$^{-1}$ and are accompanied by a strong carbonyl stretching band at around 1670 cm$^{-1}$.

**Insert Figure 1 Infrared transmission spectra of dialdehydes [1a, 1b, 1c] produced in Step 1**

*(common arbitrary vertical scale)*

This is good evidence of the presence of the aldehyde group, especially when the first overtone does not shift significantly from 1390 cm$^{-1}$. The distinctive band frequencies were used as “flags” for the presence or the absence of a characteristic group and the assignments of the absorption bands of the FT-IR spectrum of compounds 1a-c are shown in Table 2.

**Insert Table 2 FT-IR assignments for [1a, 1b, 1c] from Step 1**
\(^1\)H NMR spectroscopy was also employed to verify the presence of the respective structures and the spectra are shown in Figures 2a-c.

**Insert Figure 2 \(^1\)H NMR spectra of dialdehydes [1a, 1b, 1c] (S = shifts arising from NMR solvent)**

The \(^1\)H NMR spectrum of [1a] (Figure 2a) reveals that, while the reaction was generally successful in producing a relatively high-yielding, clean product, a small amount of work-up DCM residue was revealed at 5.27 ppm (as evidenced by the poorer agreement of the elemental analysis). The electronegativity of the oxygen atoms on either side of the ethyl backbone produced a singlet downfield from *ca.* 3.7 ppm for 1,2-dichloroethane to 4.45 ppm, due to the deshielding effects of the ether oxygens and benzene rings, while the inductive effect of the oxygen on the aldehyde further deshields the two protons on the benzene ring closest to the aldehyde causing the protons to shift downfield. The effect of the ether backbone causes the ring protons closest to it to move upfield.

The \(^1\)H NMR spectrum of product [1b] (Figure 2b) demonstrates that the reaction was successful and produced a relatively high-yielding, clean product with a small amount of work-up DCM residue at 5.27 ppm. The methylene groups are now non-equivalent, the effects of the electronegativity of the aryl ether oxygen atoms on either side of the backbone have been reduced, producing a triplet downfield from 4.45 ppm [Ha] to 4.26-4.23 ppm. The reduced deshielding effects of the ether oxygens and benzene rings are due to the electropositive methylene from the aliphatic ether link. There is now only one oxygen atom affecting the shielding of the aliphatic ether methylenes, thus the triplet is more upfield at 3.99-3.96 ppm. The effects on the aldehyde and benzene ring protons are apparently minimal as a very slight change was recorded.
The $^1$H NMR spectrum of product [1c] (Figure 2c) indicates that the reaction was successful and produced a relatively high-yielding, clean product with a small amount of work-up DCM residue at 5.27 ppm. The methylene groups are inequivalent, the electronegativity effects of the aryl ether oxygen atoms on either side of the backbone have further been reduced, producing a triplet downfield from 4.26-4.23 ppm in [1b] to 4.23-4.19 ppm. The deshielding effects of the ether oxygens and benzene rings have only slightly reduced because of the increase in electropositive influence of the backbone. Shielding of the methylene protons next to the aryl ether methylene has also increased to give a triplet at 3.91-3.88 ppm. The ethyl protons at the centre of the molecule are affected most by the electronegativity of the surrounding oxygens and because of their symmetry, a single is observed at 3.76 ppm.

**Analysis of Step 2**

Analysis of the structural features suggest that the bands of interest in this second step are those produced by the formate and ether backbone structures. As can be seen from the spectra (Figure 3) the CH$_2$ stretching bands for the alkyl ether backbone appear at 2900 cm$^{-1}$, along with the aromatic and aliphatic ether stretching at around 1200 cm$^{-1}$ and 1100 cm$^{-1}$ respectively.

**Insert Figure 3 Infrared transmission spectra of diformates [2a, 2b, 2c] produced in Step 2 (common arbitrary vertical scale)**

The formation of the formate has not significantly shifted the absorption of these bands from the precursor compounds, indicating that the backbone structure remained intact during the reaction, although as expected, the two aldehydic C-H stretching bands (ca. 2800 cm$^{-1}$ in Figure 1) are now absent from the spectra. The carbonyl stretching band is now observed at around 1700 cm$^{-1}$ for the formates and is accompanied by a ‘C-O’ stretch (a combination band) at ca. 1280 cm$^{-1}$. The distinctive band frequencies for the presence of a characteristic group and the assignments of the absorption bands of are shown in Table 3.
The $^1$H NMR spectra for the oxyaldehydes produced in Step 3 are shown in Figures 4a-c respectively. For [2a], the inductive and anisotropic effects of the C=O appear to have a minimal affect on the ring protons (Figure 4a), although the introduction of the oxygen *para* to the ethereal oxygen has increased the electronegativity on the ring protons causing them to move upfield 7.08-7.05 ppm and 6.97-6.94 ppm relative to shifts for unsubstituted benzene at 7.27 ppm. Calculated substituent effects for –OH on a 1,4-disubstituted benzene forces the signal upfield by a *ca.* 0.2 ppm.

The same effect serves to move the ethyl signals upfield from 4.45 ppm to 4.31 ppm and the insertion of an oxygen atom at the centre of the backbone affects the ring protons very slightly. Predictably, those most affected are the closer methylene protons, which are shifted upfield from 3.99-3.96 ppm to 3.94-3.91 ppm, and the aryl ether methylene protons from 4.26-4.23 ppm to 4.16-4.13 ppm. However, the presence of this oxygen atom does not cause any significant shift in the position of the proton on the carbonyl fragment of products [2b, 2c] (shown in Figures 4b and 4c respectively). Once again, the slight increase in electronegativity of the backbone has caused a shift of all protons upfield; most clearly affected are the ring protons $H_e$ having shifted upfield from 7.84-7.81 ppm to 7.05-7.02 ppm, this is due to the reduced inductive and anisotropic effects of the carbonyl oxygen.
Analysis of Step 3

The infrared spectra shown in Figure 5 reveal that the CH\_2 stretching bands for the alkyl ether backbone again appear at ca. 2900 cm\(^{-1}\), accompanied by the aryl and aliphatic ether stretching bands at around 1200 cm\(^{-1}\) and 1100 cm\(^{-1}\) respectively. The formate group has now been replaced and this is most clearly evident from the presence of bands due to the terminal hydroxyl groups, which appear in the spectra at around 3340 cm\(^{-1}\), and the absence of the carbonyl groups (that were previously visible at 1600-1700 cm\(^{-1}\)).

Insert Figure 5 Infrared transmission spectra of diphenols [3a, 3b, 3c] produced in Step 3 (common arbitrary vertical scale)

The distinctive band frequencies for the presence of a characteristic group and the assignments of the absorption bands of are shown in Table 4 for the FT-IR spectra [3a-c].

Insert Table 4 FT-IR assignments for [3a, 3b, 3c] from Step 3

The \(^1\)H NMR spectra for the diphenols produced in Step 3 are shown in Figures 6a – 6c respectively. Now that all the effects from the any carbonyl group have been removed, only the electronegativity of the oxygen atoms present result in upfield shifts of the ring protons from 7.08-7.05 ppm to 6.82-6.69 ppm and from 6.97-6.94 ppm to 6.72-6.69 ppm. From the spectral analysis, it is evident that the cleavage of the protecting group to form terminal hydroxyl groups has been successful in producing a clean material [3a] in good yield without breaking the backbone. This is also can be said because of the downfield position of the ethyl protons and no other fragments appear in the spectrum.

Insert Figure 6 \(^1\)H NMR spectrum of diphenols [3a, 3b, 3c] (S = shifts arising from NMR solvent)
Similarly, examination of the spectrum for [3b] (Figure 6b) reveals that the removal of the carbonyl group affects the spectrum of the corresponding ring protons to a similar extent to those of [3a], i.e. moving them upfield by ca. 0.25ppm, from 7.06-7.03 ppm to 6.80-6.77 ppm and from 6.94-6.91 ppm to 6.70-6.67 ppm. Similarly, the electronegativity of the backbone oxygen shifted the ethyl protons upfield by ca. 0.1 ppm. Examination of the spectrum for the longest material [3c] in this homologous series reveals that again the electronegative effects of the oxygens have caused an upfield movement of all protons in material to the same degree (Figure 6c) as the related diphenols [3a, 3b]. One might have anticipated that the presence of hydroxyl shifts should provide useful diagnostic evidence, but whilst the hydroxyl protons are present in materials (as evidenced by the IR spectra), they are obscured by the deuterated methanol used as NMR solvent (ca. 4.88 ppm).

**Analysis of Step 4**

Analysis of the final step of the scheme involves the cyanation of the diphenols to produce the desired monomers. As can be seen from the infrared spectra in Figure 7, the CH$_2$ stretching bands for the alkylene ether backbone again appear at around 2900 cm$^{-1}$, along with the aryl and aliphatic ether stretches at around 1200 cm$^{-1}$ and 1100 cm$^{-1}$ respectively. The removal of the hydroxyl group is evident from the spectra, accompanied by the presence of the characteristic O-C≡N stretching bands at ca. 2270 cm$^{-1}$.

**Insert Figure 7 Infrared transmission spectra of dicyanates [4a, 4b, 4c] produced in Step 4 (arbitrary vertical scale)**

It is well known that the O-C≡N stretching bands may appear as a two or more fully or partially resolved bands, although the origin of this splitting is not currently well understood [13], but the influence of steric hindrance and crystal packing will have some influence. Thus, the O-C≡N stretching band for [4a] appears to be split into two fully resolved bands, while [4b] has two fully resolved bands with a shoulder on the band appearing at 2285 cm$^{-1}$. Three full resolved bands are
observed for [4c], suggesting a greater degree of rotational freedom compared with [4a] and [4b]. The characteristic band frequencies and the corresponding assignments are shown in Table 5.

**Insert Table 5 FT-IR assignments for [4a, 4b, 4c] from Step 4**

The ¹H NMR spectra for the diphenols produced in Step 3 are shown in Figures 7a-c respectively. The diphenol [3a] appears to have been converted successfully to the corresponding dicyanate [4a] in reasonable purity as the ¹H NMR spectrum (Figure 7a) shows no evidence of any hydroxylated precursor remaining in the dicyanate product. The aryl protons are observed to have moved downfield as a result of the incorporation of the cyanate group. Similarly, the ¹H NMR spectrum arising from the cyanation of [3b] to yield a clean, high yielding product [4b] is seen in Figure 7b. Addition of the cyanate group serves to shift the ring protons downfield by ca. 0.3 ppm from the shift recorded for [4b] and this is consistent with other observations in the literature [23, 24]. The same effect is also observed in the spectra of materials [4b] and [4c] (Figures 7b and 7c respectively). For all the dicyanates produced in the course of this work, the presence of the cyanate group was observed to exert a downfield shift on all the ethyl protons in the backbone of ca. 0.1 ppm.

*Thermal analysis of dicyanate monomers*

The commercial dicyanate monomer, AroCy B10, based on bisphenol A was chosen as the second component in the proposed blending in this work. The DSC thermograms arising from the analysis of uncatalysed and catalysed monomers are shown in Figure 8.

**Insert Figure 8 Composite DSC thermogram (10 K/min) of (a) uncatalysed (4a), (b) catalysed (4a), (c) uncatalysed (4b), (d) catalysed (4b), (e) uncatalysed (4c), (f) catalysed (4c)**

In order to determine the internal self consistency, a catalysed sample of 2,2-*bis*(4-cyanatophenyl)propane (AroCy B10), for which much data have been reported, was analysed using
DSC and revealed a narrow endothermic peak (peak minimum 76°C, $\Delta H = 55$ J/g or 15 kJ/mol). The polymerisation exotherm spans 92–307°C (peak maximum at 192°C) with a $\Delta H$ value of 638 J/g or 178 kJ/mol.; the thermal data are collected in Table 6.

Insert Table 6 Dynamic DSC data (10 K min$^{-1}$) for dicyanate monomers

The uncatalysed samples of the homologous series (4a), (4b), and (4c) were analysed to give the thermograms shown in Figure 8. Relatively sharp melting endotherms were observed for all three monomers: (4a), peak minimum 125°C and $\Delta H = 41$ kJ/mol. cyanate; (4b), peak minimum 120°C and $\Delta H = 64$ kJ/mol. cyanate; (4c), peak minimum 66°C and $\Delta H = 65$ kJ/mol. cyanate. Examination of Figure 8 also reveals broad polymerisation exotherms for all the uncatalysed monomers, but extremely good agreement for the total polymerisation enthalpies ($87 \pm 2$ kJ/mol. cyanate), despite the variation in the temperature regime in which the process occur. As a measure of internal consistency, values reported for the thermal (i.e. ‘uncatalysed’) polymerisation of AroCy B10 using DSC are typically 101.7 kJ/cyanate [25], 107.5 [26], 113.5 [27], 101.6 [28], 98.7 [29], suggesting that the values here are a little depressed.

The DSC analyses of the catalysed monomers are also presented in Figure 8 for direct comparison. It is observed that the melting endotherms occur essentially at identical temperatures to the uncatalysed monomers, and display similar enthalpies of fusion: (4a), $\Delta H = 46$ kJ/mol. cyanate; (4b) $\Delta H = 50$ kJ/mol. cyanate; (4c) $\Delta H = 63$ kJ/mol. cyanate. In contrast with the melting behaviour, the exothermic polymerisation peaks occur at significantly lower temperatures than the uncatalysed analogues and have much narrower slightly skewed profiles, but tend occur in a similar temperature regime (i.e. the peak maxima fall within 11 K (205°C - 216°C). It is noticeable that the shapes of the exotherms are quite symmetrical and unimodal, unlike some data that have been obtained previously [30] for catalysed commercial monomers. The recorded polymerisation enthalpies for the catalysed monomers fall within a similar range 93 ± 9.9 kJ/mol. cyanate.
However, it should be noted that for the catalysed monomers (particularly for (4b) and to a lesser extent (4a), the fusion precedes polymerisation directly and consequently the initial part of the polymerisation exotherm is not lost. The onset limits for all catalysed monomers were taken as the turning points (inflections in the baseline) of the affected monomers and the decision was taken to present the catalysed data for comparative purposes only. Even small quantities of catalyst (e.g. Al(acac)$_3$: dodecylphenol: monomer 1:25:2000) significantly lowered the peak maxima of the monomers, particularly in the case of (4a) and (4b). The addition of the catalyst also reduced the cure onset temperatures by 50-80 K and at the same time increasing the polymerisation enthalpy of a cyanate group (Table 6).

*Thermogravimetric analysis of the homopolymers*

AroCy B-10 (albeit using a different batch and different curing conditions: 180°C / 1h and 230°C / 1h) was again chosen as the second component in the proposed blends for this TG work. The TG data for the homopolymers and blends are given in Table 7.

**Insert Table 7 TG data for the thermal degradation (in flowing nitrogen) of homopolymers of AroCy B10 and newly reported dicyanates**

The TG analysis (in flowing nitrogen) of the polycyanurate of AroCy B-10 revealed an onset of thermal degradation (defined as a 5% weight loss) at 348°C and a multi-stage decomposition within which few stable intermediates are formed [31]. This initial degradation step accounted for around 15% of the mass and yielded a slowly declining rate of weight loss, a second faster degradation step overlaps with the first and continues up until 530°C. An apparently slower degradation step overlaps with the second and continues up to 800°C, at which point the polycyanurate has not undergone complete thermal degradation and leaves a residual mass of 29%. Upon examination of the AroCy B10 degradation curve (Figure 9) it can be seen that at around 850°C the slope is still in very slow decline. This pattern is in agreement with other published studies for this polycyanurate [32,30].
Insert Figure 9 TG data for homopolycyanurates of AroCy B10, (4a), (4b), and (4c).

The possibility that the sample was not fully cured should not be excluded from the discussion, as ‘normal’ (i.e. proscribed) cure schedules for AroCy B10 are typically more forcing depending on the eventual application and thus the $T_g$ required [33]. Consequently, the initial degradation step might also hide some post cure process and this was confirmed by FT-IR analysis of the cured material, showing weak O-C≡N stretching peaks at 2283 cm$^{-1}$ and 2220 cm$^{-1}$ (Figure 10) the peaks are not well defined, but clearly indicate the presence of small quantities of uncured material.

Insert Figure 10 FT-IR (ATR) spectra of AroCy B10 homopolymer cured at 180 °C / 1h and 230 °C / 1h

FT-IR analysis of the cured alkyl ether type dicyanates did not provide conclusive evidence for the presence of any residual monomer, suggesting that the monomers were fully converted to their corresponding polycyanurates (Figure 11).

Insert Figure 11 FT-IR (ATR) spectra of newly reported dicyanate homopolymers (4a), (4b), and (4c) cured at 180°C / 1h and 230°C / 1h

TG analysis plots for these homopolymers showed onsets of thermal degradation (defined as a 5% weight loss) at 366°C (4a), 346°C (4b) and 357°C (4c). All three thermograms have similar patterns of decomposition to the AroCy B10 homopolymer [31], but predictably, thermal stability increased with decreasing backbone chain length, leaving residual masses of 25 % (4a), 18 % (4b), and 16 % (4c). A similar examination of the FTIR spectra was performed to determine the degree of cure. The expansion of the spectra in both Figures 10 and 11 places the features close to the
limits of discrimination for the spectral analysis and it is difficult to determine whether cyanate bands are still present in the three blends. However, it is possible to say that if the spectra do contain residual cyanate groups then there are fewer cyanate groups than in the preceding polymers, and that (4c) < (4a) < (4b) (where < = contains fewer cyanate groups). If this assumption is correct, then the effect of the alkylene ether component on the reactivity of AroCy B10 falls in the reverse order i.e. (4c) > (4a) > (4b), which correlates well with the order of polymerisation enthalpies observed using DSC (Table 6).

*Dynamic mechanical thermal analysis of the homopolymers*

The thermograms arising from the dynamic mechanical thermal analysis (DMTA) of the catalysed polymers are shown in Figure 12. In order to determine the internal self consistency, a catalysed sample of 2,2-*bis*(4-cyanatophenyl)propane (AroCy B10), for which much data have been reported, was analysed using DMTA and revealed a glass transition temperature, \( T_g \) (the \( \alpha \) transition) of 277\(^\circ\)C (determined from the maximum value of the loss tangent, \( \tan \delta \)). Other low temperature transitions (\( \beta \) and \( \gamma \)) were also present; the thermal data are collected in Table 8. The storage modulus falls noticeably (\( E' = 2.14 \) GPa at 25\(^\circ\)C and \( E' = 1.70 \) GPa at 150\(^\circ\)C) prior to the glass transition.

Insert Figure 12 DMTA data for homopolymers of AroCy B10 and (4a), (4b) and (4c)

The \( T_g \) values of the homopolymers of (4a), (4b) and (4c) were also determined from the peak maxima of the loss tangent, \( \tan \delta \) (Error! Reference source not found.) and the values of 221\(^\circ\)C (4a), 139\(^\circ\)C (4b), and 121\(^\circ\)C (4c) fall in the expected order of \( T_g \) decreasing as the backbone chain length and hence flexibility is increased. Examination of the storage moduli revealed more mixed results: (4a), \( E' = 1.77 \) GPa at 25\(^\circ\)C, 1.60 GPa at 50\(^\circ\)C and 1.13 GPa at 150\(^\circ\)C; (4b), \( E' = 2.67 \) GPa

\[2\] A typical casting procedure for cyanate ester resins incorporating zinc naphthenate (60-150 ppm metal) and nonyl phenol (2 phr) involves a gelling step (104-150\(^\circ\)C), followed by curing at 177\(^\circ\)C (1 hr) + 210\(^\circ\)C (1 hr) and a free-standing post cure at 250\(^\circ\)C (2 hr)
at 25°C, 2.38 GPa at 50°C and 1.81 GPa at 100°C; \(4c\), \(E' = 1.80\) GPa at 25°C and 1.62 GPa at 50°C.

Insert Table 8 DMTA data for poly(2,2-bis(4-cyanatophenyl)propane) and the newly reported dicyanates.

Direct (quantitative) comparison of the three backbones is difficult, due to the nature of the onset temperatures of glassy to rubbery states. However, when considering storage modulus, a general trend is observed \(i.e. (4b) > \text{AroCy B10} >> (4c) > (4a)\), where \(4b\) the storage modulus is significantly higher than that of AroCy B10 by ca. 0.4 GPa and ca. 0.8 GPa higher than \(4c\) and \(4a\). This observation is contrary to the corresponding \(T_g\) values for the homopolymers, for which the order \(4a > 4b > 4c\) is observed \(i.e.\) directly reflecting the length of the backbone and crosslink density). The relative heights of the tan \(\delta\) peaks suggest that \(4b\) is a less brittle material as evident of the high storage modulus of 2.10 GPa at 80°C, while \(4a\) is perhaps the most brittle, which is consistent with the higher crosslink density generated in the polymer.

Conclusions

It is evident from the data and analysis presented in this paper that the method used in this study was more efficient and less demanding than that of Jiang \textit{et al.} [19] who prepared the dialdehyde \[1a\] under more forcing conditions \(i.e.\) dibromoethane and 4-hydroxybenzaldehyde with LiH as the reducing agent at -78 °C in EtOH) over a longer timescale > 2.5 days) in poorer yield (63%). The same is true of the method employed to produce \[3a\], which was previously synthesised by Guilani \textit{et al.} [21] using sodium metal dissolved in EtOH and refluxed overnight to yield 40%. In contrast, in the current work, each individual step for all three backbone types produced excellent yields of over 70%, thus giving an overall reaction yield for all four steps as 42% for \[4a\], 44% for \[4b\] and 50% for \[4c\]. The main difficulty encountered in the preparation represented in Scheme 1 was, in all cases, step 2. The addition of MCPBA produced a strongly exothermic reaction, although the violent reactivity decreased as the backbone chain length increased progressively and this was
accompanied by an increase in the reaction time. Future work with this structure requires some caution to be employed when carrying out this step and some investigation will be made as to whether the reaction might not be usefully carried out at reduced temperature, rather than at room temperature.

ACKNOWLEDGEMENTS

We thank Hitachi Chemical Co. Ltd. for funding this work in the form of a studentship (PK). At the University of Surrey we thank Ms. Nicola Walker for performing the elemental analyses and Mr James P Bloxsidge for obtaining some of the NMR spectra.
Table 1 Catalyst and monomer molar ratios

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Al(acac)$_3$</th>
<th>Dodecylphenol</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>AroCy B10</td>
<td>1</td>
<td>25</td>
<td>1000</td>
</tr>
<tr>
<td>4a</td>
<td>1</td>
<td>25</td>
<td>2000</td>
</tr>
<tr>
<td>4b</td>
<td>1</td>
<td>25</td>
<td>2000</td>
</tr>
<tr>
<td>4c</td>
<td>1</td>
<td>25</td>
<td>2000</td>
</tr>
</tbody>
</table>
Table 2 FT-IR assignments for [1a, 1b, 1c] from Step 1

<table>
<thead>
<tr>
<th>Assignment</th>
<th>1a</th>
<th>2a</th>
<th>3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-H stretch</td>
<td>3066</td>
<td>3078</td>
<td>3079</td>
</tr>
<tr>
<td>-CH$_2$- stretch (ethoxy)</td>
<td>2946-2925</td>
<td>2938-2886</td>
<td>2956-2899</td>
</tr>
<tr>
<td>-C-H stretch (aldehyde)</td>
<td>2855-2760</td>
<td>2842</td>
<td>2839-2751</td>
</tr>
<tr>
<td>Ring skeleton</td>
<td>1600-1507</td>
<td>1601-1510</td>
<td>1600-1509</td>
</tr>
<tr>
<td>Aliphatic CH$_2$ scissor</td>
<td>1463-1455</td>
<td>1481-1459</td>
<td>1478-1457</td>
</tr>
<tr>
<td>First overtone aldehydic C-H bending vibrations</td>
<td>1394</td>
<td>1399</td>
<td>1395</td>
</tr>
<tr>
<td>Ar-O-R (asymmetric)</td>
<td>1244-1211</td>
<td>1255-1216</td>
<td>1250-1216</td>
</tr>
<tr>
<td>Ar-O-R (symmetric)</td>
<td>1155-1066</td>
<td>1153-1080</td>
<td>1158-1042</td>
</tr>
<tr>
<td>1,4-disubstituted benzene ring (out-of-plane bending)</td>
<td>829-818</td>
<td>840</td>
<td>836</td>
</tr>
</tbody>
</table>
Table 3 FT-IR assignments for [2a, 2b, 2c] from Step 2

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Compounds/observed bands (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-H stretch</td>
<td>2a: 3075</td>
</tr>
<tr>
<td></td>
<td>2b: 3079</td>
</tr>
<tr>
<td></td>
<td>2c: 3089</td>
</tr>
<tr>
<td>-CH(_2)- stretch (ethoxy)</td>
<td>2a: 2954-2931</td>
</tr>
<tr>
<td></td>
<td>2b: 2943-2833</td>
</tr>
<tr>
<td></td>
<td>2c: 2948-2878</td>
</tr>
<tr>
<td>C=O formate stretching</td>
<td>2a: 1737-1696</td>
</tr>
<tr>
<td></td>
<td>2b: 1739-1716</td>
</tr>
<tr>
<td></td>
<td>2c: 1732-1695</td>
</tr>
<tr>
<td>Ring skeleton</td>
<td>2a: 1609-1506</td>
</tr>
<tr>
<td></td>
<td>2b: 1609-1502</td>
</tr>
<tr>
<td></td>
<td>2c: 1608-1506</td>
</tr>
<tr>
<td>Aliphatic CH(_2) scissor</td>
<td>2a: 1453-1380</td>
</tr>
<tr>
<td></td>
<td>2b: 1476-1449</td>
</tr>
<tr>
<td></td>
<td>2c: 1457-1447</td>
</tr>
<tr>
<td>Ar-O-R (asymmetric)</td>
<td>2a: 1246-1185</td>
</tr>
<tr>
<td></td>
<td>2b: 1250-1195</td>
</tr>
<tr>
<td></td>
<td>2c: 1251-1221</td>
</tr>
<tr>
<td>R-O-R (symmetric)</td>
<td>2a: 1168-1068</td>
</tr>
<tr>
<td></td>
<td>2b: 1166-1120</td>
</tr>
<tr>
<td></td>
<td>2c: 1173-1070</td>
</tr>
<tr>
<td>1,4-disubstituted benzene ring (out-of-plane bending)</td>
<td>2a: 821-810</td>
</tr>
<tr>
<td></td>
<td>2b: 824</td>
</tr>
<tr>
<td></td>
<td>2c: 807</td>
</tr>
</tbody>
</table>
Table 4 FT-IR assignments for [3a, 3b, 3c] from Step 3

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Compounds/observed bands (cm(^{-1}))</th>
<th>3a</th>
<th>3b</th>
<th>3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H stretch</td>
<td></td>
<td>3330</td>
<td>3353</td>
<td>3352</td>
</tr>
<tr>
<td>Ar-H stretch</td>
<td></td>
<td>3068-3041</td>
<td>3101-3038</td>
<td>3088-3036</td>
</tr>
<tr>
<td>-CH(_2)- stretch (ethoxy)</td>
<td></td>
<td>2945-2876</td>
<td>2927-2881</td>
<td>2956-2879</td>
</tr>
<tr>
<td>Ring skeleton</td>
<td></td>
<td>1608-1509</td>
<td>1609-1506</td>
<td>1603-1513</td>
</tr>
<tr>
<td>Aliphatic CH(_2) scissor</td>
<td></td>
<td>1452-1369</td>
<td>1456-1448</td>
<td>1475-1444</td>
</tr>
<tr>
<td>Ar-O-R (aryl ether)</td>
<td></td>
<td>1268-1209</td>
<td>1265-1210</td>
<td>1269-1221</td>
</tr>
<tr>
<td>R-O-R (aliphatic ether)</td>
<td></td>
<td>1172-1069</td>
<td>1175-1159</td>
<td>1175-1111</td>
</tr>
<tr>
<td>1,4-disubstituted benzene ring (out-of-plane bending)</td>
<td></td>
<td>829-815</td>
<td>832-819</td>
<td>820</td>
</tr>
</tbody>
</table>
Table 5 FT-IR assignments for [4a, 4b, 4c] from Step 4

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Compounds/observed bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4a</td>
</tr>
<tr>
<td>Ar-H stretch</td>
<td>3119-3070</td>
</tr>
<tr>
<td>-CH₂- stretch (ethoxy)</td>
<td>2952-2891</td>
</tr>
<tr>
<td>O-C≡N stretching</td>
<td>2279-2238</td>
</tr>
<tr>
<td>Ring skeleton</td>
<td>1598-1501</td>
</tr>
<tr>
<td>Aliphatic CH₂ scissor</td>
<td>1456-1375</td>
</tr>
<tr>
<td>Ar-O-R (aryl ether)</td>
<td>1244-1181</td>
</tr>
<tr>
<td>R-O-R (aliphatic ether)</td>
<td>1169-1092</td>
</tr>
<tr>
<td>1,4-disubstituted benzene ring (out-of-plane bending)</td>
<td>819</td>
</tr>
<tr>
<td>Sample</td>
<td>m.p. (°C)</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
</tr>
<tr>
<td>AroCy B10 (cat)</td>
<td>76</td>
</tr>
<tr>
<td>4a (no cat)</td>
<td>125</td>
</tr>
<tr>
<td>4a (cat 2000)</td>
<td>125</td>
</tr>
<tr>
<td>4b (no cat)</td>
<td>121</td>
</tr>
<tr>
<td>4b (cat 2000)</td>
<td>119</td>
</tr>
<tr>
<td>4c (no cat)</td>
<td>66</td>
</tr>
<tr>
<td>4c (cat 2000)</td>
<td>66</td>
</tr>
</tbody>
</table>
Table 7 TG data for the thermal degradation (in flowing nitrogen) of homopolymers of AroCy B10, newly reported dicyanates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C) for given mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>AroCy B10</td>
<td>348</td>
</tr>
<tr>
<td>4a</td>
<td>366</td>
</tr>
<tr>
<td>4b</td>
<td>346</td>
</tr>
<tr>
<td>4c</td>
<td>357</td>
</tr>
</tbody>
</table>
Table 8 DMTA data for poly(2,2-\textit{bis}(4-cyanatophenyl)propane) and the newly reported dicyanates.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\alpha) transition (°C)</th>
<th>(\beta) transition(^a) (°C)</th>
<th>(\gamma) transition (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AroCy B10</td>
<td>277</td>
<td>30</td>
<td>-80</td>
</tr>
<tr>
<td>4a</td>
<td>221</td>
<td>24</td>
<td>-68</td>
</tr>
<tr>
<td>4b</td>
<td>139</td>
<td>-55</td>
<td>-115</td>
</tr>
<tr>
<td>4c</td>
<td>121</td>
<td>-55</td>
<td>-115</td>
</tr>
</tbody>
</table>

\(^a\) with the exception of 4b this transition is ill defined and very broad
Scheme 1 synthetic route to the dicyanate monomers [4a, b, c]
Figure 1 Infrared transmission spectra of dialdehydes [1a, 1b, 1c] produced in Step 1

(common arbitrary vertical scale)
Figure 2a $^1$H NMR spectrum of dialdehyde [1a] ($S$ = shifts arising from NMR solvent)
Figure 2b $^1$H NMR spectrum of dialdehyde [1b] ($S$ = shifts arising from NMR solvent)
Figure 2c $^1$H NMR spectrum of dialdehyde [1c] ($S =$ shifts arising from NMR solvent)
Figure 3 Infrared transmission spectra of diformates [2a, 2b, 2c] produced in Step 2 (common arbitrary vertical scale)
Figure 4a $^1$H NMR spectrum of dioxyaldehyde [2a] (S = shifts arising from NMR solvent)
Figure 4b $^1$H NMR spectrum of dioxyaldehyde [2b] (S = shifts arising from NMR solvent)
Figure 4c ¹H NMR spectrum of dioxyaldehyde [2c] (S = shifts arising from NMR solvent)
Figure 5 Infrared transmission spectra of diphenols [3a, 3b, 3c] produced in Step 3 (common arbitrary vertical scale)
Figure 6a $^1$H NMR spectrum of diphenol [3a] (S = shifts arising from NMR solvent)
Figure 6b $^1$H NMR spectrum of diphenol [3b] ($S =$ shifts arising from NMR solvent)
Figure 6c $^1$H NMR spectrum of diphenol [3c] ($S$ = shifts arising from NMR solvent)
Figure 7 Infrared transmission spectra of dicyanates [4a, 4b, 4c] produced in Step 4 (arbitrary vertical scale)
Figure 8a $^1$H NMR spectrum of dicyanate [3a] (S = shifts arising from NMR solvent)
Figure 8b ¹H NMR spectrum of dicyanate [3b] (S = shifts arising from NMR solvent)
Figure 8c $^1$H NMR spectrum of dicyanate [3c] (S = shifts arising from NMR solvent)
Figure 9 Composite DSC thermogram (10 K/min) of (a) uncatalysed (4a), (b) catalysed (4a), (c) uncatalysed (4b), (d) catalysed (4b), (e) uncatalysed (4c), (f) catalysed (4c)
Figure 10 TG data for homopolymers of AroCy B10 and dicyanates (4a), (4b), and (4c).
Figure 11 FT-IR (ATR) spectrum of AroCy B10 homopolymer cured at 180 °C / 1h and 230 °C / 1h (showing expansion of cyanate region)
Figure 12 FT-IR (ATR) spectra of newly reported dicyanate homopolymers (4a), (4b), (4c) cured at 180°C / 1h and 230°C /
REFERENCES


