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Studies on a dicyanate containing four phenylene rings and polycyanurate blends. 1. Synthesis and polymerization of the monomers and characterization of the polymer blends using thermal and mechanical methods

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Abstract

The two-step preparation of bis-4-(4-cyanatophenoxy)phenyl sulphone, in good yield and high purity, is reported. Characterization of the monomer is undertaken using spectroscopic and chromatographic methods and elemental analysis. Blends of bis-4-(4-cyanatophenoxy)-phenyl sulphone with a commercial dicyanate, 2,2-bis(4-cyanatophenyl)propane are analyzed using differential scanning calorimetry at a variety of heating rates and the thermal data compared with those of the discrete monomers. The cured homopolymers and blends are further analyzed using thermogravimetry, dynamic mechanical thermal analysis and thermomechanical analysis. The effects of blend composition on the thermal stability, glass transition temperature and thermal expansion are discussed. © 2002 Published by Elsevier Science Ltd.

Keywords: Cyanate esters; Polycyanurates; Synthesis

1. Introduction

Cyanate ester resins are a family of thermosetting resins that are used within a variety of electronic and microelectronic applications. The cyanate monomers offer low toxicity ($LD_{50} \geq 3$ g/kg), ease of processing and versatile cure and blending options and undergo conventional thermal cure via the formation of cyanurate rings (*sym*-triazine rings linked by aryl ether linkages to a polymer, correctly termed a polycyanurate). A simplified reaction is depicted in Scheme 1 for 2,2-bis(4-cyanatophenyl)propane (a range of catalyst packages may be used, but these generally comprise a transition metal carboxylate or chelate and an alkyl phenol, such as dodecylphenol). The single largest application for polycyanurates is in the formation of lamination substrates for printed circuits and their assembly via prepreg adhesives into high-density, high-speed multilayer boards for supercomputers, mainframes and high-speed workstation mother units [1]. In these applications cured polycyanurates have a number of desirable characteristics: relatively high glass transition temperature, good fracture toughness, good hot/wet performance, low dielectric and low moisture absorption [2].

However, the problem of thermal stresses, which arise during the cure cycle process of the aforementioned lamination substrates, can give cause for concern during manufacture. Simon notes [3] that there are two (independent) components to stress development in thermosetting polymers: *cure* stresses arising from volume changes that are associated with chemical reaction during cure and *thermal* stresses arising from the mismatch of thermal expansion coefficients (TECs) between, e.g. a polymer matrix and the adjoining or confining material [4,5]. The development of thermal stresses has been well documented [6–8] and is particularly pertinent to the current study for, in complex electronic packages, wherein both dielectric polymer and, e.g. a silica substrate may be in direct contact, severe delamination and warping may arise as a result. For instance, the TEC of a typical commercial polycyanurate lies between 62 and 71 ppm/°C [9], over 20 times the magnitude of the TEC for silicon wafer [10]. The current work seeks to extend the knowledge in this area with the eventual aim of designing polymer matrices with a greater

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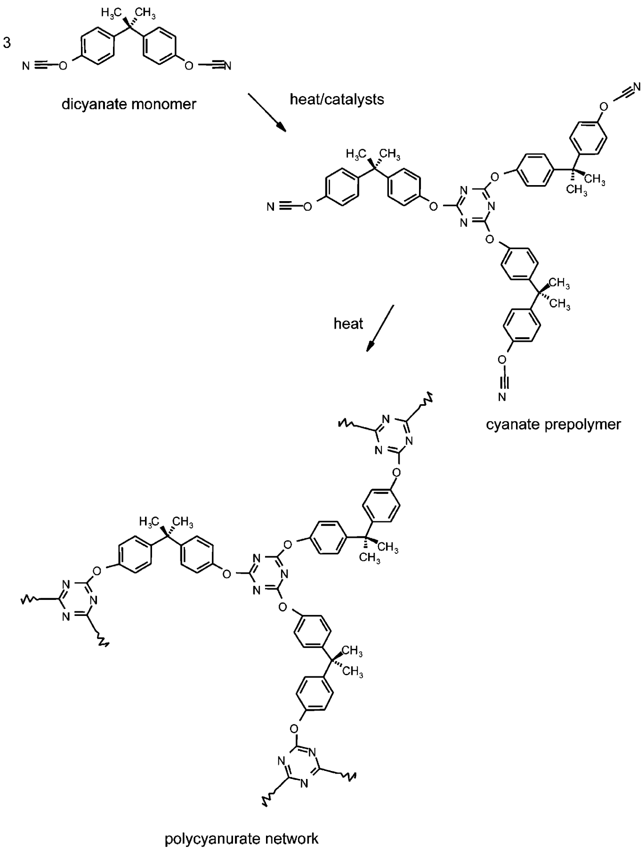


Scheme 1. Simplified cyclotrimerization reaction to produce polycyanurate network (shown for 2,2-bis(4-cyanatophenyl)propane).

degree of molecular flexibility and also to minimize TEC (to improve the match with the substrate). In this way thermal stresses might be dissipated during the processing stage, thus reducing the propensity for warpage and delamination.

In this paper we discuss the preparation, characterization and thermal properties of an aryl dicyanate, containing four ether-bridged phenylene rings in its backbone, bis-4-(4-cyanatophenoxy)phenyl sulphone, with the eventual aim of assessing the potential of the monomer for use in microelectronic applications. The selection of this monomer for incorporation in commercial dicyanate blends was based on previous molecular simulation work [11–13] that examined the inherent flexibility of similar structures in poly(arylene ether sulphone)s. The relationship between the structures of the blend components and bulk mechanical performance is also addressed. The discussion of the kinetics and mechanisms of the polymerization and thermal degradation of the blends will be the subject of a subsequent paper.

2. Experimental

2.1. Materials

The commercial dicyanate, 2,2-bis(4-cyanatophenyl)-propane (AroCy B-10) was obtained from Ciba Speciality Chemicals and was used as received. The following reagents 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, methanol, petroleum ether (40–60 °C), anhydrous potassium carbonate and glacial acetic acid (all of GPR grade and obtained from Fisher Scientific). *N*,*N*-Dimethylacetamide (99%), triethylamine (99%), $CDCl_3$, CD_3OD and D_6-acetone (Aldrich Chemical Co.). Cyanogen bromide (97%) and 4-methoxyphenol (99%) (Acros Organics). Hydrobromic acid (48% w/w aqueous solution) and bis(4-fluorophenyl)sulphone (98 + %) (Lancaster). Anhydrous magnesium sulphate and acetone (both GPR grade and obtained from BDH).

2.2. 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. The samples were presented on an ATR module, 16 scans, at a resolution of $4\ cm^{-1}$, were recorded and coadded to produce the final spectrum. ^1H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC300 spectrometer operating at 300 MHz. Samples were prepared in $CDCl_3$, CD_3OD or D_6-acetone according to solubility and spectra were acquired at 298 K using tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed using a Leeman Labs, Inc. CE 440 elemental analyzer. Melting temperatures were determined using a Kopfler flat bed micro melting point apparatus and a heating rate of $4\ K\ min^{-1}$. Differential scanning calorimetry (DSC) was carried out using a Perkin–Elmer *Pyris* 1 on samples (ca. 2.5 ± 0.5 mg) over the range 40–350 °C at a variety of heating rates (5, 10, 15, and $20\ K\ min^{-1}$). Measurements were made under N_2 ($20\ cm^3\ min^{-1}$) using sealed, crimped aluminium pans. Thermogravimetry (TG) was performed using a ULVAC Sinku-Riko differential thermogravimetric analyzer TGD 7000 on samples (ca. 8.7 ± 0.5 mg) at a heating rate of $10\ K\ min^{-1}$ between 25 and 800 °C. Measurements were made under N_2 ($20\ cm^3\ min^{-1}$) using a platinum boat. Dynamic mechanical analysis (DMA) measurements were undertaken in tensile mode, at a frequency of 1 Hz ($6.28\ rad\ s^{-1}$), on cured neat resin samples of $5 \times 0.5 \times 35\ mm^3$ using a Rheometrics solids analyzer RSAII with Rheometrics environmental controller unit. Scanning experiments were performed between − 150 and 350 °C at a heating rate of $5\ K\ min^{-1}$. Thermomechanical measurements were undertaken using a Seiko Instruments, Inc. EXSTAR6000 TMA/SS6000 on cured neat resin samples of between 0.7 and 1.1 mm thickness. A probe weight of 0.5 g (4.9 mN) was used on an analysis area of $9.026\ mm^2$ while being scanned at a heating rate of $5\ K\ min^{-1}$.

2.3. Synthesis and characterization

2.3.1. Bis-4-(4-methoxyphenoxy)phenyl sulphone (**1**)

A round bottom flask, equipped with a magnetic stirrer bar and air condenser, was charged with 4-methoxyphenol (5.71 g, 46 mmol), bis(4-fluorophenyl)sulphone (5.85 g, 23 mmol) and DMAc (75 cm^3). The resulting mixture was stirred under reflux (135 °C) for 16 h after which time the reaction mixture was allowed to cool to room temperature, before distilled water (65 cm^3) was added. The product was extracted into dichloromethane (150 cm^3) and given a final wash with distilled water (200 cm^3), before the organic layers were combined and dried over magnesium sulphate. The solvent was removed by rotary evaporation to yield a light brown liquid, which solidified as a white product on successive additions of methanol/water (50/50, v/v) (300 cm^3) and petroleum ether (300 cm^3). The white solid (mp 112–114 °C) was produced in good yield on the small scale (7.57 g, 71.1%), but purity and yield were improved on scale up (27.21 g, 85.3%, mp 112–114 °C). Subsequent analytical data are given for the scaled up preparation.

2.4. Analytical data

Elemental analysis, calculated for $C_{26}H_{22}O_6S$: 67.52% C, 4.79% H; found: 67.35% C, 4.60% H.

300 MHz ^{1}H NMR δ_H ($CDCl_3$, ppm from TMS) 7.84–7.81 (4H, d, $J_H = 8.9$ Hz, Ar-H$_a$), 7.00–6.97 (4H, d of d, $J_H = 8.2$ Hz, Ar-H$_b$), 6.94–6.93 (4H, d of d, $J_H = 8.2$ Hz, Ar-H$_c$), 6.92–6.89 (4H, d of d, $J_H = 9.7$ Hz, Ar-H$_d$), 3.82 (6H, s, CH_3O–Ar).

2.4.1. Bis-4-(4-hydroxyphenoxy)phenyl sulphone (**2**)

A round bottom flask, equipped with stirrer bar and air condenser, was charged with bis-4-(4-methoxyphenoxy)-phenyl sulphone (**1**) (5 g, 10.8 mmol), acetic acid (30 cm^3) and hydrobromic acid (48% aqueous, 15 cm^3). The resulting mixture was stirred under reflux (135 °C) for 16 h after which time the reaction mixture, a clear light brown solution, was allowed to cool to room temperature. The cooled solution was poured into stirred water (50 cm^3) and dissolved in methanol (50 cm^3). Addition of further water (50 cm^3) yielded a white precipitate, which was washed with petroleum ether (150 cm^3). The product was dried in vacuo at 80 °C (6 h) to yield a white solid (2.97 g, 63.2%). The preparation was subsequently scaled up to yield 19.79 g (84.2%) of the desired product (mp 184–186 °C). Subsequent analytical data are given for the scaled up preparation.

2.5. Analytical data

Elemental analysis, calculated for $C_{24}H_{18}O_6S$: 66.35% C, 4.18% H; found: 66.04% C, 3.90% H.

300 MHz ^{1}H NMR δ_H (CD_3OD, ppm from TMS) 7.85–7.82 (4H, d, $J_H = 8.8$ Hz, Ar-H$_a$), 7.00–6.97 (4H, d, $J_H = 8.8$ Hz, Ar-H$_b$), 6.92–6.89 (4H, d, $J_H = 8.8$ Hz, Ar-H$_c$), 6.84–6.81 (4H, d, $J_H = 8.8$ Hz, Ar-H$_d$), 4.88 (s, partially obscured by CD_3OD, Ar–OH$_e$).

2.5.1. Bis-4-(4-cyanatophenoxy)phenyl sulphone (**3**)

A three-neck round bottom flask, equipped with a magnetic stirrer bar, dropping funnel and a drying tube, was charged with bis(4-hydroxyphenyl-4′-phenoxy)sulphone (10 g, 23.02 mmol) and cyanogen bromide (5.36 g, 50.64 mmol). The reactants were dissolved in *N*,*N*-dimethylacetamide (DMAc, 4 cm^3) and acetone (40 cm^3) and the solution cooled below −5 °C using a methanol/-card-ice bath. Triethylamine (5.13 g, 50.64 mmol) 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 the triethylamine, the reaction mixture was left stirring for 30 min and then allowed to warm to room temperature. The mixture was washed, by fast stirring, with water (150 cm^3) to remove triethylamine hydrobromide and DMAc—the product was then extracted with dichloromethane (100 cm^3). The organic layer was dried over magnesium sulphate and the solvent removed by rotary evaporation to give a light brown liquid (containing occluded DMAc). The addition of a 50/50 (v/v) mixture of methanol and water yielded a solid, which was then washed with petroleum ether (100 cm^3) to yield 10.40 g (93.3%) of a white solid product (mp 104–106 °C, [lit. 107 °C [14]]).

2.6. Analytical data

Elemental analysis, calculated for $C_{26}H_{16}N_2O_6S$: 64.46% C, 3.33% H, 5.78% N; found: 64.35% C, 2.99% H, 5.67% N.

300 MHz ^{1}H NMR δ_H ($CDCl_3$, ppm from TMS) 7.92–7.90 (4H, d, $J_H = 8.9$ Hz, Ar-H$_a$), 7.36–6.33 (4H, d, $J_H = 8.8$ Hz, Ar-H$_b$), 7.14–7.12 (4H, d, $J_H = 9.9$ Hz, Ar-H$_c$), 7.05–7.02 (4H, d, $J_H = 9.8$ Hz, Ar-H$_d$).

2.6.1. Procedure for blending of dicyanates and cocatalysts and cure schedule employed to effect cure

Prior to selecting the blend compositions for analysis, an initial assessment was made of the compatibility of the individual components within the proposed blends. This assessment was based on a calculation reported by Fedors [15] (and based on the Hildebrand solubility parameter, δ)

$$\delta = (\Delta E_v/V)^{1/2}$$

where

$$\Delta E_v = \sum_i \Delta e_i \text{ and } V = \sum_i \Delta v_i$$

(Δe_i and Δv_i are the additive atomic group contributions for the energy of vaporization and the molar volume, respectively, at a given temperature). This additive method essentially produces a calculated solubility parameter, δ

(not to be confused with the NMR chemical shifts reported herein), which depends on the nature of functional groups/moieties within the monomer/polymer blend structure(s). Where the calculated values of δ for the two components are similar, this implies that they will be compatible. This simple method should only be taken as an initial guide to the ambient temperature compatibility of the components of the blend. It is not intended to determine the dynamics of the mixing of the components during the cure, which may be influenced by a number of factors and may lead to a complex phase diagram. On this basis for AroCy B-10, δ is calculated as 25.20 $\mathrm{MPa}^{1/2}$ in the monomer and 26.69 $\mathrm{MPa}^{1/2}$ in the polymer, whereas the figure is 26.99 and 28.23 $\mathrm{MPa}^{1/2}$, respectively, for the monomer and polymer of bis-4-(4-cyanatophenoxy)phenyl sulphone. Hence, one would expect the two components to be compatible and indeed AroCy B-30, which being a prepolymer contains a larger proportion of triazine rings, should be more compatible with the bis-4-(4-cyanatophenoxy)phenyl sulphone monomer.

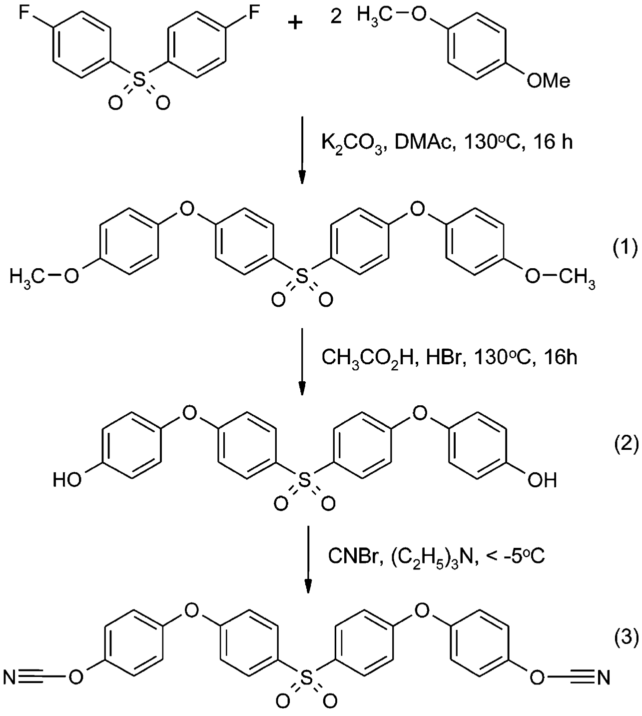
Prior to incorporation in the dicyanate, the cocatalyst package, comprising aluminium(III) acetylacetonate, $\mathrm{Al(acac)_3}$, and dodecylphenol in the molar ratio of 1:25, was first homogenized by heating to 80 °C (in a vial in a water bath) before cooling to room temperature. The cocatalysts were then introduced into the dicyanate monomer (typically at a molar ratio of $\mathrm{Al(acac)_3}$/-dodecylphenol/monomer of 1:25:1000) by mixing in a pestle and mortar at room temperature to a homogeneous mixture. The ensuing blends were used in the thermal analyses directly after incorporation of the cocatalysts. Storage of catalyzed blends was undertaken in a refrigerator (<5 °C) with care being taken to minimize the exposure of the blend to atmospheric moisture.

3. Results and discussion

3.1. Synthesis and characterization

Whilst the dicyanate (**3**) has been reported before [14,16,17], the characterization presented was less detailed than that undertaken in this work and no blend studies were undertaken. The preparative route employed in the work to produce (**3**) is shown in Scheme 2. The initial step, involving the preparation of bis-4-(4-methoxyphenoxy)phenyl sulphone (**1**) was based on a reported procedure [17,18], but modified to accommodate these reagents. The use of 4-methoxyphenol facilitates a relatively low reaction temperature (130 °C) and produces high yields (in excess of 70%). The methoxy groups prevent further chain extension via condensation and these are cleaved using acid hydrolysis during the second step to produce bis-4-(4-hydroxyphenoxy)phenyl sulphone (**2**).

In the final step, cyanation of bis-4-(4-hydroxyphenoxy)phenyl sulphone was carried out using a modification of a well reported method [19]. Unfortunately, at the low



Scheme 2. Preparative procedures used in this study.

(subzero) temperatures required to effect cyanation, the bis-phenol precipitated from both acetone (a preferred cyanation solvent) and dichloromethane, typically when the temperature approached −5 °C. In order to maintain the solution, a small volume of DMAc (ca. 10 $\mathrm{cm^3}$) was added to the mixture to effect complete solution. The addition of DMAc was kept to a minimum since removal of large volumes of this solvent would be problematic at the conclusion of the synthesis. An additional point to note with this particular preparation involves the immersion of the newly cyanated monomer in a methanol/water mixture during work-up. It was found, during an early experiment, that hydrolysis of the cyanate (to form the corresponding phenol) was appreciable even at ambient temperature and so a brief washing step was employed. The crude, solid dicyanate was placed in a vacuum desiccator at room temperature with phosphorus pentoxide to remove any adsorbed moisture and eliminate residual bromoethane (another side product arising from the von Braun reaction [20] when using cyanogen bromide). Observation of these minor modifications yielded a dicyanate monomer in high purity as evidenced by the analytical data presented herein.

The principal means of determining whether the cyanation step has been effected successfully involve FT-IR and ^{1}H NMR spectroscopy. In the dicyanate new bands at 2238 and 2285 $\mathrm{cm^{-1}}$, characteristic of C≡N stretch, coupled with the absence of the broad O–H stretch at 3350 $\mathrm{cm^{-1}}$ (arising in the bis-phenol precursor) (Fig. 1) support this conclusion.

Furthermore, ^{1}H NMR spectra of both the bis-phenol and dicyanate (Fig. 2) show a pronounced downfield shift (by ca. 0.2 ppm) in the chemical shifts associated with the aromatic protons, particularly those *ortho* to the cyanate group and the OH group in the precursor ($\delta = 4.88$ ppm, partially obscured by the CD_3OD proton signal). The spectra also show clearly the absence of appreciable levels of contaminants as the remaining chemical shifts can be assigned to either the internal standard (TMS) or NMR solvent.

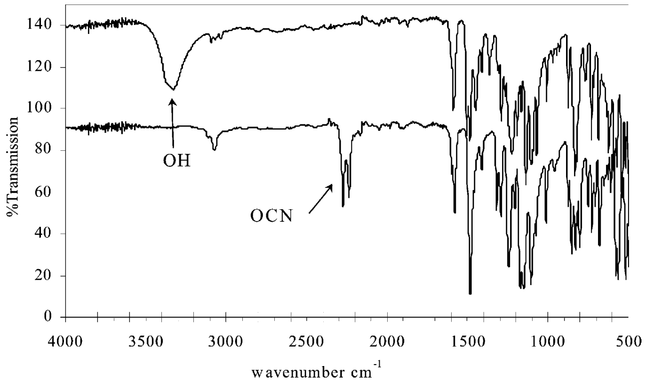


Fig. 1. FT-IR spectra of (a) bis-4-(4-hydroxyphenoxy)phenyl sulphone and (b) bis-4-(4-cyanatophenoxy)phenyl sulphone.

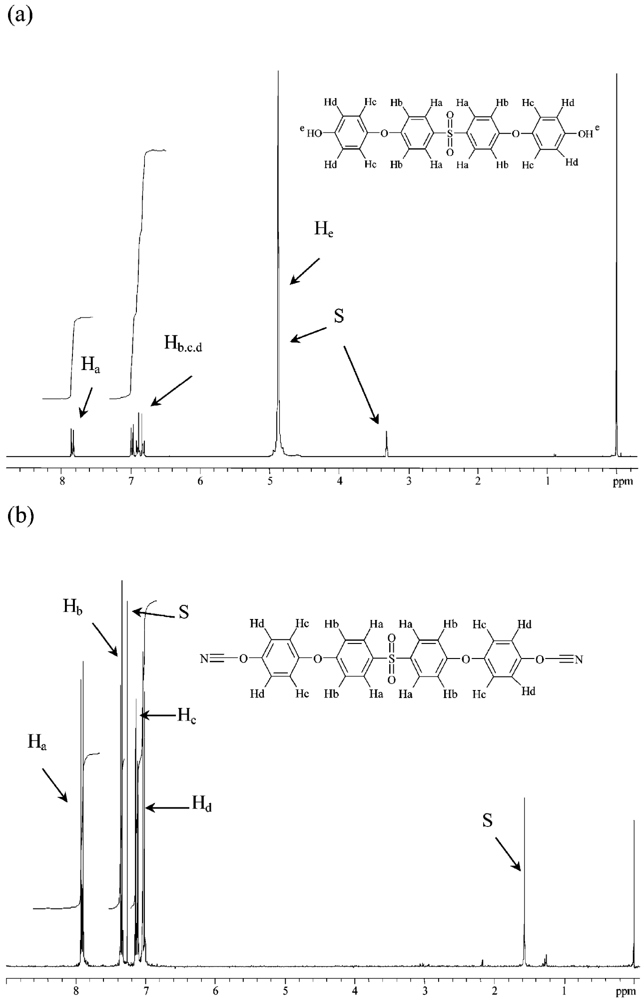


Fig. 2. ^{1}H NMR spectra of (a) bis-4-(4-hydroxyphenoxy)phenyl sulphone and (b) bis-4-(4-cyanatophenoxy)phenyl sulphone (S = chemical shifts associated with the NMR solvents).

3.2. Thermal analysis of the monomers and blends

3.2.1. Analysis of the individual dicyanate monomers

A common dicyanate, 2,2-bis(4-cyanatophenyl)propane (available commercially as AroCy B-10 and shown in Scheme 1) was chosen as the second component in the proposed blends for this work. 2,2-Bis(4-cyanatophenyl)-propane has the additional advantage of having been studied extensively and so its physical, thermal and mechanical properties are well known, making it an ideal material for comparative purposes.

In the first instance, an 'uncatalyzed' sample of 2,2-bis(4-cyanatophenyl)propane was analyzed individually using DSC (a typical dynamic scan, 10 K min^{-1}, is shown in (Fig. 3(a)). A sharp melting endotherm is evident (peak minimum 84 °C, $\Delta H = 83$ J g^{-1} or 21 kJ mol^{-1}) indicating a reasonably high degree of purity. This precedes an exothermic peak spanning 207–349 °C (with a main peak maximum at 309 °C and a lower temperature shoulder at around 230 °C). The shape of the peak and the polymerization enthalpy ($\Delta H = -661$ J g^{-1} or -184 kJ mol^{-1} accord well with literature values for this monomer [21–23]. The DSC analysis of the catalyzed dicyanate monomer (Fig. 3(b)) reveals noticeable differences: the melting endotherm occurs at a slightly lower temperature and is somewhat broader than before (peak minimum 81 °C, $\Delta H = 74$ J g^{-1} or 21 kJ mol^{-1}). More significantly, the polymerization exotherm has been reduced to a much lower temperature regime as it now spans 120–335 °C (with a main peak maximum at 191 °C and a lower temperature shoulder at around 155 °C). The value of ΔH is now -692 J g^{-1} or -193 kJ mol^{-1}, presumably partly due to the difficulty in defining the true end point of this broad thermal event.

Bis-4-(4-cyanatophenoxy)phenyl sulphone (**3**) was also analyzed in the absence of an added catalyst (Fig. 3(c)). A reasonably sharp melting endotherm is evident (peak minimum 105 °C, $\Delta H = 46$ J g^{-1} or 22 kJ mol^{-1}). This precedes a broad exothermic peak spanning 184–349 °C (with a main peak maximum at 292 °C and a lower temperature shoulder at around 260 °C). In this instance, a polymerization enthalpy of $\Delta H = -388$ J g^{-1} or -188 kJ mol^{-1}) was recorded. The DSC analysis of the catalyzed dicyanate monomer (**3**) (Fig. 3(d)) revealed a similar picture to the commercial dicyanate: the melting endotherm occurs at a slightly lower temperature and is slightly broader than before (peak minimum 103 °C, $\Delta H = 41$ J g^{-1} or 20 kJ mol^{-1}). The polymerization exotherm now spans 134–290 °C (with a main peak maximum at 211 °C). The value of ΔH is now -385 J g^{-1} or -187 kJ mol^{-1}. As each monomer is a dicyanate then the enthalpy is halved to yield the value in kJ mol^{-1} of cyanate group (see Table 1, entries for blends 100:0 and 0:100). These data compare well with literature values for the polymerization enthalpy [23] and Hamerton and Takeda

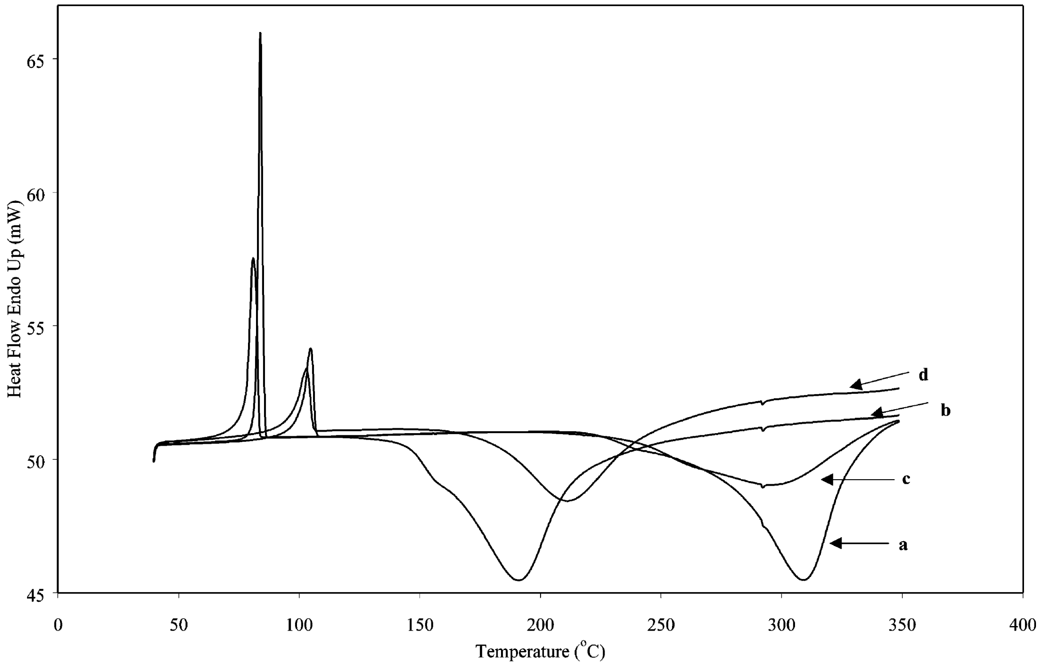


Fig. 3. Composite DSC thermogram (10 K min^{-1}) of (a) uncatalyzed 2,2-bis(4-cyanatophenyl)propane; (b) catalyzed 2,2-bis(4-cyanatophenyl)propane; (c) uncatalyzed bis-4-(4-cyanatophenoxy)phenyl sulphone; (d) catalyzed bis-4-(4-cyanatophenoxy)phenyl sulphone.

[24] have recently reported a value of 90 kJ mol^{-1} OCN for the Al(acac)$_3$/dodecylphenol catalyzed polymerization of AroCy L-10 (1,1-bis(4-cyanatophenyl)ethane) using DSC.

3.2.2. *Analysis of bis(4-cyanatophenyl)propane/bis-4-(4-cyanatophenoxy)phenyl sulphone blends*

Having analyzed the monomers individually, a series of catalyzed dicyanate blends was prepared and analyzed using DSC. The data are given in Table 1 and several features are worthy of note. Predictably, the melting behavior of the individual monomers is altered during the formation of the binary blend (Fig. 4), however, the composition containing 75% bis-4-(4-cyanatophenoxy)phenyl sulphone displays two discrete melting endotherms: the first occurring over a reasonably narrow temperature range, while the second is bimodal at higher temperature. This suggests a possible change in the miscibility of the components at this composition and is surprising since the remaining compositions all display only a single event. The behaviour persisted despite several analyses being undertaken and the enthalpy of melting was similar in magnitude to the other binary blends.

3.3. *Thermo-mechanical analysis of the cured homopolymers and polymeric blends*

A variety of techniques was employed to assess the thermal and mechanical characteristics of the blends and these were assessed with respect to polycyanurate homopolymers.

3.3.1. *TG analysis of the individual monomers: 2,2-bis(4-cyanatophenyl)propane and bis-4-(4-cyanatophenoxy)phenyl sulphone and selected blends*

The TG data for the homopolymers and blends are shown in Fig. 5 and TG analysis (in flowing nitrogen) of

Table 1
Dynamic DSC data (10 K min^{-1}) for dicyanate blends as a function of blend composition

Molar ratio AroCy B/(**3**)	Melting point (°C)	Cure onset[a] (°C)	Peak max (°C)	−Δ*H* polymerization	
				Blend (J g^{-1})	OCN (kJ mol^{-1})
100:0	81	152	191	692	96.5
75:25	73	157	195	578	95.5
50:50	69	160	197	501	95.5
25:75	71, 85[b]	167	203	417	90.5
0:100	103	176	212	385	93.5

AroCy B: 2,2-bis(4-cyanatophenyl)propane; (**3**): bis-4-(4-cyanatophenoxy)phenyl sulphone.

[a] Onset defined as tangent extrapolated from half peak height to baseline.

[b] Two melting transitions were recorded.

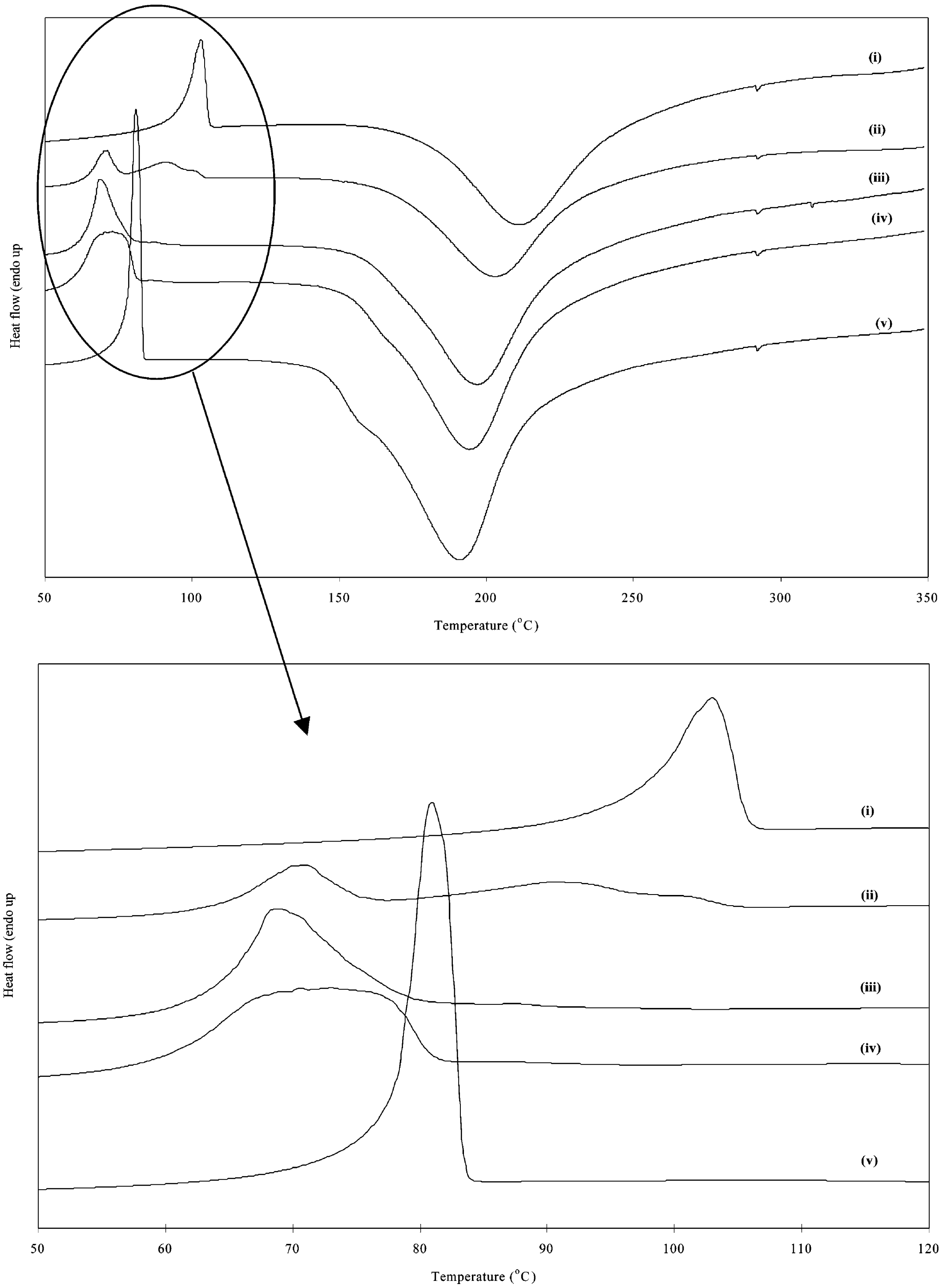


Fig. 4. DSC thermograms (10 K min^{-1}, exothermic transitions are shown with peak maxima facing downwards) of selected blends of 2,2-bis(4-cyanatophenyl)propane (AroCy B) and bis-4-(4-hydroxyphenoxy)phenyl sulphone (**3**) showing entire data and expansion of the melting region. Key: molar ratios for AroCy B/(**3**) (i) 0:100; (ii) 25:75; (iii) 50:50; (iv) 75:25; (v) 100:0.

poly(2,2-bis(4-cyanatophenyl)propane) (i.e. the polycyanurate of AroCy B-10) revealed an onset of thermal degradation (defined as a 5% weight loss) at 344 °C. This initial degradation step accounted for around 50% of the mass and yielded the most rapid rate of weight loss, a second apparently slower degradation step overlaps with the first and continues up until 642 °C, at which point the polycyanurate has undergone complete degradation.

This form of TG plot shown in Fig. 5 is typical for polycyanurates and has been observed for poly(2,2-bis(4-cyanatophenyl)propane) [25,26]. It may be generally described as a Type (v) curve [27] indicating multi-stage

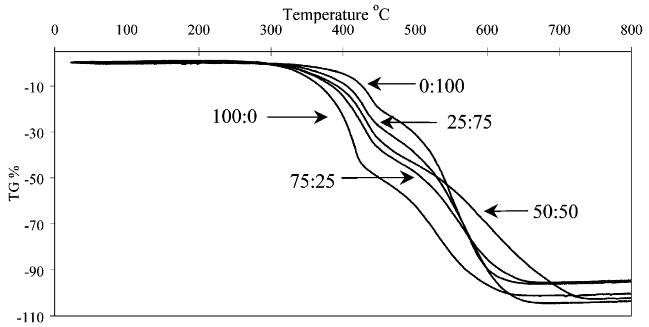


Fig. 5. TG data for homopolymers and selected blends of 2,2-bis(4-cyanatophenyl)propane (AroCy B-10) and bis-4-(4-cyanatophenoxy)phenyl sulphone (**3**). Key: molar ratios shown for (AroCy B-10)/(**3**).

decomposition yielding unstable intermediates. The decomposition reaction of polycyanurates in both air and nitrogen is exothermic and has been observed to proceed in several stages (although the reaction in an inert atmosphere takes place in a higher temperature regime and gives rise to a larger char yield, as might be expected). Pankratov and coworkers [28] reported that the degradation products of polycyanurates consisted mainly of carbon dioxide, carbon monoxide, hydrogen, cyanuric acid and its phenyl esters, phenol and bis-phenols. The thermal degradation mechanism that has been proposed by Pankratov et al. initially involves hydrolytic cleavage of the cyanurate linkage prior to homo- and hetero-lytic decomposition of the triazine ring.

Two groups have independently put forward alternative degradation mechanisms that are gaining acceptance. Shimp and Ising [29] have suggested that the thermal degradation proceeds with the elimination of carbon dioxide in a decarboxylation mechanism at temperatures above 200 °C (Scheme 3(a)), whereas Pascault and coworkers [30] have evidence to support the evolution of cyanic acid as a significant degradation product (Scheme 3(b)). The two mechanisms have in common the formation of a thermally unstable carbamate intermediate from unreacted, sterically hindered cyanate groups within the polymer network. The action of adventitious moisture and transition metal compounds (used to effect polymerization) serve ultimately to effect the transformation [31]. Whichever mechanism ensues (and unfortunately no ‘hyphenated’ techniques were available to us to determine the nature of the decomposition products evolved), both serve to underline the importance of achieving the highest degree of polymerization through the correct choice of catalyst and processing conditions, in order to achieve optimum thermal stability.

More recently, Ramirez et al. [26] have studied the thermal decomposition mechanisms of a series of aromatic polycyanurates using infrared analysis, TG, and pyrolysis GC–MS. They found that, for the compounds studied, the thermal stability of the polycyanurates was essentially independent of the chemical structure of the monomers studied with the major mass loss occurring at ca. 450 °C for all materials, although it should be noted that in the case of an isothermal experiment this event may occur at much lower temperatures after a lengthy thermal exposure. The thermal degradation mechanism was proposed to involve three consecutive processes: (i) random scission and cross-linking of the hydrocarbon backbone between 400 and 450 °C with negligible mass loss; (ii) decyclization of the triazine ring between 450 and 500 °C, with the liberation of low molecular weight volatile compounds and the formation of a primary solid residue; and (iii) decomposition of the primary residue between 500 and 750 °C.

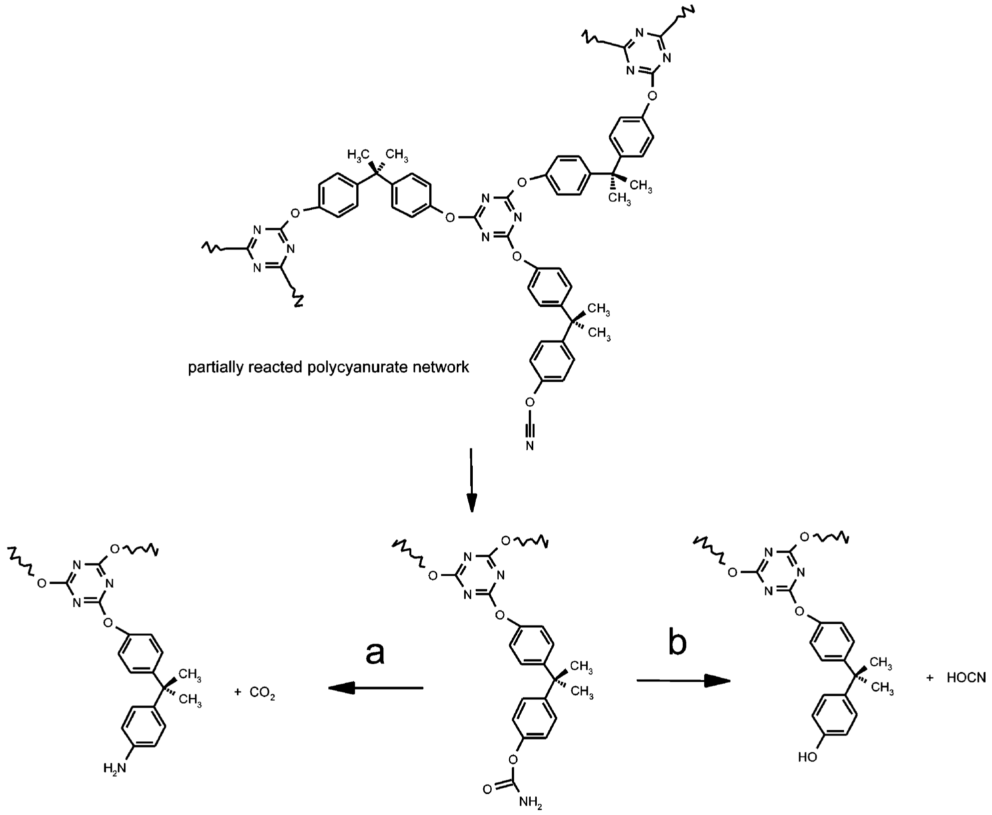
In the current work, poly(bis-4-(4-cyanatophenoxy)phenyl sulphone) was also subjected to TG analysis under the same conditions. In this case, the onset of thermal degradation (defined as a 5% weight loss) commenced at 402 °C and was a somewhat shorter thermal event. This initial (relatively slow) degradation step accounted for around 15–20% of the mass. A second degradation step (with a slower rate of weight loss) overlaps with the first and continues up until 642 °C, at which point the polycyanurate has undergone complete degradation (i.e. around 96% of the mass had been lost, leaving a small residual char). While not directly comparable, McGrath and coworkers [32] determined the thermo-oxidative stability (in air) of poly(bis-4-(4-cyanatophenoxy)phenyl sulphone) and found that the polymer had lost 5% of it mass by 448 °C, while no residual mass remained at 750 °C.

The TG data for the blends of the two comonomers are also depicted in Fig. 5 and even a cursory examination of the TG data reveals that the initial onset of degradation rises in line with the bis-4-(4-cyanatophenoxy)phenyl sulphone content. The same is broadly true for the temperature at which 50% weight loss is recorded and suggests that the two homopolymers undergo different degradation mechanisms (this is particularly evident when the first derivative traces are studied), presumably related to the different polymer backbone structures. For instance, in the case of AroCy B-10, there is a significant aliphatic content that is absent in bis-4-(4-cyanatophenoxy)phenyl sulphone and this would accord with the mechanism proposed by Ramirez et al. [26].

Within the blends the mechanism that the blend adopts largely reflects its composition (i.e. the blend comprising 75% dicyanate (**3**) displays a similar plot to its homopolymer). However, it is evident that 2,2-bis(4-cyanatophenyl)propane is more sensitive to the addition of the second component of the blend. For instance, the addition of 25% dicyanate (**3**) to 2,2-bis(4-cyanatophenyl)propane raises the thermal stability significantly over that of the 2,2-bis(4-cyanatophenyl)propane homopolymer. In contrast, the thermal stability of the blend comprising 25% 2,2-bis(4-cyanatophenyl)propane compares favorably with the homopolymer of dicyanate (**3**).

3.3.2. DMA of the individual monomers: 2,2-bis(4-cyanatophenyl)propane and bis-4-(4-cyanatophenoxy)phenyl sulphone and selected blends

The homopolymer of 2,2-bis(4-cyanatophenyl)propane shows an α transition (the T_g) at 262 °C (determined from



Scheme 3. Two degradation mechanisms proposed for polycyanurates (shown for 2,2-bis(4-cyanatophenyl)propane) (after Refs. [29,30]).

the maximum value of the loss modulus, E'') (Fig. 6). This value is in line with that recorded in the literature [33] for the same polymer.

It is recognized that the measurement of T_g (at best a temperature range rather than a single temperature event) is fraught with difficulty, particularly when making comparison between different studies and published values of T_g for AroCy B-10 vary between 250 and 290 °C, depending on the conditions employed to measure the data. For example, in a recent review [34] it was stated that, at 97% conversion, 2,2-bis(4-cyanatophenyl)propane (equivalent to AroCy B-10), catalyzed with zinc naphthenate (0.15 phr) and nonyl phenol (2 phr), achieved a T_g of ca. 245 °C. Furthermore, extrapolation to a notional 100% conversion on the same published graph yields an ultimate T_g of 260–265 °C. In previous research [35], 2,2-bis(4-cyanatophenyl)propane has been found to yield a T_g ($E''_{\max}$) of 272 °C (at an oscillation frequency of 10 Hz and heating rate of 2 K min^{-1}); the latter are both of importance as they can affect the value obtained, e.g. in the present study a frequency of 1 Hz was employed.

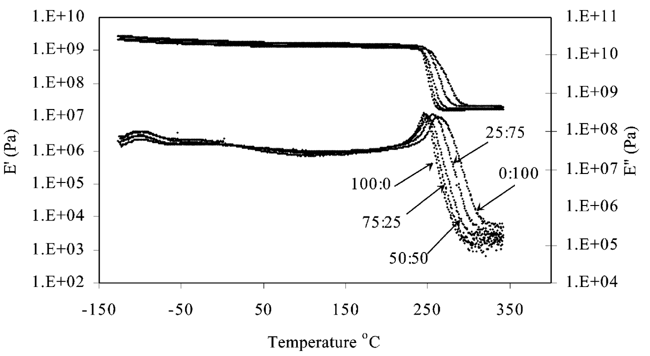


Fig. 6. DMA data for homopolymers and selected blends of 2,2-bis(4-cyanatophenyl)propane (AroCy B-10) and bis-4-(4-cyanatophenoxy)phenyl sulphone (**3**). Key: molar ratios shown for (AroCy B-10)/(**3**) against the E'' data.

The DMA data presented indicate an apparently high degree of conversion for all of the blends studied (examination of the rubber modulus also shows that the polymer shows no signs of undergoing further cure during the analysis), but additional confirmation was provided by performing spectroscopic analysis of the cured polymers and corresponding monomer blends.

FT-IR spectroscopy was employed to ascertain whether the polymeric samples had achieved full conversion by using an accepted method [36], involving the comparison of characteristic cyanate and cyanurate bands. As polymerization proceeds, prominent bands arising from the triazine (ca. 1560 cm^{-1}) and cyanurate (ca. 1365 cm^{-1}) structures—N.B., both are indicated on the lower spectrum of Fig. 7—increase at the expense of the cyanate bands (ca. 2200–2300 cm^{-1}—upper spectrum). By comparing the intensity (or by inserting a baseline and performing an integration of the areas bounded by these bands in the spectrum), it is possible to assess reliably the extent to

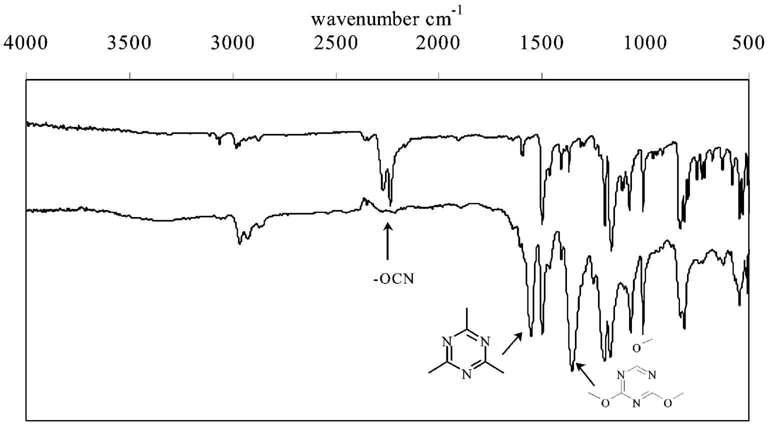


Fig. 7. FT-IR (ATR) spectra of 2,2-bis(4-cyanatophenyl)propane monomer (upper spectrum) and polycyanurate of 2,2-bis(4-cyanatophenyl)propane (lower spectrum) showing signal intensity versus wavenumber. N.B., the characteristic vibrational bands for the cyanate group and cyanurate/*s*-triazine structures are indicated.

which the cyclotrimerization has progressed. An example is shown for the 2,2-bis(4-cyanatophenyl)propane monomer (Fig. 7, top) and the corresponding polycyanurate (Fig. 7, bottom). The presence of cyanate bands within the polymer is negligible, indicating that the majority of cyanate groups have undergone reaction.

Other secondary (sub-ambient) transitions are also apparent in the DMA traces (Table 2) associated with conformational changes that do not require main chain movement (e.g. rotation of *gem*-dimethyl groups within the isopropyl bridges). The polymer shows only a relatively small loss in storage modulus ($E' = 1.48$ GPa at 20 °C and $E' = 1.34$ GPa at 151 °C), prior to the glass transition. These data compare well with literature values recorded for AroCy B-10 (E' at 25 and 200 °C were 1.62 and 1.30 GPa, respectively) [33], giving some confidence in the application of the technique to the novel blends.

The α transition of the homopolymer of dicyanate (**3**) is apparent at 246 °C (determined from the maximum value of the loss modulus, E''), lower than that recorded for 2,2-bis(4-cyanatophenyl)propane reflecting the lower cross-link density and lower barriers to rotation afforded by the ether bridges of the former. Again, the polymer shows no signs of undergoing further cure during the analysis. Other transitions are also apparent at ca. 0 °C (a very broad, ill-defined β transition) and − 100 °C (γ transition). This homopolymer not only shows higher storage modulus compared to 2,2-bis(4-cyanatophenyl)propane, but also a greater retention of storage modulus over a wider temperature range ($E' = 1.76$ GPa at 0.33 °C and $E' = 1.57$ GPa at 150 °C), prior to the glass transition.

Table 2
DMA data for cured homopolymers and blends

Sample (AroCy B-10)/(**3**)	α transition (°C)	β transition[a] (°C)	γ transition (°C)
100:0	262	− 25	− 99
75:25	256	0	− 100
50:50	250	− 10	− 103
25:75	247	− 25	− 98
0:100	246	0	− 100

AroCy B: 2,2-bis(4-cyanatophenyl)propane; (**3**): bis-4-(4-cyanatophenoxy)phenyl sulphone.

[a] This transition is ill-defined and very broad (typically spanning 100 K).

In the case of the binary blends, the behaviour generally reflects the blends' compositions (e.g. the α transition is certainly sensitive to the blend composition). However, interestingly, the storage modulus appears to reach a maximum (of those materials tested) for the blend containing 25% dicyanate (**3**), which yields a figure (1.62 GPa at 150 °C) that is significantly higher than that recorded for either homopolymer.

3.3.3. *TMA of the individual monomers: 2,2-bis(4-cyanatophenyl)propane and bis-4-(4-cyanatophenoxy)phenyl sulphone and selected blends*

The TMA data for the homopolymers and blends are presented in Fig. 8. There is reasonably good agreement between the values of T_g derived from DMA (Table 3) and those determined using TMA. In view of the proposed application of the materials to the electronics industry, the

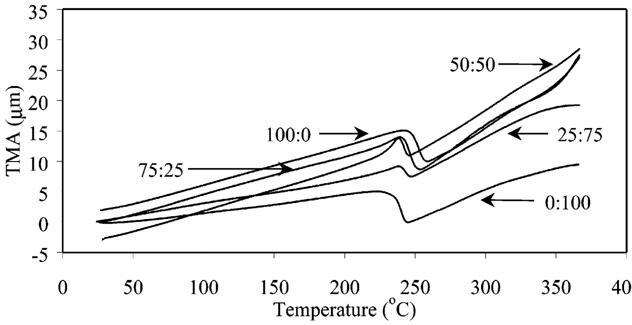


Fig. 8. TMA data for homopolymers and selected blends of 2,2-bis(4-cyanatophenyl)propane (AroCy B-10) and bis-4-(4-cyanatophenoxy)phenyl sulphone (**3**). Key: molar ratios shown for (AroCy B-10)/(**3**).

Table 3
Thermo-mechanical data for homopolymers and blends and commercial resin systems [33]

Samples	DMA		TMA	
	T_g (°C)	E' (GPa) at 25/200 °C	T_g (°C)	TEC (ppm/°C) 40–200 °C
*Blends (**1**)/(**2**)*				
100:0	262	1.48/1.34	246–257	57
75:25	256	1.92/1.62	242–251	54
50:50	250	1.45/1.28	239–245	63
25:75	247	1.71/1.42	240–246	41
0:100	246	1.76/1.57	235–255	39
Commercial polymers[a]				
AroCy B	289	1.62/1.30	257	64
AroCy M	252	1.61/1.07	244	71
AroCy L	258	1.34/1.01	259	64
XU71787	244	1.75/1.32	223	68
TGDDM-DDS	246	1.97/1.13	210	67
BMI-MDA	320	1.65/1.30	297	62
BMI-DABA	288	1.90/1.35	263	63

AroCy B: 2,2-bis(4-cyanatophenyl)propane; AroCy M: bis(4-cyanato-3,5-dimethylphenyl)methane; AroCy L: 1,1-bis(4-cyanatophenyl)ethane; XU71787: dicyanate monomer of phenol–dicyclopentadiene adduct; TGDDM-DDS: copolymer of bis(4-tetraglycidylaminophenyl)methane and bis(4-aminophenyl)-sulphone; BMI-MDA: copolymer of bis(4-maleimidophenyl)methane and bis(4-aminophenyl)methane; BMI-DABA: copolymer of bis(4-maleimidophenyl)methane and 2,2-bis(3-allyl-4-hydroxyphenyl)propane.

[a] DMA/TMA analysis conditions for the commercial polymers were not specified in the original reference [33].

range of TEC values displayed by the polymers is of great interest.

In Section 1 it was stated that polycyanurates are finding increasing application in complex electronic packages, comprising layers of dielectric polymer and silica substrate sandwiched together. The issues of delamination and warping arising from mismatched TECs have already been highlighted as a potential problem. Consequently, it is the ultimate aim of this work to produce polymer blends that offer the lowest possible TEC (or at least as close to that of silicon as possible), while retaining an acceptable T_g and a high modulus that is retained until the onset of the glass transition. It should be borne in mind that the commercial polymers shown in Table 3 represent the current 'state of the art' and the blend data should be evaluated in this context. The blends reported here offer the opportunity to tailor the properties of the ensuing resin—they may yield dry T_g and modulus values that compare favourably with epoxy resins based on tetraglycidylamines, along with lower TEC values (see, for instance, TGDDM/DDS and the 75:25 blend). Similarly, 'first generation' BMI resins (polyaspartimides such as BMI-MDA) yield superior T_g to all of the polycyanurates shown here, but are inherently more brittle and yield higher TEC values than the blends reported in this work. Toughened BMIs (BMI-DABA) fare better than BMI-MDA in terms of fracture toughness (at the expense of dry T_g), but the modulus is similar to the newly reported blends and the TEC is again significantly higher than all but the 50:50 blend.

The formation of simple, binary blends offers the potential to optimize mechanical properties such as T_g, modulus and TEC, depending on the intended application. For example, the lowest TEC reported here is for the bis-4-(4-cyanatophenoxy)phenyl sulphone homopolymer, but this is accompanied by only moderate values of dry T_g and modulus.

4. Conclusions

This work has demonstrated that it is feasible to prepare bis-4-(4-cyanatophenoxy)phenyl sulphone, in good yield and high purity via a two-step preparation. The dicyanate may be blended with a commercial dicyanate, 2,2-bis(4-cyanatophenyl)propane, and copolymerized thermally in the presence of a conventional catalyst package (aluminium(III) acetylacetonate and dodecylphenol). Analysis of the monomers and a variety of blends, using DSC, demonstrated that the onset of thermal polymerization was significantly altered in the binary blends. The formation of binary blends of the commercial dicyanate AroCy B-10 may yield copolymers with improved thermal stability and improved thermo-mechanical properties. Work now continues to examine the effect of blending on the kinetics and mechanism of polymerization and degradation.

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