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Studies on a dicyanate containing four phenylene rings and polycyanurate blends. 2. Application of mathematical models to the catalysed polymerization process

Ian Hamerton[a,*], Alan M. Emsley[a], Brendan J. Howlin[a], Paul Klewpatinond[a], Shinji Takeda[b]

[a]*Department of Chemistry (C4), School of Biomedical and Life Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK*
[b]*Research and Development Strategy Office, Hitachi Chemical Co., Ltd, 48 Wadai, Tsukuba, Ibaraki 300-4247, Japan*

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Abstract

Selected blends of *bis*-4-(4-cyanatophenoxy)phenyl sulphone with a commercial dicyanate, 2,2-*bis*(4-cyanatophenyl)propane are analysed using differential scanning calorimetry (DCS) to examine the processes of the aluminium-catalysed thermal polymerisation. Kinetic treatment of these data show that the kinetics of the formation of the *bis*-4-(4-cyanatophenoxy)phenyl sulphone homopolymer were fitted with just two processes, but three processes were required for the 2,2-*bis*(4-cyanatophenyl)propane homopolymer, for which a more complex thermogram was obtained. When considering the polymerisation kinetics of binary blends of the monomers it was necessary to select the minimum number of kinetic parameters to obtain the best fits to the data. The binary blends generally show trends in the data that reflect the monomer composition. The parameters derived from two kinetic methods are broadly in agreement; the kinetic treatment of the thermal data for 2,2-*bis*(4-cyanatophenyl)propane monomer suggests the presence of at least one impurity and this is supported by spectroscopic and chromatographic analyses. The latter was not observed for *bis*-4-(4-cyanatophenoxy)phenyl sulphone, a monomer found to be of a higher purity by chromatography. From the kinetic analysis of the thermal data (from dynamic DSC), the mathematical model predicts that, following an isothermal cure regime at 450 K, *bis*-4-(4-cyanatophenoxy)phenyl sulphone should reach a conversion of 90% after ca. 33 min. The empirical data for this isothermal experiment show that *bis*-4-(4-cyanatophenoxy)phenyl sulphone reaches a conversion of 73% after 33 min and 87% after 2 h at 450 K.

Keywords: Cyanate esters; Polycyanurates; Polymerization kinetics

1. Introduction

Cyanate ester resins (polycyanurates) are a family of thermosetting resins that are used within a variety of technological applications. Cured polycyanurates offer high performance, including relatively high glass transition temperature (T_g for AroCy B-10 is ca. 260 °C, depending on degree of cure), good fracture toughness (typically $G_{IC} = 140$ J m^{-2} for cured neat AroCy B-10 or 500 J m^{-2} when blended with poly(arylene ether sulphone) [1]) and low moisture absorption (polycyanurates typically gain less than 3 wt% in short-medium term conditioning studies).

The combination of good thermo-mechanical and dielectric properties (e.g. dielectric constant, $\varepsilon = 2.2-2.7$ and dissipation factor, $D_f = 0.003$ at GHz frequencies) makes cyanate esters attractive competitors for epoxy resins and polyimides in many electronic (as well as adhesive and advanced structural composite) applications. Currently, the single largest application for polycyanurates is as lamination substrates for printed circuits and their assembly via prepreg adhesives into high-density, high-speed multi-layer boards, which are produced commercially for supercomputers, mainframes and high speed workstation mother units [2].

In a previous paper we demonstrated the benefits of blending a commercial dicyanate with *bis*-4-(4-cyanatophenoxy)phenyl sulphone by examining the thermo-mechanical properties (as evidenced by increases in thermal stability, modulus and glass transition temperature and reductions in thermal expansion behaviour). In this paper we examine the

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* Corresponding author. Tel.: +44-1483-259587; fax: +44-1483-876851.
E-mail address: i.hamerton@surrey.ac.uk (I. Hamerton).

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application of different mathematical models to elucidate the kinetics of the catalysed thermal polymerisation of these monomers and binary blends. The data will be discussed in the context of the mechanisms proposed for these processes.

2. Experimental

2.1. Materials

2,2-*Bis*(4-cyanatophenyl)propane (available commercially as AroCy B-10, 96.5% pure by HPLC) (**1**) was obtained from Ciba Speciality Chemicals and was used as received; the details of the preparation and characterization of *bis*-4-(4-cyanatophenoxy)phenyl sulphone (98.3% pure by HPLC) (**2**) and the blending of the monomer(s) and catalysts are reported elsewhere [3]. The co-catalyst package comprised aluminum(III) acetylacetonate:dodecylphenol:dicyanate monomer in the molar ratio of 1:25:1000 throughout the study.

2.2. Apparatus

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}). Isothermal DSC analysis was performed on a sample (ca. 4 mg) under N_2 (20 cm^3 min^{-1}) using sealed, crimped aluminium pans; highly pure indium was used as a calibration standard. The 'isothermal' programme comprised a 10 K min^{-1} ramp from 35–100 °C followed by a short equilibration period and then a further ramp to 177 °C (450 K). The sample was held isothermally at this temperature for a period of 2 h before a dynamic rescan (35–100 °C at 10 K min^{-1}) was performed to determine the magnitude of any residual exotherm. Nuclear magnetic resonance spectroscopy was performed using a Brucker AC300 spectrometer operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C nuclei. Samples were prepared in $CDCl_3$ and spectra were acquired at 298 K using tetramethylsilane (TMS) as an internal standard. Reverse-phase, high performance liquid chromatography (HPLC) was carried out on samples (dissolved in acetonitrile) using a Millipore system. The latter comprised a Kontron Instruments T-414 LC pump, Waters 490E programmable multiwavelength detector, a Phenomenx Phenosphere 5 ODS-2 (250 × 3.20 mm, 5 μ) column and using acetonitrile/water (70/30) as the eluent (flow rate 1 cm^3 min^{-1}). The differential kinetic equations were solved by using a commercial software package (Model-Maker v3.0.4 from Cherwell Electronics).

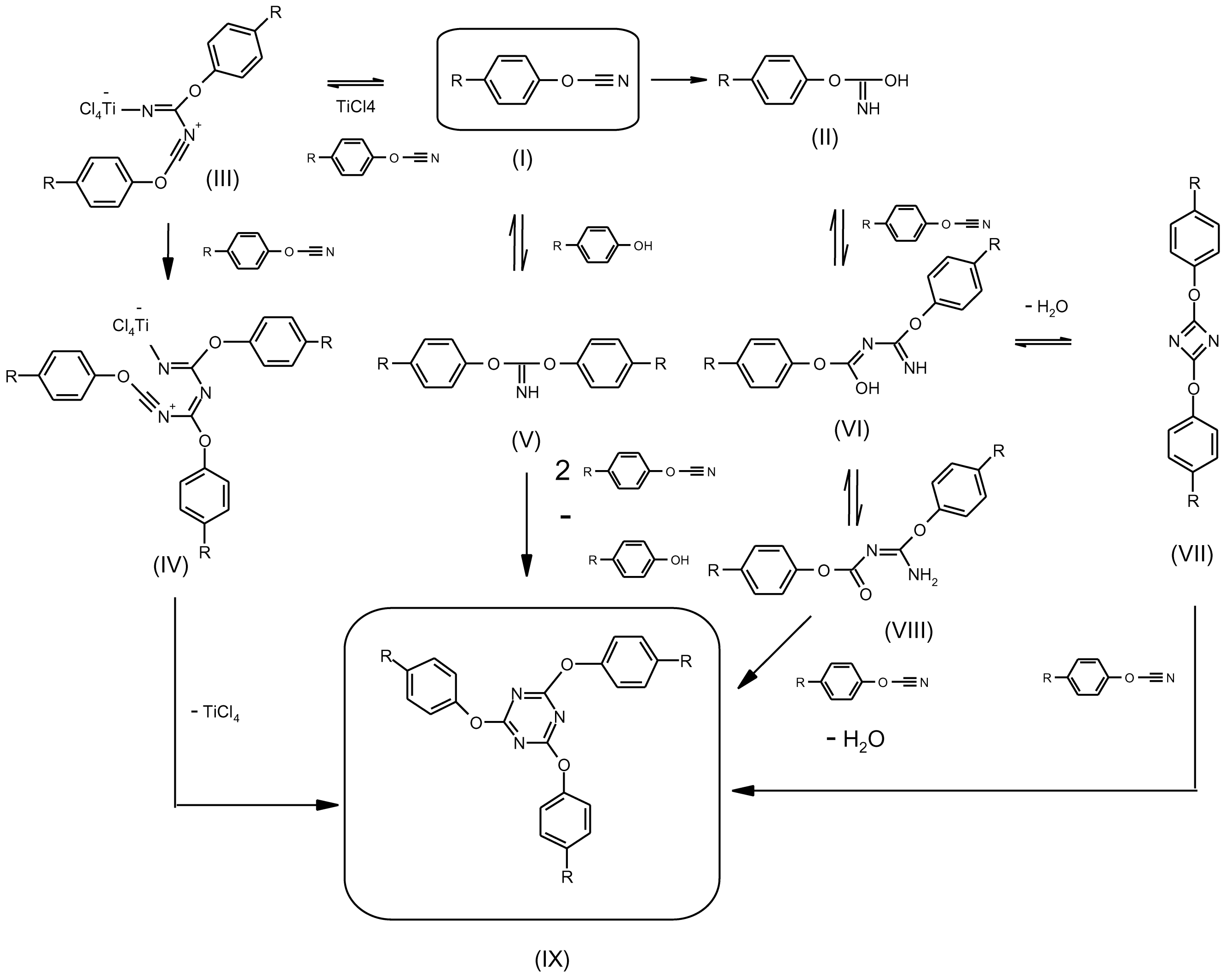
3. Results and discussion

3.1. The cyclotrimerisation reaction of cyanate monomers

The polymerisation of multi-functional cyanate monomers (structure I, Scheme 1) is generally accepted to proceed predominantly via a step growth, addition cyclotrimerisation mechanism to form a thermoset network comprising *s*-triazine rings linked by oxygen bridges (forming a polycyanurate, structure IX in Scheme 1). A range of catalyst packages may be used to effect cure and these generally comprise a transition metal carboxylate or chelate and an alkyl phenol [4]. Together with an appropriate stimulus (e.g. heat or UV radiation in the presence of a suitable initiator [5]) the reaction is generally high efficiency and achieves a high degree of conversion, although it is now recognised that the earlier claims for the exclusive formation of cyanurate rings [6] were somewhat optimistic. Indeed, despite the many studies conducted in recent years to examine the polymerisation of cyanates there is still debate about the exact nature of the polymerization mechanism. Many routes have been proposed to acknowledge the effects of different catalysts and reaction intermediates.

Furthermore, some of the characteristics of the ensuing polycyanurate networks are somewhat unexpected. For instance, there has been considerable discussion concerning the gelation behaviour, or more precisely the degree of conversion at which gelation occurs. Several studies have found that the growth of the polymer network deviates from the expected random branching behaviour. According to the mean field theory, developed by Flory [7] and Stockmayer [8], for a difunctional monomer, with groups of equal reactivity, the theory would predict that gelation should occur at a conversion of 0.50, but gel conversions of between 0.60 and 0.64 have been found for polycyanurates. It has been proposed that the reaction becomes diffusion controlled before gelation and there is some support for this point of view [9–11]. Bauer and Bauer [12] have already made the point that exact knowledge of the position of the gel point is important, as the critical conversion at the gelation threshold is very sensitive to violations of the assumptions made for the meanfield approximation (e.g. substitution effects, intramolecular cyclization or diffusional hindrance).

Kasehagen and Macosko have written a particularly good, concise account [13] of this aspect of the cyclotrimerisation reaction. They conclude that side reactions are responsible for the observed deviations from prediction (i.e. those species mentioned above that contribute to a reduction in the degree of network formation and which might account for the observation of delayed gelation behaviour, e.g. the formation of phenol-substituted cyanurates [14] and bicyclophane cages (II, Scheme 2) [15]. For this reason, the atmosphere in which the cyanate is polymerised (i.e. whether air or perhaps nitrogen) has also been observed to



Scheme 1. Various independently proposed polymerization mechanisms for cyclotrimerisation, R = alkyl or aryl residue, e.g. NCO-ph-$(CH_3)_2C$ for AroCy B10.

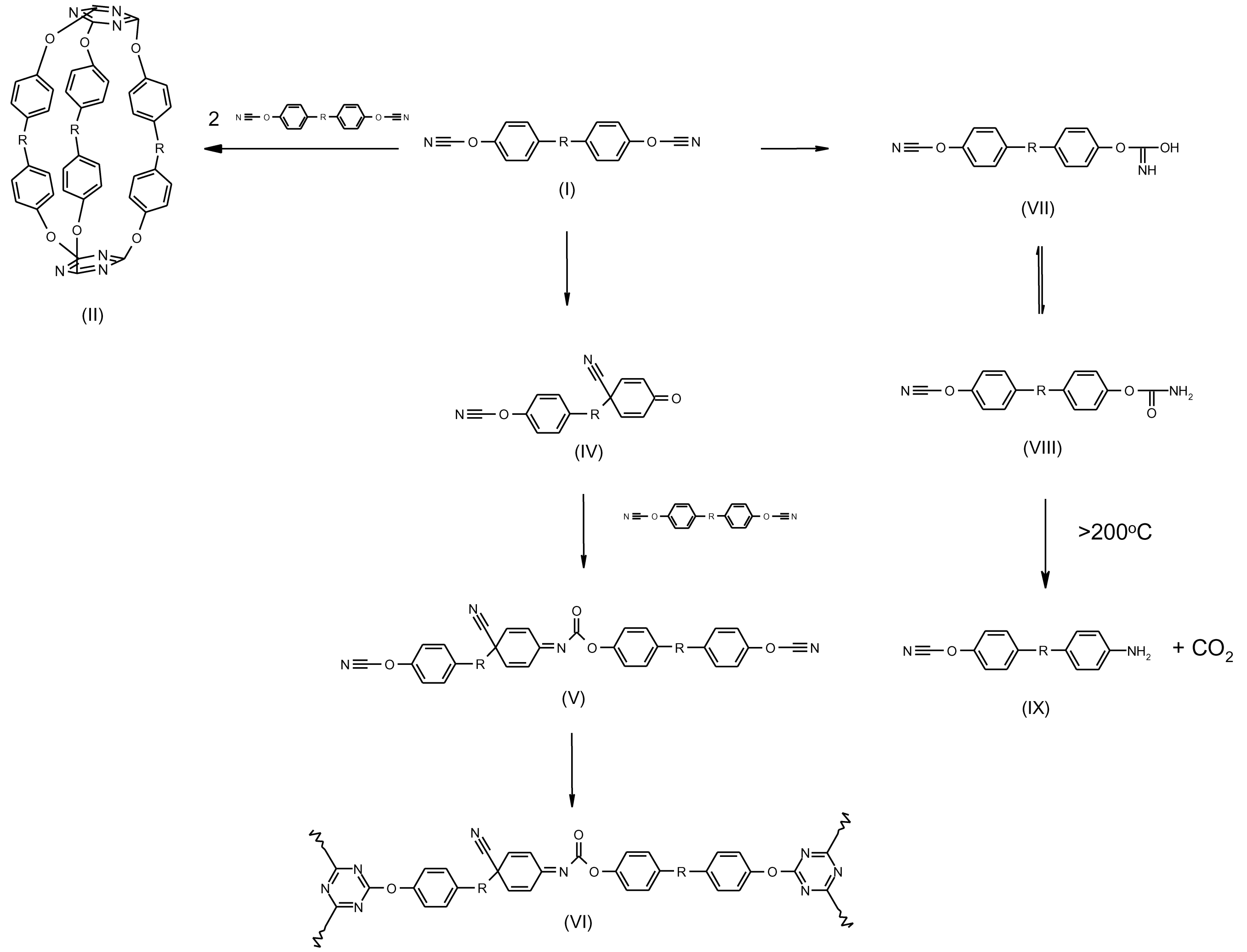
have an effect on the nature of the side reactions and, hence, on gelation behaviour.

3.2. General background to previous kinetic studies of the cyclotrimerisation reaction of cyanate monomers

The kinetics of the 'uncatalysed' polymerisation of cyanate monomers has been reported [9] to follow a second order autocatalytic model, although in some cases both catalysed and uncatalysed systems have been found to conform to an *n*th order reaction model [16–20]. One published exception to this general statement involves the polymerisation of a cyanate monomer comprising a flexible backbone based on phenylene sebacate [21]. In this case, the first order reaction was observed to undergo gelation at the theoretical value (0.50) with an overall activation energy of 21.8 kcal mol^{-1} (91.2 kJ mol^{-1}), the latter remaining practically constant for an apparent conversion range of 0.30–0.70. The apparent absence of autocatalysis was attributed to self-catalysis by the ester groups in the backbone.

In fact, given the extreme sensitivity of the cyanate group to catalysis by a range of different species, including protic acids, Lewis acids and bases, metallic species and atmospheric moisture [22], the notion of a truly uncatalysed reaction is somewhat academic; highly purified cyanates have been reported to be relatively unreactive to cyclotrimerisation [12]. As a result, the autocatalysis reaction can be neglected when considering catalysed systems (as are under study here) and the reaction is traditionally considered to follow a classical *n*th order model. Fig. 1 shows the effect of catalysis on the thermal behaviour of both dicyanate monomers studied in the current work.

It is clearly evident that the addition of the catalyst not only reduces the temperature regime in which polymerisation occurs, but also alters the profile of the exothermic peak recorded for the polymerisation. In the case of 2,2-*bis*(4-cyanatophenyl)propane (**1**) the catalysed mixture



Scheme 2. Various side reactions and byproducts that have been proposed to occur during cyclotrimerisation.

displays a ‘shoulder’ at lower temperature and is consistent with observations made on this (and other dicyanates) [20, 23]. In the analysis of *bis*-4-(4-cyanatophenoxy)phenyl sulphone (**2**), the effect of catalysis is to make the exothermic peak markedly less broad.

In order to simplify the study and focus on the numerical analysis, we have concentrated on using a single co-catalyst package (aluminium(III) acetylacetonate:dodecylphenol:dicyanate monomer in the molar ratio of 1:25:1000), although this does limit the extent to which these findings (in absolute terms) may be compared with other studies, using other catalysts. It is well known that the catalyst employed (i.e. the nature and oxidation state of the metal and the concentration) may have a significant effect on the kinetics of the polymerisation process, but reported studies often neglect to make comparisons of data obtained from thermal analyses performed under similar catalytic conditions. Both Nair et al. [24] and Hamerton and Takeda [25] have reported the effects of changing carefully monitored catalyst concentrations on the thermal behaviour of cyanate monomers and blends, but importantly making direct comparisons only between similar catalyst packages. Nair et al. [24] found a linear relationship between the activation energy with gel time at a fixed cure temperature for *bis*-(4-cyanatophenyl)propane cured with different catalyst systems. Although their data did not cover aluminium-catalysed formulations (used in this study), the activation energy (prior to gelation) for the system comprising e.g. zinc was ca. 150 kJ mol^{-1} (compared with ca. 173 kJ mol^{-1} for the system containing no added catalyst). Furthermore, Bauer et al. [26] have found that the use of catalysed formulations occasionally promote the formation of byproducts during cyanate cyclotrimerization (structures IV, V and VI in Scheme 2). The latter give rise to characteristic bands in the infrared at 2215 cm^{-1} and which persist even at high degrees of cyanate conversion. However, careful analysis of the cyanato/nitrile region of the infrared spectra of *bis*-4-(4-cyanatophenoxy)phenyl sulphone and its homopolymer yielded no evidence of structure VI following polymerization (Fig. 2) and it is not considered that this aspect was significant in this particular study.

Bauer and Bauer have reviewed the range of Arrhenius

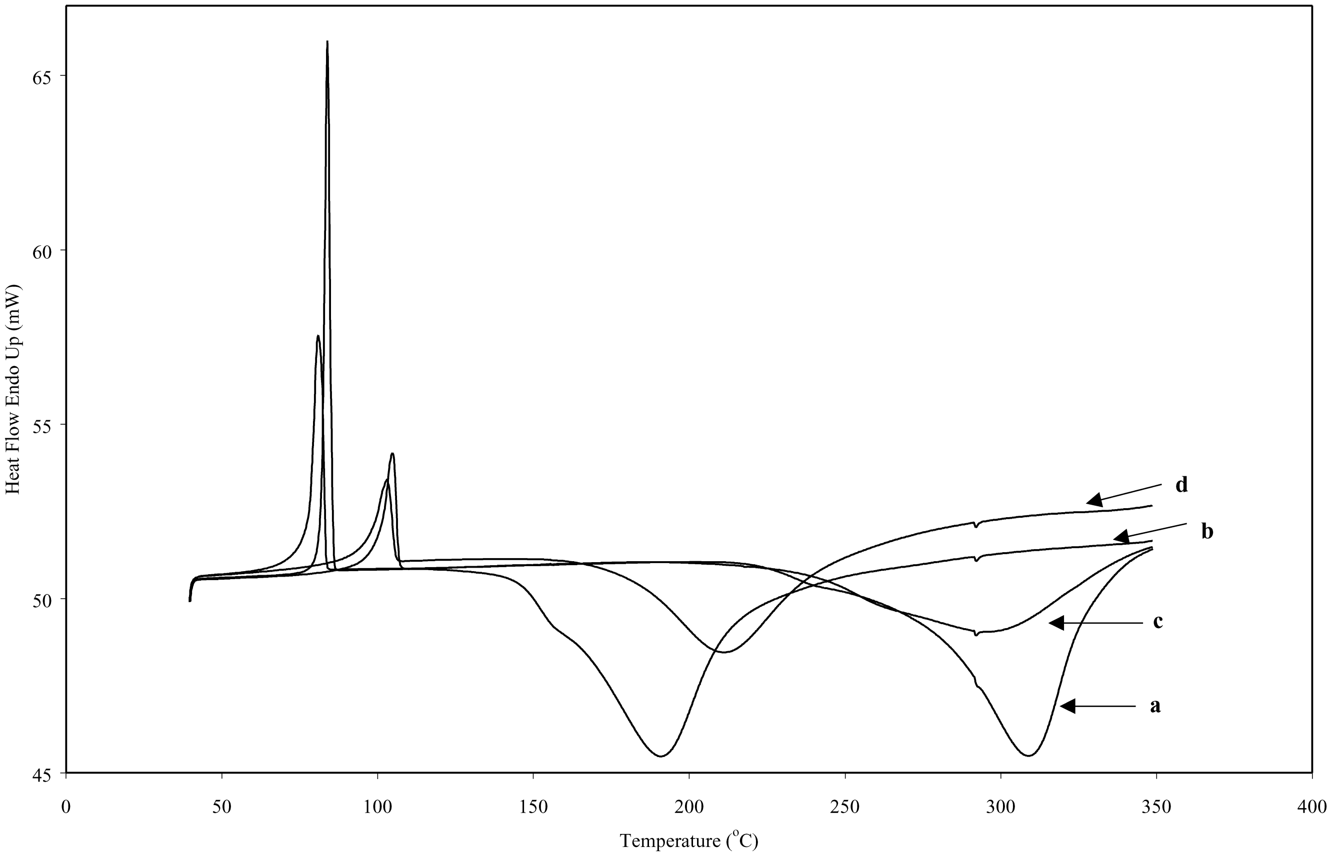


Fig. 1. DSC thermograms (10 K $\min^{-1}$) of (a) uncatalysed 2,2-*bis*(4-cyanatophenyl)propane, (b) catalysed 2,2-*bis*(4-cyanatophenyl)propane, (c) uncatalysed *bis*-4-(4-cyanatophenoxy)phenyl sulphone, (d) catalysed *bis*-4-(4-cyanatophenoxy)phenyl sulphone.

parameters reported in the literature for the catalysed (and uncatalysed) polymerisation process and summarised these in the following way [12]. The exothermic reaction of cyanate groups into cyanurates (homopolycyclotrimerisation) is almost completely selective with an enthalpic effect of ΔH ca. $-105\,\mathrm{kJ\,mol^{-1}}$ per OCN group; nearly full conversion of the functional groups can be achieved when working at sufficiently high temperatures; a catalytically active species is formed during the process that gives the reaction an autocatalytic character (with the exception noted above); the reaction rate is very sensitive to small impurities of the monomer or the added catalyst; and the overall kinetics can be described by simple equations regardless of the catalyst.

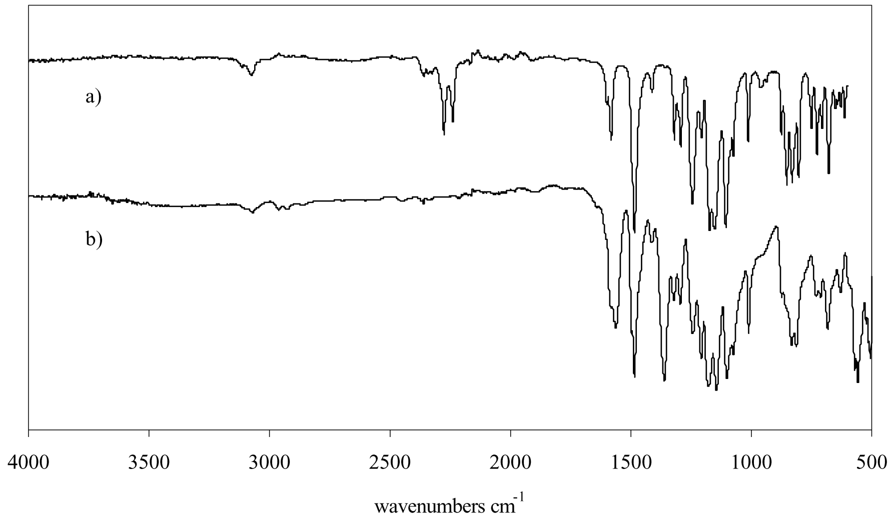


Fig. 2. Transmission FTIR spectra of (a) *bis*-4-(4-cyanatophenoxy)phenyl sulphone and (b) its homopolymer following Al(III)acac catalysed polymerization.

Simon and Gilham [27,28] have presented a kinetic scheme (Eq. (1)) for the uncatalysed polymerisation based on that originally reported by Bauer et al. [29], incorporating two terms which represent two parallel, competing second order reactions

$$d\alpha/dt = k_1(1-\alpha)^2 + k_2\alpha(1-\alpha)^2 \tag{1}$$

where α is the conversion of the cyanate groups and k_1 and k_2 are the rate constants for second order reactions, one of which, k_2, is autocatalytic towards the cyanate. It has been noted [12] that k_1 and k_2 are not pure rate constants, but incorporate the effects of impurities and catalytic active species. Consequently, the activation energies determined using this method are influenced by the same species. Values of 35 and 42 kJ mol^{-1} (from Ref. [30]), 44 kJ mol^{-1} (for k_1) and 88 and 89 kJ mol^{-1} (from Refs. [27,28]), 134 kJ mol^{-1} (from Ref. [27]), and 120 kJ mol^{-1} (from Ref. [28]) (for k_2) have been reported using this method.

3.3. Use of a traditional method to determine the kinetics of the catalysed thermal polymerization of the dicyanate monomer blends in the current work

The thermal characterization of the monomers and blends using DSC was initially reported in a previous paper [3], but the raw DSC data are presented in Table 1 to allow a direct comparison to be made with the kinetic treatment of the data.

Heat flow and temperature data were obtained through the DSC exothermic reaction peaks at a variety of heating rates. The data were initially analyzed using a traditional approach using the simple *n*th-order kinetic model shown in equation [2,31]

$$\ln(r) - n\ln(1-\alpha) = \ln(A) - \Delta E/RT \tag{2}$$

where r is the rate of conversion ($d\alpha/dt$), n is the order of reaction, α is the fractional conversion, A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant and T is the absolute temperature. Bauer and Bauer have already stated [12] that a simple *n*th order kinetic scheme can yield a satisfactory description of the kinetics, provided that the reaction temperature or the catalyst concentration are sufficiently high to allow the behaviour during the initial phase of the reaction can be neglected.

Consequently, a plot of the left-hand side of Eq. (2) against $10^3/T$ for the correct value of n should be linear if the data are well fitted to the model. The best fit values of $\ln A$ and E may be found from the intercept and slope, respectively, obtained by a linear regression analysis. The analyses were carried out predominantly over the 0.05–0.95 conversion range and the data are displayed for monomer (**2**) (Fig. 3) for three integer values of the reaction order n : 1, 2 and 3.

It can be seen from the plots that these data are best fitted by a second order ($n = 2$) model. However, it is also apparent that the data begin to diverge from linearity outside the analysis range, indicating that there is an apparent change in reaction order at these points. The kinetic analyses (using Eq. (2)) for the remaining binary blends are shown in Table 2.

Despite the fact that these figures compare favourably with the published data using a similar approach, they do not represent the entire process and are hence average values.

The obvious limitation with this approach is that it presupposes that the order of reaction is known (and is an integer value) and does not vary throughout the polymerisation process. Considering the foregoing discussion of the cyclotrimerisation process, this is clearly not realistic for such a complex series of reactions involving different intermediates. Other studies have attempted to apply e.g. the Coats-Redfern [32] or related equations to different sectors of the DSC thermogram to yield cure kinetics either prior to or after gelation [24].

3.4. Use of an improved method to determine the kinetics of the catalysed thermal polymerization of the dicyanate monomer blends in the current work

In this paper we have taken another approach to determining the kinetics of the polymerisation process(es). The polymer is assumed to consist of a number of reactive species, reacting independently of each other to form a

Table 1

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

Molar ratio (**1**):(**2**)	m.p. (°C)	Cure onset[a] (°C)	Peak max (°C)	$-\Delta H$ polymerization	
				J g^{-1} blend	kJ mol^{-1} OCN
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

(**1**) = 2,2-*bis*(4-cyanatophenyl)propane; (**2**) = *bis*-4-(4-cyanatophenoxy)phenyl sulphone.

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

[b] Two melting transitions were recorded.

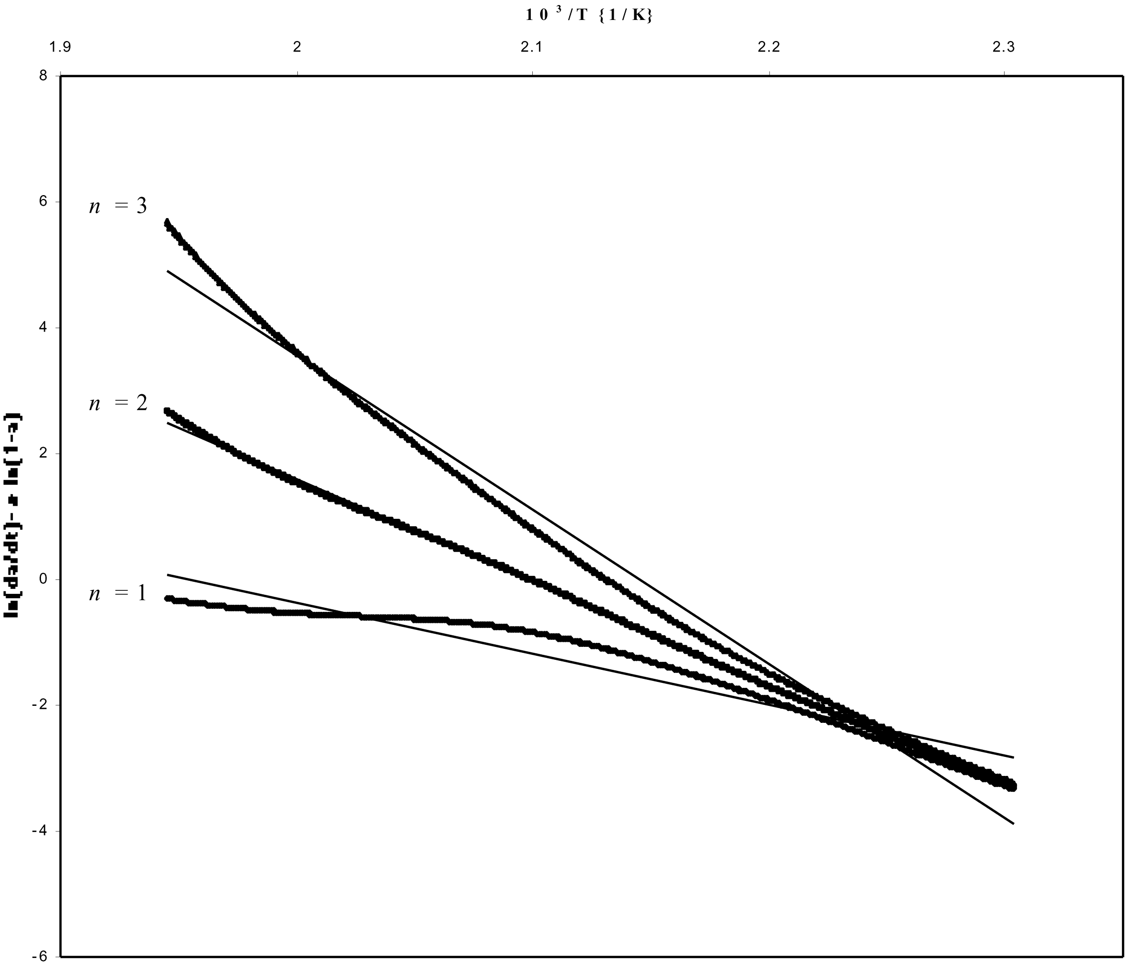


Fig. 3. Plots of $\ln(d\alpha/dt) - n\ln(1-\alpha)$ versus reciprocal absolute temperature for (**2**) over the apparent conversion range $\alpha = 0.05$–0.95 for three fixed reaction orders (n)—fitted data shown as thinner lines.

single product by simple Arrhenius kinetics with activation energies and orders of reactions of $A_1, E_1, n_1, A_2, E_2, n_2$, etc.

We can thus write the kinetic equation for the ith process as:

$$k_i = A_i\,e^{-E_i/RT} \tag{3}$$

where k_i is the rate constant at temperature T and R is the universal gas constant.

The rate of reaction at temperature T is then:

$$\frac{d(\text{reactant}_i)}{dt} = k_i[\text{reactant}_i]^{n_i} \tag{4}$$

Differentiating Eq. (3) with respect to temperature gives:

$$\frac{dk_i}{dT} = \frac{E_i}{RT^2}A_i\,e^{-E_i/RT} = \frac{E_i}{RT^2}k_i \tag{5}$$

and, if we plot extent of reaction against temperature, we can use the relationship $dT/dt = 1$ to solve Eqs. (4) and (5)

Table 2

Summary of DSC kinetic parameters for the dicyanate monomers/blends as a function of heating rate over the apparent conversion $\alpha = 0.05$–0.95 using Eq. (2)

Parameter	Sample blend (**1**):(**2**)				
	100:0	75:25	50:50	25:75	0:100
A	1.59×10^{22}	1.27×10^{18}	1.01×10^{21}	9.73×10^{13}	7.43×10^{14}
E	193	161	187	129	139
n	4	3	3	2	2

(**1**) = 2,2-*bis*(4-cyanatophenyl)propane; (**2**) = *bis*-4-(4-cyanatophenoxy)phenylsulphone; A = pre-exponential factor (s^{-1}); E = activation energy (kJ mol^{-1}); n = reaction order.

simultaneously for any number of concurrent processes, using numerical methods.

The kinetics of the formation of the *bis*-4-(4-cyanatophenoxy)phenyl sulphone homopolymer were fitted with just two processes and the kinetic parameters are given in Table 3 (analysed in duplicate as a function of DSC heating rate). There is good agreement across the range of heating rates and examples of the best fits to the DSC data are also displayed in Fig. 4. The key point to consider is that the quality of the raw thermal analysis data is of paramount importance. This should be self evident, but it is often not common practice to validate the thermal data before analysis (a point which has been made before in connection with DSC analysis (of *bis*-maleimides) [33]). Barton [31] also discusses (and stresses) the importance of selecting/constructing a suitable baseline to allow the quantitative analysis of DSC data to be valid.

In the present work, most of the thermal data yield fairly flat baselines, however there are notable exceptions, particularly when a slower heating rate (e.g. 5 K min^{-1}) is being used or when large changes in heat capacity are observed during the polymerization process. Consequently, the raw DSC data were evaluated using both a linear baseline (selected by eye using the instrumental DSC software package) and also a third order parabolic baseline to enable changes in baseline to be modelled successfully. In the latter case, the analysis was performed twice. Initially, the process was modelled with just one set of Arrhenius parameters which yielded a consistent activation energy of ca. 154 kJ mol^{-1}, but the agreement to the DSC curve was poorer. In the second analysis, two sets of Arrhenius parameters were used and this yielded two distinct processes for the 5 and 20 K min^{-1} data, although the existence of a second peak at 20 K min^{-1} is marginal, but only one at 10 and 15 K min^{-1}. The results of the second data set are given in Table 3. The second peak at 5 K min^{-1} seems to be required to account for the long high temperature tail in the data.

The thermal analysis of monomer (**1**), *bis*-(4-cyanatophenyl)propane, yielded a thermogram with a small shoulder preceding the main exothermic peak (see Fig. 5, which also contains data for the copolymers). The first (near fourth order) process yielded an activation energy of 152 kJ mol^{-1} ($A = 2.56 \times 10^{23}$ s^{-1}), the second reaction ($n = 1.5$) had an activation energy of 238 kJ mol^{-1} ($A = 3.28 \times 10^{27}$ s^{-1}), while the third approximately second order process yielded an activation energy of 362 kJ mol^{-1} ($A = 5.58 \times 10^{43}$ s^{-1}).

Unlike monomer (**1**), the *bis*-4-(4-cyanatophenoxy)phenyl sulphone monomer (**2**) yielded a thermogram with a more Gaussian-shaped exothermic peak with no discernible shoulder. The first (near first order) process yielded an activation energy of 154 kJ mol^{-1} ($A = 3.39 \times 10^{15}$ s^{-1}) and the second (with a similar reaction order) an activation energy of 110 kJ mol^{-1} ($A = 2.35 \times 10^{12}$ s^{-1}).

The polymerisation kinetics of the blends could not be obtained simply by adding together the appropriate number of processes from each of the constituents in the appropriate proportions. Rather, it was necessary to select the minimum number of kinetic parameters to obtain the best fits to the data. The results displayed in Table 4 show only the parameters that contribute to each process, grouped by similarities in activation energy. The binary blends generally show trends in the data that reflect the monomer composition. The addition of 25 mol% of *bis*-4-(4-cyanatophenoxy)phenyl sulphone monomer (**2**) to 2,2-*bis*(4-cyanatophenyl)propane (**1**) yields a blend that displays thermal behaviour that is very similar to a single sample of dicyanate (**1**). In contrast the remaining binary blends (containing 50 and 75 mol% of (**2**), respectively) behave essentially like (**2**), although both require two Arrhenius equations to model the polymerisation. In this respect, the parameters derived from both kinetic methods are broadly in agreement in that the values of reaction order (n) compare well. For instance, the treatment of the thermal data for monomer (**1**) using a traditional approach (Eq. (2)) yields a value of $n = 4$, while the mathematical models yields three process with reaction

Table 3
Summary of DSC kinetic parameters for *bis*-4-(4-cyanatophenoxy)phenylsulphone as a function of heating rate (K min^{-1})

Parameter	Linear baseline				Third order parabolic baseline			
	5	10	15	20	5	10	15	20
A_1	7.38×10^{15}	2.76×10^{14}	1.33×10^{15}	4.83×10^{13}	5.47×10^{15}	1.00×10^{16}	2.10×10^{16}	1.57×10^{15}
E_1	147	132	152	140	154	155	154	154
n_1	2.94	2.03	2.06	1.88	2.81	2.20	1.90	1.90
$^*A_1$					6.64×10^{16}	4.71×10^{16}	3.57×10^{16}	4.28×10^{16}
$^*E_1$					154	148	165	167
$^*n_1$					1.78	2.22	2.08	2.17
$^*A_2$					3.52×10^{3}			2.39×10^{6}
$^*E_2$					49			85
$^*n_2$					1.00			0.61

A_i = pre-exponential factor (s^{-1}) for ith process, E_i = activation energy (kJ mol^{-1}) for ith process, n_i = reaction order for ith process, $*$ = repeat analysis on same data using two sets of Arrhenius parameters.

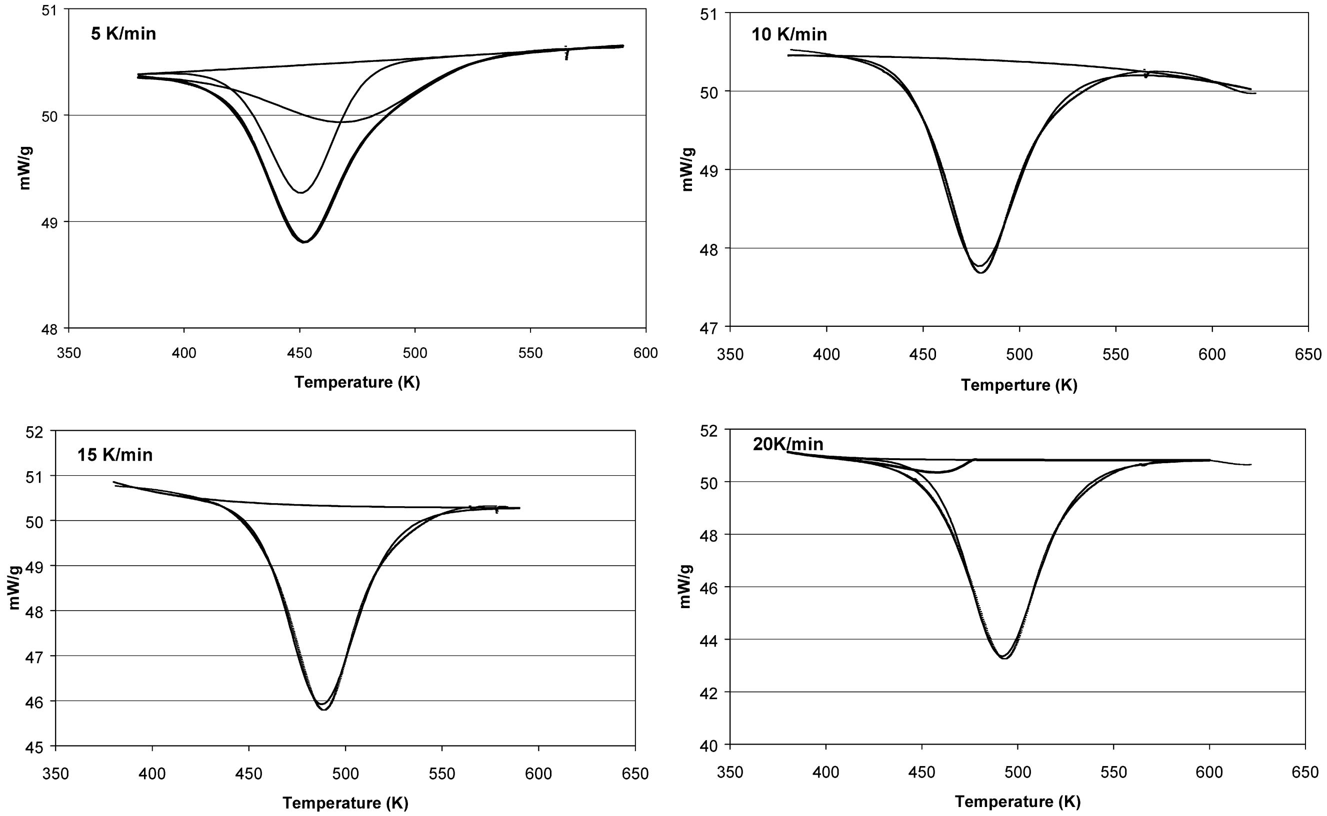


Fig. 4. Plots of DSC thermograms (exothermic heat flow shown downwards) for catalysed *bis*-4-(4-cyanatophenoxy)phenyl sulphone shown at a variety of heating rates. The fitted data are shown superimposed on each of the thermograms.

orders of 1.5, 3.8 and 1.8, respectively. The apparently high order of the process ($n > 3$) models the low temperature shoulder on the DSC curve and the high n value suggests a thermal event that is not necessarily a chemical reaction, but could be related, for instance, to changes in thermal heat capacity of the system in the early stages of polymerization.

3.5. The role of impurities in the cyclotrimerisation process

The presence of a shoulder on the low temperature side of the exothermic peak in the DSC thermogram of the 2,2-*bis*(4-cyanatophenyl)propane monomer (**1**) has already been noted and is consistent with the presence of a catalytic species. Analysis of (**1**) using HPLC revealed that the cyanate (eluting after 3.21 min) contained two 'impurities' (one eluting after 1.19 min, somewhat before the dicyanate and accounting for 3.08% of total; another eluting after 3.69 min and accounting for the remaining 0.46%). It is possible that the latter is due to a higher oligomer, albeit of relatively low molecular weight, since Venditti et al. [34] reported that the higher molecular weight oligomers were insoluble in acetonitrile during HPLC analysis. Spectroscopic analysis did not provide conclusive identification of the species present, but for example the FTIR spectrum of 2,2-*bis*(4-cyanatophenyl)propane (Fig. 6) shows evidence of some moisture (as evidenced by a broad band centred at 3300 cm^{-1} due to O–H stretch and a weak band at 1641 cm^{-1}, possibly due to O–H bend).

There is no conclusive evidence of appreciable amounts of the parent bisphenol (2,2-*bis*(4-hydroxyphenyl)propane, bisphenol A) in the FTIR spectrum and this is supported by the corresponding ^{1}H NMR spectrum (not shown) (in which the aromatic protons are consistent with two 1,4-disubstitued rings, corresponding to the dicyanate (Table 5)—the presence of the parent bisphenol would yield a more complex aromatic region as the deshielding effects of both cyanato and hydroxyl groups differ appreciably).

Furthermore, there is no strong spectral evidence for the presence of diethylcyanamide or bisphenol A dicarbamate. ^{13}C NMR was also undertaken and revealed a very clean spectrum with no detectable impurities using this technique. The chemical shifts (shown in Table 6) are consistent with the proposed structure.

A number of studies, including those of Bauer et al. [29], Simon and Gillham [9], and Grenier-Loustalot et al. [14], have discussed the effect of an active hydrogen donor such as phenol on the polymerisation reaction (see Scheme 1) in introducing a competing mechanism to produce an imidocarbonate (Scheme 1, structure V). This may, in turn, undergo reaction with another cyanate monomer to cyclotrimerise and liberate a bisphenol molecule. The alternative route (reaction of the cyanate group with water to yield an iminocarbonate (II), prior to reaction with two

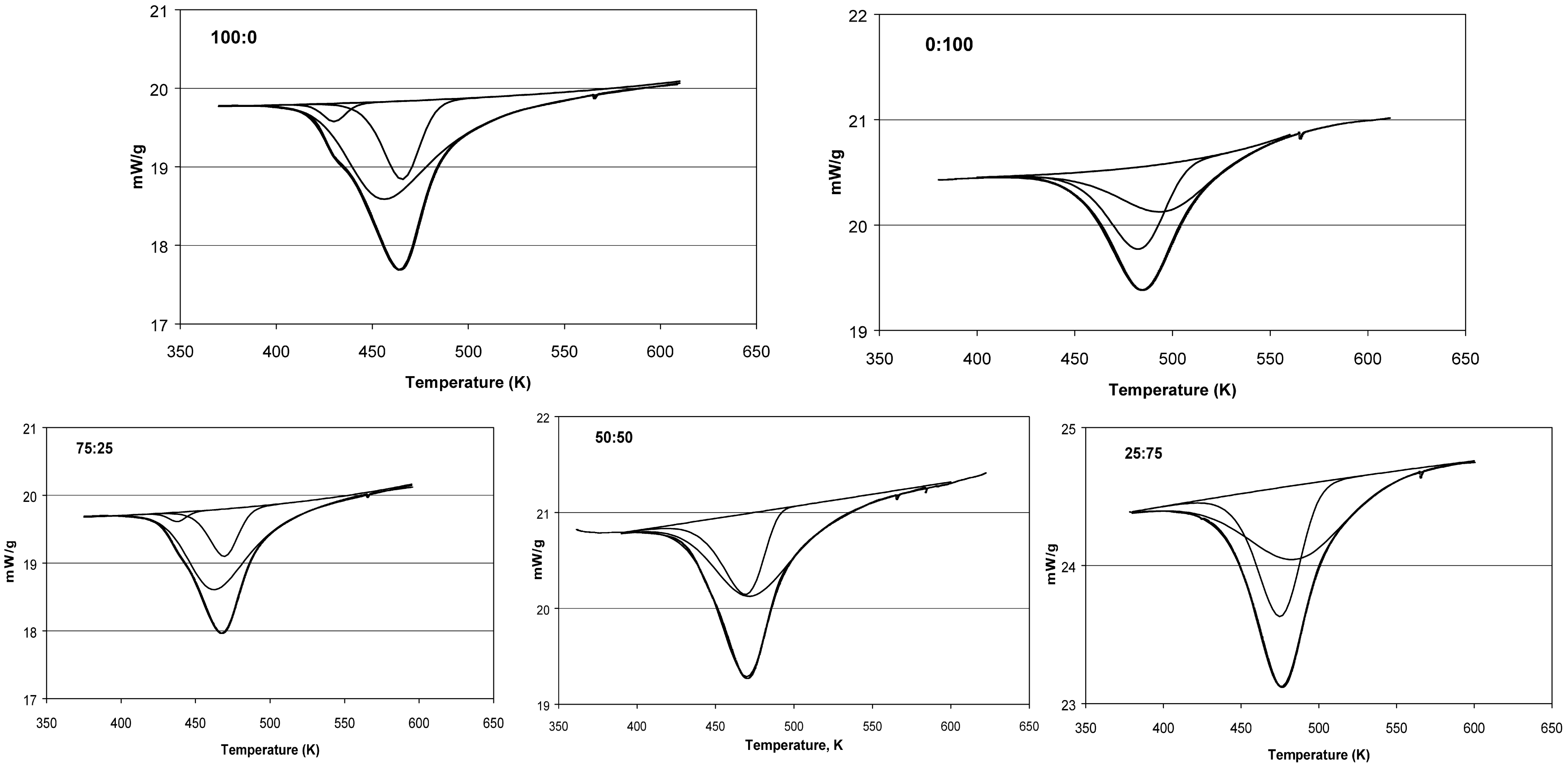


Fig. 5. Plots of DSC thermograms (10 K min^{-1}, exothermic heat flow shown downwards) for catalysed blends containing 2,2-*bis*-(4-cyanatophenyl)propane (**1**) and *bis*-4-(4-cyanatophenoxy)phenyl sulphone (**2**). The fitted data are shown superimposed on each of the thermograms.

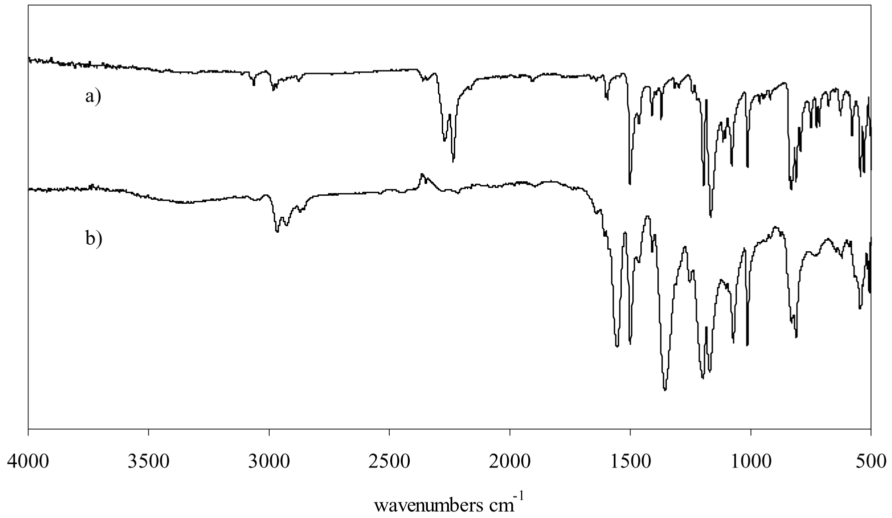


Fig. 6. Transmission FTIR spectra of 2,2-*bis*(4-cyanatophenyl)propane and its homopolymer.

further cyanate groups to effect cyclotrimerisation appears to be more likely in this instance. In contrast, the *bis*-4-(4-cyanatophenoxy)phenyl sulphone monomer (**2**) was found to be significantly more pure by HPLC (98.4%) than dicyanate (**1**) and the NMR evidence support this (Tables 5 and 6).

3.6. Using the improved method to predict the catalysed thermal polymerization of a dicyanate monomer under isothermal conditions

Having obtained dynamic DSC data at a variety of heating rates for the catalysed polymerization of (**2**), it was informative to verify whether these data would yield a reasonable prediction for the isothermal polymerization process (a more realistic representation of the actual cure process that this monomer would experience in use). To this end, a suitable temperature (450 K) was chosen and the data used at each heating rate to predict the fractional conversion of the monomer. These data (Fig. 7) demonstrate that the monomer is predicted to reach a conversion of ca. 90% after a period of 2000 s (ca. 33 min) at this temperature. The corresponding isothermal DSC experiment was carried out to ascertain the verisimilitude of this prediction. Following a 2-h isothermal dwell at 450 K, an enthalpy of 346 J g^{-1} was recorded for the *bis*-4-(4-cyanatophenoxy)phenyl sulphone monomer (Fig. 8a); a rescan experiment on the quenched monomer revealed a residual exotherm of ca. 48 J g^{-1} (Fig. 8b).

The reaction enthalpy for this monomer determined from a dynamic experiment (with a rescan showing no residual exotherm) was 397 J g^{-1}, hence yielding a figure of around 87% for the isothermal experiment; the residual exotherm accounts for a further 12%. While this appears to agree well with the final predicted figure, after a period of 2000 s the isothermal experiment had produced a conversion of 73%. The discrepancy can be accounted for in several ways, but the most obvious is that the model generated from dynamic DSC data agrees closely with the isothermal data up to around

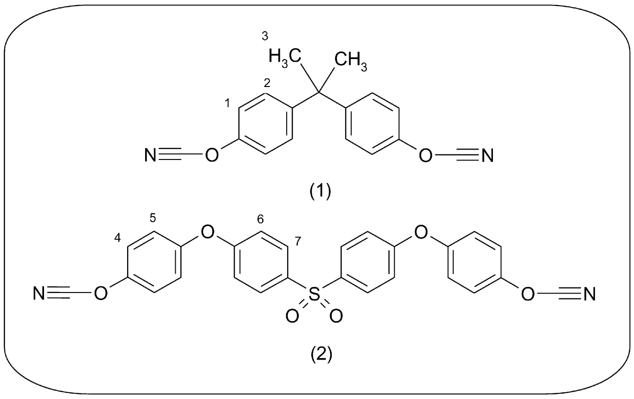
Table 4
Arrhenius parameters for the thermal polymerization of the monomers and blends (using Eqs. (4) and (5) and third order parabolic baseline)

Parameter	Sample blend (**1**):(**2**)				
	100:0	75:25	50:50	25:75	0:100
A_1	2.56×10^{23}				
E_1	152				
n_1	3.8				
A_2	3.28×10^{27}	6.62×10^{24}	5.33×10^{14}	3.31×10^{16}	3.39×10^{15}
E_2	238	187	142	159	154
n_2	1.5	1.9	1.0	1.3	1.2
A_3	5.58×10^{43}	1.74×10^{30}	1.42×10^{11}	3.39×10^{6}	2.35×10^{12}
E_3	362	278	112	72	110
n_3	1.8	3.5	2.5	1.5	1.5

(**1**) = 2,2-*bis*(4-cyanatophenyl)propane; (**2**) = *bis*-4-(4-cyanatophenoxy)phenylsulphone; A_i = pre-exponential factor for the *i*th process (s^{-1}); E_i = activation energy for the *i*th process (kJ mol^{-1}); n_i = reaction order for the *i*th process.

Table 5

^{1}H NMR data for the dicyanate monomers used in this work

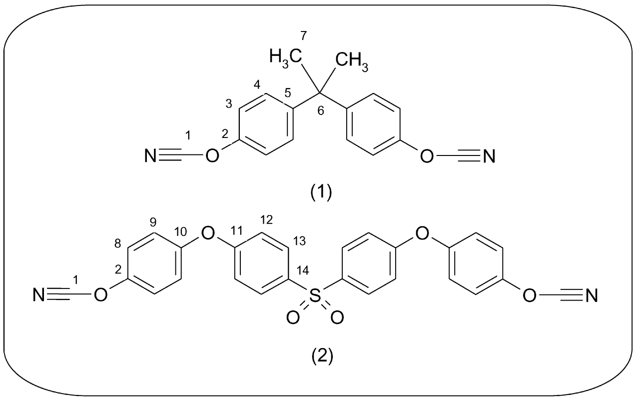


Chemical shift (for sample)		Multiplicity	J (Hz)	Assignment
(**1**)	(**2**)			
–	7.92–7.90	d of d	8.9	H7
–	7.36–6.33	d of d	8.8	H6
–	7.14–7.12	d of d	9.9	H5
–	7.05–7.02	d of d	9.8	H4
7.29–7.26	–	d of d	9.2	H1
7.23–7.20	–	d of d	9.2	H2
1.69	–	singlet	–	H3

d of d = doublet of doublets; J = coupling constant.

Table 6

^{13}C NMR data for the dicyanate monomers used in this work



Chemical shift (for sample)		Assignment
(**1**)	(**2**)	
–	161.28	C11
150.87	153.42	C10
–	149.32	C2
–	136.17	C14
148.71	–	C5
–	130.01	C13
128.70	–	C4
	122.05	C9
114.89	–	C3
–	118.09	C12
–	117.25	C8
108.66	108.69	C1
42.51	–	C6
30.63	–	C7

50% conversion, but does not take into account the effects of vitrification. It is well known that once the T_g of the curing mixture reaches the cure temperature then the polymerization reaction will effectively stop or slow considerably. The rescan data (Fig. 8b) reveal that the partially converted dicyanate has achieved a T_g of ca. 166 °C (439 K) after the isothermal period (compared with a reaction temperature of 450 K). Partridge et al. [35] used an empirical fit to model the isothermal cure of a commercial epoxy resin (RTM 6) used for resin transfer moulding. They used a non-linear least squares regression analysis method (based on Marquardt's algorithm) to fit the DSC reaction rate data. The Di Benedetto equation was then used to establish the relationship between conversion and glass transition temperature in order to model the latter (diffusion controlled) part of the reaction. Further work would be required to modify this preliminary model to account for changes in the viscosity as the kinetically controlled reaction gives way to a diffusion controlled one at higher conversions and future work will investigate whether this approach can be incorporated into the present model.

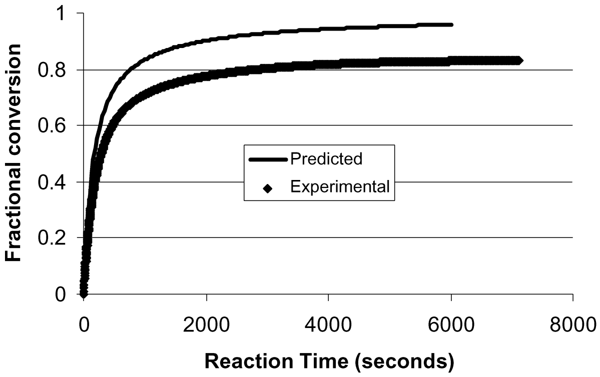
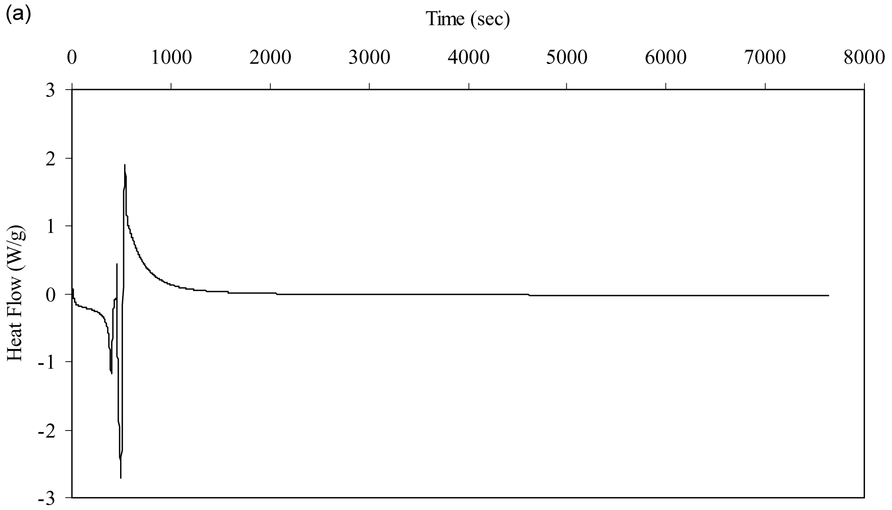


Fig. 7. Polymerization of *bis*-4-(4-cyanatophenoxy)phenyl sulphone (**2**) to its corresponding homopolymer at 450 K showing empirical isothermal data and modelled dynamic DSC data for the catalysed monomer.

Furthermore, it should be borne in mind that DSC data must be treated with some caution—isothermal experiments are notoriously difficult to analyse quantitatively if the monomer is undergoing reaction either near or within the initial set up temperature. This serves to truncate the beginning of the peak and yield a lower total exotherm—and hence a lower fractional conversion when compared with a dynamic experiment (in which the limits of the reaction exotherm can be more readily determined). The reproducibility of the technique also limits the accuracy of the prediction. Nevertheless, this approach yields reasonable agreement in this case.

It is extremely important to maximise the degree of



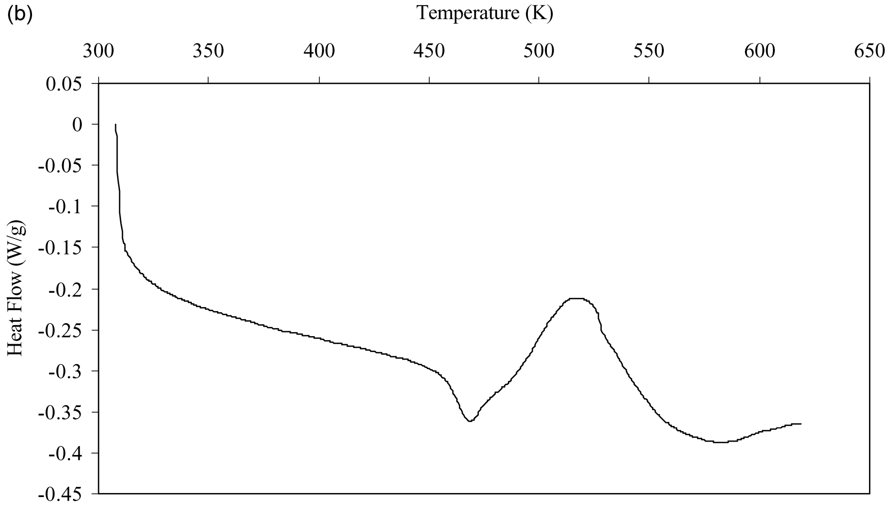


Fig. 8. (a) Isothermal DSC data acquired at 450 K for the polymerization of *bis*-4-(4-cyanatophenoxy)phenyl sulphone (**2**); (b) a dynamic DSC rescan on the same material following a quench after two hours at 450 K.

conversion to polycyanurate since the (well-documented) conversion of sterically isolated, unreacted cyanate groups (in the gelled network) to form carbamate [36]. The latter undergo decarboxylation at temperatures above 200 °C, leading to potentially catastrophic blistering the polymer composites. Naturally, in designing an appropriate cure schedule for such a monomer, an additional higher temperature post cure step would be introduced to enable the reaction temperature to exceed the T_g of the vitrified reaction mixture, increase molecular mobility and encourage further reaction to take place.

4. Conclusions

It has been possible to apply successfully a kinetic treatment, using numerical methods to analyse differential equations of reaction to data obtained from DSC on dicyanate monomers and blends and obtain Arrhenius parameters for the polymerization processes that are in agreement with published literature. The thermal polymerization of the *bis*-4-(4-cyanatophenoxy)phenyl sulphone monomer (nominally 98.4% pure) is well fitted by the model incorporating two equations, whereas the 2,2-*bis*(4-cyanatophenyl)propane monomer (nominally 96.5% pure) requires three equations to do so adequately and yields higher values of the reaction order as a result. The total kinetics of the blends show characteristics of the constituent parts, allowing trends in reactivity to be related to blend composition and purity. An isothermal polymerization reaction profile, generated using modelled dynamic DSC data predicts that the *bis*-4-(4-cyanatophenoxy)phenyl sulphone monomer should reach a conversion of 90% after a period of 33 min at 450 K. An isothermal experiment under these conditions yielded a conversion of 73% after this period of time (but a conversion of 87% after ca. 2 h at 450 K).

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Further Reading

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