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Studies on a dicyanate containing four phenylene rings and polycyanurate copolymers. 3. Application of mathematical models to determine the kinetics of the thermal degradation processes

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

[a]*Chemistry Division School of Biomedical and Molecular 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 copolymers of bis-4-(4-cyanatophenoxy)phenyl sulphone with a commercial dicyanate, 2,2-bis(4-cyanatophenyl)propane are analysed using thermogravimetry to examine the processes of thermal degradation. Kinetic treatment of the data from these thermal analyses yields three Arrhenius equations for each monomer individually. The kinetics are consistent with a three-stage degradation mechanism, but the total kinetics of the copolymers cannot be derived simply from the sum of the constituent parts added together in proportion to their concentration. Each copolymer reacts slightly differently and must therefore be treated individually.

Keywords: Cyanate esters; Copolymers; Degradation kinetics

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 undergo cure via the formation of cyanurate rings (*sym*-triazine rings linked by aryl ether linkages to a polymer, correctly termed a polycyanurate) involving a step growth addition mechanism (the polymer network is depicted in Scheme 1). A range of catalyst packages may be used to effect cure, but these generally comprise a transition metal carboxylate or chelate and an alkyl phenol.

The 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 $G_{IC} = 140\ \mathrm{J\ m^{-2}}$ for cured AroCy B-10 although this can be raised significantly to $500\ \mathrm{J\ m^{-2}}$ by blending with engineering thermoplastics, such as poly(arylene ether sulphone) [1]) and good hot/wet performance and low moisture absorption (polycyanurates typically gain less than 3 wt% in short-medium term conditioning studies). Cyanate esters are generally termed as high temperature/high performance polymers, although the thermal stability, of most cured commercial dicyanate monomers, places them intermediate between epoxies (with somewhat poorer hot/wet performance) and polyimides (both pyromelitimides and addition polyimides). Cyanate esters have been examined as potential candidates for ultra-high thermal performance (i.e. possessing medium-long term stability at temperatures in excess of 300 °C) by the introduction of heteroatoms such as silicon [2], boron [3] and phosphorus [4,5], but to date these monomers have not found widespread application in the market place.

The combination of 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 an attractive competitor for epoxy resins and polyimides in many technological applications including (micro)electronics and aerospace composites. Indeed, the single largest application for polycyanurates is the use as lamination substrates for printed circuits and their assembly via prepreg adhesives into high-density, high-speed multilayer boards, which are produced commercially for supercomputers, mainframes and high speed workstation mother

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* Corresponding author. Address: Chemistry Division, School of Biomedical and Molecular Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK. Tel.: +44-1483-259587; fax: +44-1483-876851.
E-mail address: i.hamerton@surrey.ac.uk (I. Hamerton).

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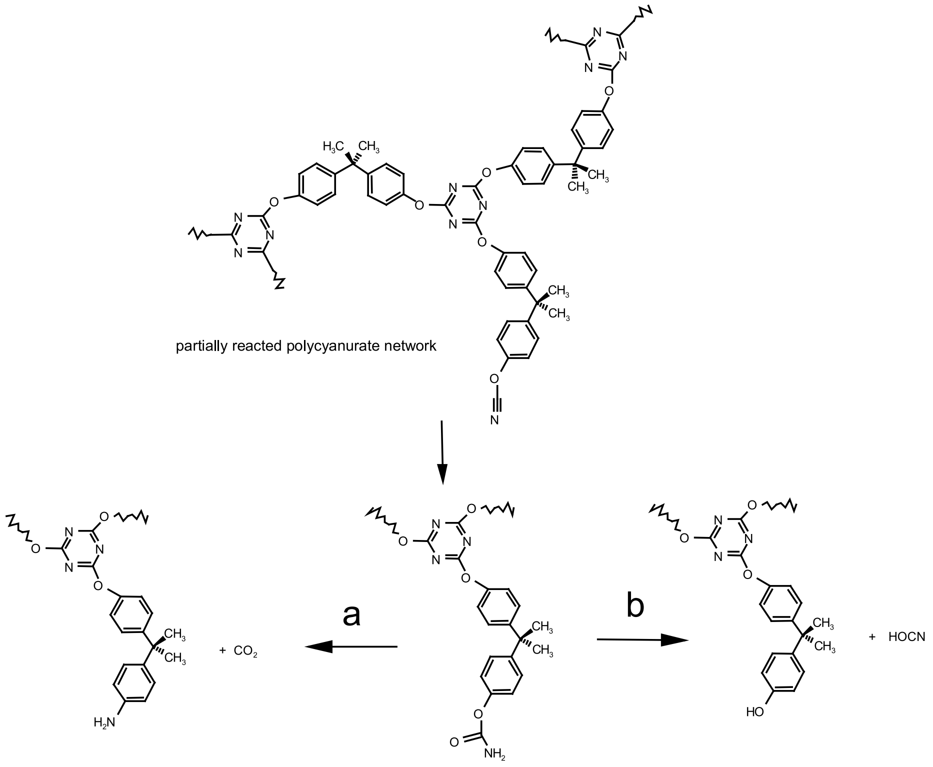

Scheme 1. Two degradation mechanisms proposed for polycyanurates (shown for 2,2-bis(4-cyanatophenyl)propane) (after Refs. [16,17]).

units [6]. In this context the need for high thermal stability (and steam resistance) is of paramount importance when carrying out die attach or soldering operations.

The selection of bis-4-(4-cyanatophenoxy)phenyl sulphone for incorporation in commercial dicyanate copolymers was based on previous molecular simulation work [7–10] that examined the inherent flexibility of similar structures in thermoplastic poly(arylene ether sulphone)s. In a previous paper we demonstrated the benefits of blending these two co-reactive monomers in terms of thermomechanical properties (as evidenced by increases in thermal stability and glass transition temperature and reductions in thermal expansion behaviour). In this paper we examine the application of different mathematical models to elucidate the kinetics of the thermal degradation of the cured polymers. The data will be discussed in the context of mechanisms proposed for these processes.

2. Experimental

2.1. Materials

The dicyanate, 2,2-bis(4-cyanatophenyl)propane (available commercially as AroCy B-10) (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 (2) and the blending of the comonomer and catalysts are reported elsewhere [11]. The co-catalyst package comprised aluminium(III) acetylacetonate: dodecylphenol: monomer in the molar ratio of 1:25:1000 throughout the study.

2.2. Apparatus

Thermogravimetry (TG) was performed using a ULVAC Sinku-Riko differential thermogravimetric analyzer TGD 7000 on ground, cured samples (ca. 8.7 ± 0.5 mg) at heating rates of 5, 10, 15 and 20 K min^{-1} between 25 and 800 °C. Measurements were made under N_2 (20 $\mathrm{cm}^3\ \mathrm{min}^{-1}$) using a platinum boat. The kinetic equations were solved by numerical methods using a commercial software package (ModelMaker v3.0.4 from Cherwell Electronics).

3. Results and discussion

3.1. Mechanisms of degradation of the cured dicyanate homopolymers

The form of TG plot shown in Fig. 1 below is typical for polycyanurates and has been observed for poly(2,2-bis-(4-cyanatophenyl)propane) [12,13]. It may be generally described as multi-stage decomposition yielding unstable intermediates [14]. 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

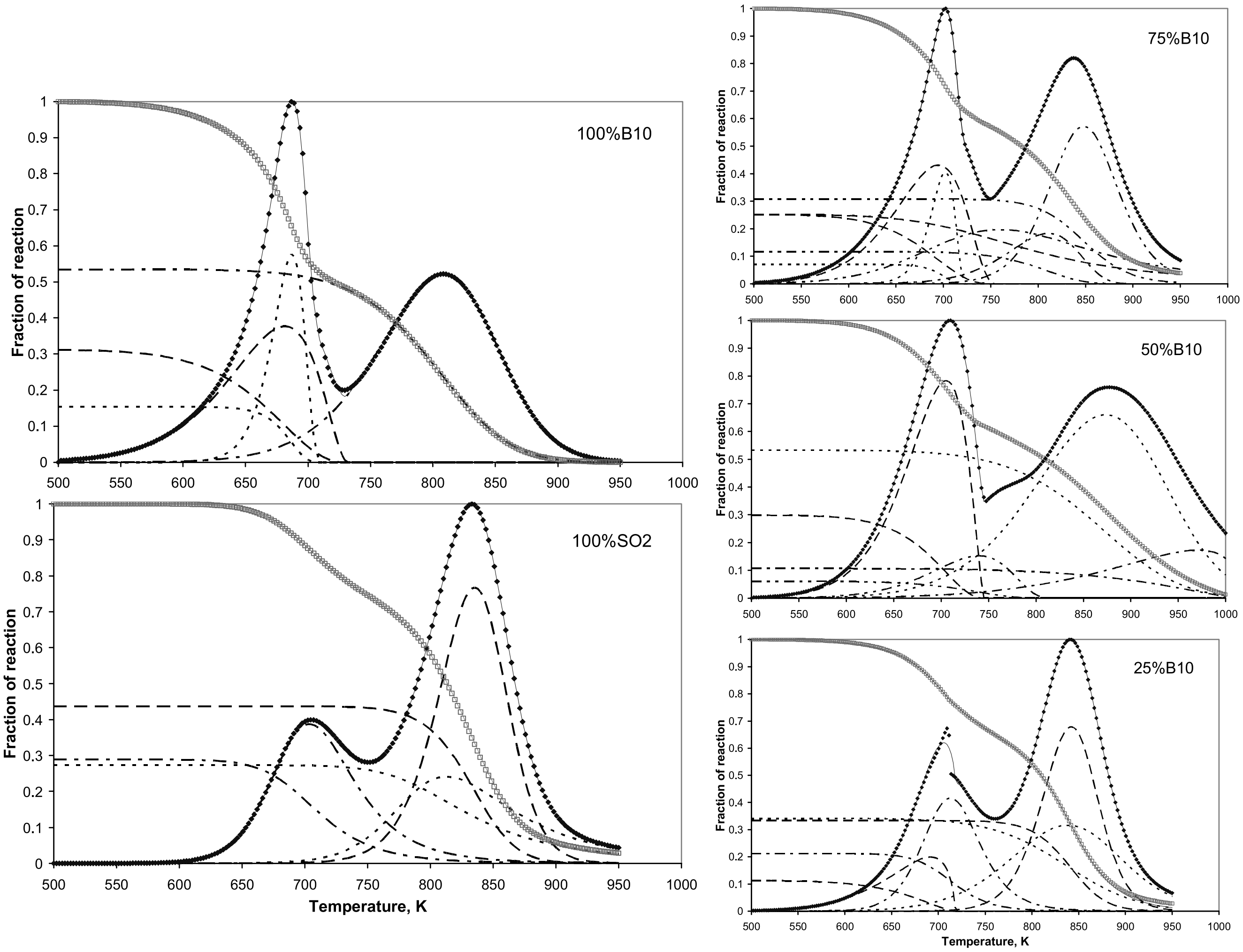

Fig. 1. TG data representing mass loss data, differential plots and derived rate parameters for homopolymers and selected copolymers of 2,2-bis-(4-cyanatophenyl)propane (B10) and bis-4-(4-cyanatophenoxy)phenyl sulphone (SO2). Percentage denotes blend composition (or homopolymer) giving rise to TG data.

temperature regime and gives rise to a larger char yield, as might be expected). Pankratov et al. reported [15] 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 additional degradation mechanisms that are gaining acceptance. Shimp and Ising [16] have suggested that the thermal degradation proceeds with the elimination of carbon dioxide in a decarboxylation mechanism at temperatures above 200 °C (Scheme 1a), whereas Pascault et al. [17] have evidence to support the evolution of cyanic acid as a significant degradation product (Scheme 1b). 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 residual transition metal compounds (used to effect polymerization) serve ultimately to effect the transformation. 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.

Lyon et al. [13] 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 monomer with the major mass loss occurring at ca. 450 °C for all materials. The thermal degradation mechanism was proposed to involve three consecutive processes: (i) random scission and crosslinking of the hydrocarbon backbone between 400–450 °C with negligible mass loss; (ii) decyclization of the triazine ring between 450–500 °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 500–750 °C.

3.2. TG analysis of degradation of the cured dicyanate homopolymers

The TG data (obtained in flowing nitrogen) were initially reported in a previous paper [11] along with a detailed discussion of the effect of varying the monomer composition on the stability of the resulting copolymer. The TG data for the homopolymers (and also selected copolymers) are given in Fig. 1 and Table 1. It should not be inferred that the degradation temperatures quoted in Table 1 have a precision better than ± 1%; the latter is probably closer to ± 10%, given the breadth of the peaks in the raw TG data. It is not our intention to repeat the previous discussion [11], but the thermograms are included for direct comparison with the newly derived kinetic parameters.

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 ca. 400 °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 ca. 640 °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 their data are not directly comparable with those of the present study, McGrath et al. [5] determined the thermo-oxidative stability (i.e. the measurements were undertaken in air) of poly(bis-4-(4-cyanatophenoxy)phenyl sulphone) and found that the polymer had lost 5% of its mass by ca. 448 °C, while no residual mass remained at ca. 750 °C.

The mechanism proposed by Lyon et al. [13] is consistent with our findings for, 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 proposed mechanism (i.e. the commercial cyanate would initially undergo random scission and crosslinking through the alkyl moieties in the backbone, while the sulphone, lacking the alkyl groups, presumably undergoes loss of the SO_2 group). However, in order to gain a fuller understanding of the influence of structure on degradation it is also necessary to determine the kinetics of the process.

3.3. TG analysis of degradation of the cured dicyanate copolymers

The TG data for the copolymers are also depicted in Fig. 1. Even a cursory examination of the TG data (Table 1) 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. An examination of Fig. 1 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.

Within the copolymers the mechanism observed largely reflects its composition (i.e. the copolymer comprising 75% bis-4-(4-cyanatophenoxy)phenyl sulphone 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 comonomer. For instance, the addition of 25% bis-4-(4-hydroxyphenoxy)phenyl sulphone 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 copolymer comprising 25% 2,2-bis-(4-cyanatophenyl)propane compares favourably with the bis-4-(4-hydroxyphenoxy)phenyl sulphone homopolymer.

In order to gain a fuller understanding of the influence of structure on degradation it is also necessary to determine the kinetics of the degradation process and this is dealt with below.

3.4. Traditional kinetic analysis of the thermal degradation of the cured dicyanate homopolymers and copolymers

Nair and Francis [18] and have previously used the Coats–Redfern model to examine the kinetics of the

Table 1
TG data for the thermal degradation (in flowing nitrogen) of cured homopolymers and copolymers

Sample ratio 1:2	Approximate temperature (°C) for a given mass loss (%)									
	5	10	15	20	30	40	50	60	80	100
100:0	344	368	383	394	409	420	450	493	543	625
75:25	355	384	401	413	432	462	509	540	585	680
50:50	359	392	410	422	441	478	532	569	629	712
25:75	374	405	420	430	460	503	531	550	583	628
0:100	402	426	438	451	497	524	540	553	581	699

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

thermal degradation of the homopolymer of 2,2-bis-(4-cyanatophenyl)propane in argon (and also, incidentally, of blends comprising this monomer and a bismaleimide, 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane). Their approach initially required the order of reaction, n, determined by an iterative method (the best fit value for n, was determined using linear regression) in order to derive the kinetic parameters using the Coats–Redfern Eq. (1): [19]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]\frac{E}{RT} \tag{1}$$

Where n is the order of reaction ($n \neq 1,$), α is the fractional conversion (determined from the TG curve for each respective temperature), T is the absolute temperature (K), A is the Arrhenius pre-exponential factor (s^{-1}), R is the gas constant ($8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$), E is the activation energy ($\mathrm{kJ\ mol^{-1}}$) and ϕ is the experimental heating rate ($\mathrm{K\ min^{-1}}$).

In the study by Nair and Francis, the model assumed first order kinetics, since the polycyanurate underwent random decomposition, for which the Coates–Redfern Eq. is (2):

$$\ln\left[\frac{(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]\frac{E}{RT} \tag{2}$$

The data for the degradation of the polycyanurate homopolymer (covering the loss of between 7–39% of the initial mass, presumed to correspond to the degradation of the polycyanurate component) were analysed and found to conform to a linear plot. The 2,2-bis-(4-cyanatophenyl)propane homopolymer was found to yield an activation energy of $260 \pm 1\ \mathrm{kJ\ mol^{-1}}$ and a pre-exponential factor of $6.9 \times 10^{13}\ \mathrm{s^{-1}}$.

Nair et al. [20] have also reported an activation energy of around $91–92\ \mathrm{kJ\ mol^{-1}}$ for the thermal degradation (in nitrogen) of the polycyanurate of 2,2-bis-(4-cyanatophenyl)propane and a significantly lower pre-exponential factor of $2.2–2.6 \times 10^{4}\ \mathrm{s^{-1}}$. Furthermore, a rate constant of $4.9–5.3 \times 10^{-4}\ \mathrm{s^{-1}}$ (at 350 °C) was calculated for the degradation process (similar to that determined for the first study). In this later study, there are two points worthy of note (which may account for the apparent discrepancy in the parameters recorded earlier). In the first instance, the methodology differs in both cases as the earlier study relies on dynamic analysis, while the second is performed under isothermal conditions. Moreover, the mass loss range in the later study corresponds practically to the entire (major) degradation step and, as the α values differ, this leads to different activation parameters being calculated within the Coats–Redfern equation.

3.5. An alternative approach to the kinetic analysis of the thermal degradation of the cured dicyanate homopolymers and copolymers

The obvious limitation with the Coats–Redfern approach is that it presupposes that the order of reaction is known (and is an integer value) and does not vary throughout the degradation process. This is clearly not realistic for such a complex series of reactions and is graphically illustrated in Fig. 2, wherein a series of non-linear plots is presented.

In another publication [21] we have reported the determination of the kinetics of the catalysed thermal polycylotrimerisation of dicyanates by solving the differential equations simultaneously for a number of concurrent processes, using numerical methods. That paper contains a fuller discussion of the process and so the reader is referred to it for more information concerning the basis of the method. Here, we show that the approach is a general one and hence applicable to the thermal degradation process.

Consequently, we have taken another approach to determining the kinetics of the degradation processes directly from the differential equations. In practice, the minimum number of processes required to fit the TG data of the individual polymers turned out to be three (which is in agreement with Lyon et al. [13]) and the kinetic parameters are given in Table 2, wherein the data are tabulated by increasing activation energy down the table, with processes exhibiting similar activation energies grouped together horizontally. Examples of the best fits to the TG raw data are shown in Fig. 1. An independent analysis was undertaken of the effect of heating rate on the derived kinetic parameters. The modelled activation energy increased by ca. 7% with each additional increase of $5\ \mathrm{K\ min^{-1}}$ in heating rate relative to the $5\ \mathrm{K\ min^{-1}}$ data. We are aware that there is a slight increase in activation energy when the heating rate is raised and so we have avoided quoting absolute rate constants (in which case the non-isothermal data would have necessitated the inclusion of conversion (α) versus temperature plots [22]). However, since data (for both homopolymers and copolymers) were

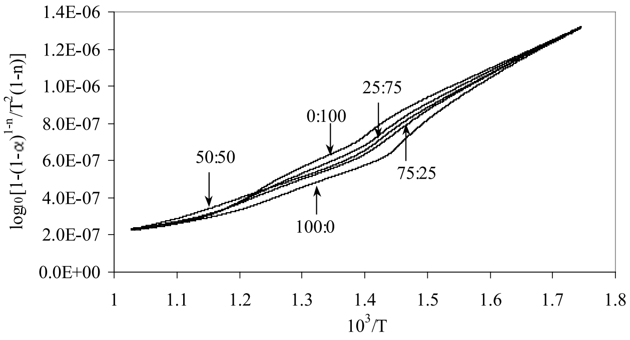

Fig. 2. Plots of $\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ versus reciprocal temperature for fixed reaction order ($n = 2$) over the temperature range 300–700 K for homopolymers and copolymers. Key-molar ratios shown for 2,2-bis(4-cyanatophenyl)propane (1): bis-4-(4-cyanatophenoxy)phenyl sulphone (2).

Table 2
Arrhenius kinetic parameters for the thermal degradation of cured homopolymers and copolymers

Parameter	Sample copolymer 1:2				
	100:0	75:25	50:50	25:75	0:100
A_1	29,940	17,705	6.995	2037	
E_1	82.30	76.30	65.70	73.90	
n_1	0.65	2.47	0.31	0.39	
A_2	13,73,211	432.76	4614	233,594	
E_2	119.90	86.00	91.50	111.00	
n_2	1.20	0.71	1.14	1.41	
A_3	9.06×10^{20}				
E_3	279.3				
n_3	0.84				
A_4		1.75×10^{7}	33392		
E_4		137.90	91.70		
n_4		0.95	0.78		
A_5			215537		
E_5			96.60		
n_5			0.60		
A_6				3.41×10^{13}	1.36×10^{14}
E_6				194.30	197.90
n_6				1.97	2.48
A_7		2.72×10^{12}			1.60×10^{13}
E_7		217.80			208.40
n_7		1.77			3.28
A_8		7.91×10^{19}		1.13×10^{14}	6.84×10^{14}
E_8		286.30		244.80	256.00
n_8		0.78		1.54	1.46

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

acquired at a single heating rate they are directly comparable in order that trends may be discerned.

The TG data of copolymers show characteristics of both constituents, but simply adding together the three processes from each of the constituents in the appropriate proportions did not reproduce exactly the shape of the copolymer curves. In reality, this is not surprising given that the 'blends' are true copolymers with their own reactive characteristics. Each copolymer was therefore treated individually to obtain the best fits to the data with the minimum number of equations, using the equations for the individual components as the starting point for an iterative solution. The results are given in Table 2 and patterns of systematic variation can be clearly seen.

For instance, at the extreme ends of the data set, the polycyanurate of 2,2-bis-(4-cyanatophenyl)propane displays three processes: the first of which (of fractional order 0.65) has a relatively low activation energy (82.3 kJ mol^{-1}) and pre-exponential factor of 29,940 s^{-1}. According to Lyon et al. this arises from the random scission and crosslinking reactions of the aliphatic (isopropylidene) residues, although this appears to be taking place at a slightly lower temperature than that quoted in their study (they stated between 400–450 °C) and, while the mass loss is arguably not 'negligible' (a rather vague term) it does preface a much more significant degradation step. A further point to note is that Lyon et al. carried out their TG analysis under nitrogen flowing at 100 cm^3 min^{-1} (whereas a rate of 20 cm^3 min^{-1} was used in the current study). The higher flow rate will undoubtedly have a greater cooling effect on the furnace temperature and consequently, may cause an apparent elevation of the degradation onset temperature. Furthermore, the samples in the literature study were analysed as neat resin plaques, rather than as powdered polymers, again leading to apparently more stable products.

In contrast with poly(2,2-bis-(4-cyanatophenyl)propane), the polycyanurate of bis-4-(4-cyanatophenoxy)phenyl sulphone displays an initial degradation process (of fractional order 2.48) with an activation energy that is much higher (197.9 kJ mol^{-1}) and significantly larger pre-exponential factor (1.36×10^{14} s^{-1}). As this cannot arise from a reaction of aliphatic components (absent from the monomer) it is presumably associated with the degradation of the (ether or sulphone) bridges, which link the aromatic rings. We did not have access to hyphenated techniques to verify this hypothesis on this occasion, but fortunately a previous study [23] had been undertaken on a polyaspartimide based on bis-(4-maleimidophenyl)methane and a structurally-related diamine, bis-4-(aminophenoxy)phenyl sulphone (i.e. the same monomer structure with the replacement of the cyanate group with an amino group). In this unpublished work the polyaspartimide (ca. 16 mg) was analysed (in nitrogen at 10 K min^{-1}) using a TGA-MS apparatus (comprising a Du Pont 9900 TGA coupled with a VG mass spectrometer). Under these conditions the evolution of SO_2 ($m/z = 64$) fragments commenced at around 358 °C and reached a peak at around 420 °C before beginning to fall off at around 480 °C. Whilst it is dangerous to make too many assumptions in this regard, the data do appear to support the observations made in the present study.

Lyon et al. attribute the second step of their degradation mechanism to the decyclization of the triazine ring (between 450–500 °C). They also detected the liberation of low molecular weight volatile compounds and the formation of a primary solid residue. In this study, we have observed differences in the degradation behaviour of the homopolymers—again the polycyanurate of 2,2-bis-(4-cyanatophenyl)propane yields a lower activation energy (120 kJ mol^{-1}) and pre-exponential factor (1.37×10^6 s^{-1}) for this process than the sulphone with an activation that is almost double ($E = 208.4$ kJ mol^{-1}, $A = 1.60 \times 10^{13}$ s^{-1}).

The final degradation step has been attributed [13] to decomposition of the primary residue. Interestingly, we have found a reversal in the behaviour of the two homopolymers in this temperature range (although this is purely academic since it is not envisaged that these materials would be used at these temperatures, having undergone such a degree of decomposition). We have determined the polycyanurate of 2,2-bis-(4-cyanatophenyl)-propane to yield a marginally higher activation energy ($279.3\ \mathrm{kJ\ mol^{-1}}$) and pre-exponential factor ($9.06 \times 10^{20}\ \mathrm{s^{-1}}$) for this process than the sulphone ($E = 256.4\ \mathrm{kJ\ mol^{-1}},\ A = 6.84 \times 10^{14}\ \mathrm{s^{-1}}$), although the difference is not as marked as in the earlier steps.

4. Conclusions

Application of 'simple' Coates–Redfern equations to the kinetics of degradation of 2,2-bis(4-cyanatophenyl)propane and bis-4-(4-cyanatophenoxy)phenyl sulphone homopolymers and their copolymers shows a multi-stage degradation process in all cases. Application of numerical methods to solve the differential equations of reaction has enabled the degradation processes to be deconvoluted into three processes (or four in the case of the 50:50 copolymer), with realistic Arrhenius parameters, although it is important to note that the quality of data is important to achieve reproducible results. The reaction kinetics can be related to known mechanistic processes, although in the current study (in the absence of a hyphenated spectroscopic technique) the model indicates the number of processes occurring within the degradation, rather than their nature. The kinetics of the copolymers exhibits some of the characteristics of the homopolymers, but the total kinetics can only be fitted by treating each one individually. This confirms that they are true copolymers (rather than interpenetrating networks) with their own characteristics. In a future publication [24] we shall demonstrate that the same approach may be applied more widely with some success to examine the mechanisms associated with the polymerisation and degradation of other, more common, polymeric systems.

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