

# A study of the polymerization of novel cyanate ester/acrylate blends

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## Abstract

Differential scanning calorimetry (DSC) has been employed to measure the thermal properties of two commercial cyanate esters (AroCy L10 and AroCy XU366) before and after blending with several commercial acrylates. DSC analysis of the cyanate homopolymerizations yields values of  $\Delta H$  and apparent conversion in the cyanate and cyanate/acrylate blends which agree well with published data. For catalysed L10 and XU366 polymerizations trends are reported for the onset of polymerizations as a function of metal ion in the catalyst. The relative effects of each acrylate on the cyanate polymerization are considered in terms of the inhibition of the cyanate polymerizations. Thermal data are related to the nature of the polymer networks produced. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Cyanate esters; Acrylates; Compatibility

## 1. Introduction

In the last decade, increasingly ‘high-tech’ applications make ever increasing demands upon candidate materials for use in both terrestrial and extra-terrestrial environments. Cyanate esters form one family of thermosetting resins whose performance characteristics (a combination of high glass transition temperatures, low moisture absorption and low dielectric loss which is superior to many current commercial materials) make them attractive competitors to epoxy and bismaleimide resins [1,2]. Dicyanate monomers are remarkable in that they polymerize via a cyclotrimerization reaction to form a polycyanurate network with a reputedly high degree of efficiency [3]; the use of metallic or amine catalysts has been reported to achieve conversions of greater than 98%. In practice, the most commonly used form of catalyst used for aryl dicyanates, such as those studied here, is the carboxylate or chelate salt of a transition metal ion in the presence of an active hydrogen co-catalyst such as nonylphenol. Despite the importance of the cyanate cyclotrimerization, the mechanism is still the subject of much debate and a number of theories have been put forward to account for the reaction mechanism [4–12]. Whatever the reaction pathway, the transition metal is believed to facilitate the cyclization of the cyanate mono-

mers, while the co-catalyst serves the dual purpose of acting as a solvent for the transition metal catalyst (which is otherwise of low solubility in molten cyanate monomer [13]) and completing ring closure of the triazine ring via hydrogen transfer at higher degrees of conversion when translational mobility of species within the gelling network is greatly reduced [13].

It is generally accepted that the rate of the cyclotrimerization of cyanate monomers is catalyst-dependent. Depending on the type and addition level, the rate of cure of cyanates may be varied over a wide range, for example metal ions such as zinc have been reported to show particularly high catalytic activity due to their low coordination number and high ligand mobility during the cure process [13]. It is also well known [14,15] that the metal ion has a relatively minor effect on the degree of conversion, and that the nonylphenol concentration employed is particularly important in this regard (higher concentrations of ca. 4 parts per hundred parts resin, phr, producing optimal results). From the results of the same study, Shimp and Craig presented a preferred ranking of metal ions ( $\text{Cu}^{2+} = \text{Co}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+}$ ) for incorporation in cyanate/catalyst formulations to minimize moisture plasticization and thermo-oxidative degradation in the cured polycyanurate. To date, however, there have been few rigorous studies of the effect of the nature of the curing agent on the polycyclotrimerization of cyanate monomers. Many published data purporting to show this effect arise from studies whose complexes contain a variety of metal ions

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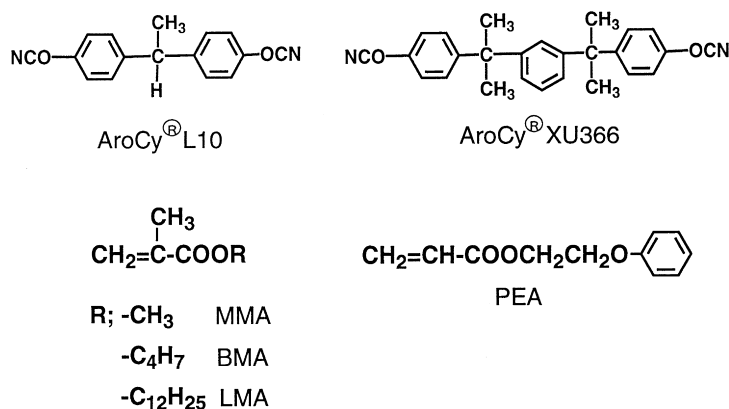


Fig. 1. Structures of the dicyanates and acrylates studied in this work.

(in different oxidation states) or at different levels of incorporation. In all the experiments reported here our data reflect a carefully calculated and controlled catalyst incorporation based on molar concentration, rather than on weight. Consequently, the current study attempts to rationalize the effect of complex ion (and purity) on the polymerization behaviour of cyanate monomers and cyanate/acrylate blends.

Cyanate esters are finding increasing use in the form of blends where their aforementioned inherent low moisture absorption and low dielectric loss properties may be allied to other blend components such as polyimides (e.g. bismaleimides [16]) or epoxy resins [17]. Where an additional component is added it may be to impart greater processability, lower cost, or increased thermo-oxidative resistance. Binary blends of cyanate esters and relatively cheap acrylates are currently eliciting interest in the microelectronics industry, due to the favourable properties of the resulting polymers. These properties include: the ability to prepare solvent-free polymer blends, due to the low viscosity of the acrylate component (this feature is particularly important as it prevents the formation of voids); the reduction of stress in the cured blend in comparison with the cured polycyanurate homopolymers; the enhancement of the polymerization rate, and consequent improvement in blend processability. All of the preceding features lead to improvements in the performance reliability of the resulting products—a key criterion in the selection of materials for this particular application where the operation of microelectronic devices may run into many hours of continuous use.

It is envisaged that careful selection of both acrylate and cyanate (as a blend) may facilitate the formation of either a co-curing (though not, it is believed, a co-reactive) blend or one which undergoes 'sequential' reaction. Both routes might offer interesting processing opportunities in the technological application of these materials in the microelectronics industry. However, little work has been done to examine the possible reaction of cyanate esters and acrylates and the current work reports the thermal and spectroscopic characterization of binary blends.

## 2. Experimental

### 2.1. Equipment

Differential scanning calorimetry (DSC) was performed at a heating rate of 10 K min<sup>-1</sup> using a TA instruments Model 2920 calorimeter. Accurately-weighed samples (of 7.5 ± 2 mg) were analysed in hermetically-sealed aluminium pans under a nitrogen purge (30 cm<sup>3</sup> min<sup>-1</sup>).

### 2.2. Materials

The commercial cyanate esters: 1,1'-bis(4-cyanatophenyl)ethane (AroCy<sup>®</sup>L-10, denoted L10 hereafter) and 1,3-bis(4-cyanatophenyl)-1-(1-methylidene)benzene (AroCy<sup>®</sup>XU-366, denoted XU366) were kindly provided by Ciba-Speciality Chemicals Corporation, Duxford (UK). Fig. 1 details the structures of the monomers studied in this work.

The methacrylates (see Fig. 1): methyl methacrylate, MMA (99%, containing 10 ppm hydroquinone monomethyl ether), *n*-butyl methacrylate, BMA (99%, containing 10 ppm hydroquinone monomethyl ether), and lauryl methacrylate, LMA (96%) were obtained from Aldrich Chemical Co.

2-(Phenoxy)ethyl acrylate, PEA (99.8%, containing 305 ppm hydroquinone monomethyl ether) was supplied by Shin-Nakamura Chemical Co. Ltd., Wakayama (Japan).

The cyanate curing agents: copper(II) acetylacetonate (97%), cobalt(II) acetylacetonate (97%, containing ≤ 3% H<sub>2</sub>O), aluminium(III) acetylacetonate (99%), titanium(IV) oxide acetylacetonate and zinc(II) acetylacetonate hydrate were also obtained from Aldrich Chemical Co.

4-Nonyl phenol (ca. 85% *p*-isomer mixed with branched side chain) was obtained from Fluka Chemie AG, Dorset (UK).

*t*-Butyl peroxybenzoate (Perbutyl Z, PBZ) was supplied by NOF Corporation, Tokyo (Japan).

All reagents were of reagent quality and were used as received without further purification.

Table 1

The compositions of the blends tested in this work. The ratios of cyanate: acetylacetonate and nonylphenol: acetylacetonate were constant for all samples studied (all samples comprised a cyanate:acetylacetonate molar ratio of 1000:1 and a nonylphenol:acetylacetonate molar ratio of 25:1. L10 blends contained 2.09 phr nonylphenol and XU366 blends contained 1.39 phr nonylphenol; acac, acetylacetonate; nonylphenol:acac, nonylphenol:acetylacetonate ratio)

Catalyst	Atomic weight (metal)	Nonylphenol:acac (wt/wt)	Metal concentration (ppm)	
			L10	XU366
Al(acac) <sub>3</sub>	26.98	16.99	102	68
TiO(acac) <sub>4</sub>	47.90	21.02	181	121
Co(acac) <sub>2</sub>	58.93	21.42	223	149
Cu(acac) <sub>2</sub>	63.55	21.05	241	160
Zn(acac) <sub>2</sub> ·H <sub>2</sub> O	65.38	19.56	248	165

### 2.2.1. Blending the materials

**2.2.1.1. Preparation of samples for DSC analysis.** Each blend comprised a complex mixture of monomers and curing agents and consequently the blending procedure involved several steps. Initially, acetylacetonates were dissolved in 4-nonylphenol at a molar ratio of 25:1 (nonylphenol:acetylacetonate) at 80°C for 1 h. Each acetylacetonate/catalyst blend was then mixed with the cyanate monomer at 60°C for 30 min. In each case the molar ratio of cyanate monomer:acetylacetonate was 1000:1. Perbutyl Z (PBZ) (1 mol%) was added to each acrylate at room temperature. Finally, each cyanate monomer (L10 and XU366), already containing acetylacetonate/4-nonylphenol, was mixed separately with the acrylate/PBZ blends. The molar ratios of cyanate:acrylate were 9:1, 1:1, and 1:2 (mol% values are given in Table 1).

## 3. Results and discussion

### 3.1. Calculation of solubility parameters

Initially, an assessment was made of the compatibility of the components within the proposed blends using a calculation (1) reported by Fedors [18] (and based on the Hildebrand solubility parameter,  $\delta$ ) and a series of experimental solubility measurements.

$$\delta = (\Delta E_v/V)^{0.5} \quad (1)$$

where

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

( $\Delta e_i$  and  $\Delta v_i$  are the additive atomic group contributions for the energy of vaporization and molar volume respectively at

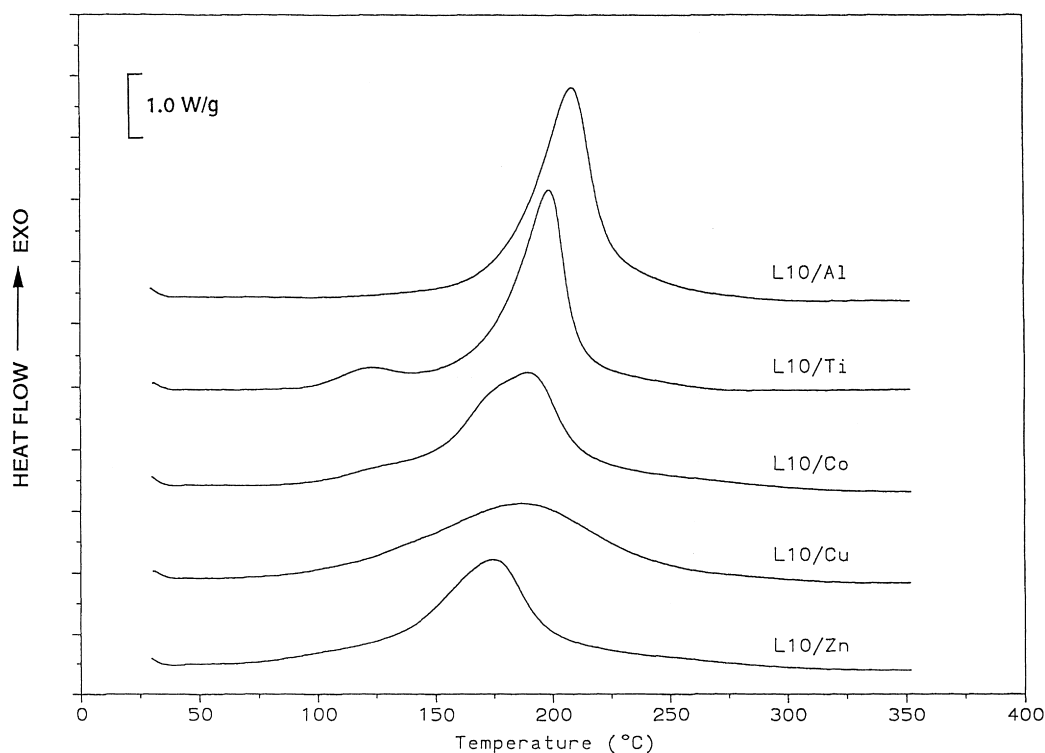


Fig. 2. DSC thermograms for catalyzed homopolymerizations of the L10 cyanate monomer, showing the effect of metal species on the polycyclotrimerization.

a given temperature). This additive method essentially produces a calculated solubility parameter,  $\delta$ , which depends on the nature of functional groups/moieties within the monomer/polymer structures. Where the calculated values of  $\delta$  ( $\text{cal cm}^{-3}$ ) for the two components are similar, this implies that they will be compatible (e.g. for L10,  $\delta$  is calculated as 12.66 in the monomer and 12.20 in the polycyanurate, whereas the figure is somewhat lower for XU366 at 11.65 and 11.02 for the monomer and polymer, respectively). On this basis, one would expect the acrylates ( $\delta$  ranging from 8.70 for LMA to 10 for PEA) to be most compatible with XU366. In order to limit the number of DSC experiments to be undertaken, a series of four representative acrylates: MMA ( $\delta = 8.93$  for monomer and 9.48 for polymer), BMA ( $\delta = 8.82$  for monomer and 9.17 for polymer), LMA ( $\delta = 8.70$  for monomer and 8.88 for polymer) and PEA ( $\delta = 10.0$  for monomer and 10.61 for polymer) was selected. It should be noted that Fedors' method predicts that the last acrylate, PEA, a special experimental vinyl monomer, should have the highest compatibility with the cyanates tested here.

### 3.2. DSC analysis

#### 3.2.1. Polycyclotrimerization of cyanate monomers

**3.2.1.1. Homopolymerization of L10.** The DSC data for the homopolymerizations of the L10 cyanate monomer are displayed in Fig. 2 which shows an overlay of the DSC thermograms on the same axes. All thermograms (with the sole exception of the aluminium-catalysed reaction) seem to display a shoulder preceding the main exothermic peak. However, in the case of the aluminium-catalysed polymerization this shoulder may simply be not discernible, rather than absent. There may be a purity issue involved as the aluminium complex is quoted as being 99% pure. Furthermore, the aluminium is also in the +3 oxidation state and it has already been reported [13,15,19] that this may have a significant effect on the latency of a polycyclotrimerization catalyst. Shimp [19] has studied the activity of both naphthenates and acetylacetonates containing different metal ions towards the liquid monomer AroCy L-10 (one of the commercial cyanates studied in the current work). He examined the pot life of the resin/catalyst systems and reported a ranking of catalysts in the order  $\text{Co}^{3+} > \text{Co}^{2+} \approx \text{Zn}^{2+} > \text{Cu}^{2+}$ . Of the polycyclotrimerization reactions monitored in this work, that catalysed by titanium has the most pronounced 'bimodal' form with a distinct peak ( $T_{\text{exo}} = 124^\circ\text{C}$ ) preceding the main exothermic peak ( $T_{\text{exo}} = 199^\circ\text{C}$ ). The entire polymerization exotherm, encompassing both peaks, totalled  $\Delta H_o = 178 \text{ kJ mol}^{-1}$  of difunctional monomer ( $\Delta H_o$  denotes the observed polymerization exotherm). Again, it may be significant that the form in which titanium was used was as titanium(IV) oxide acetylacetonate—the additional oxygen atom in the ligand may offer another active site towards the cyclotrimerization

reaction, leading to an enhanced reactivity (and perhaps account for the first exothermic peak). Brownhill et al. [12] have studied the  $\text{TiCl}_4$  catalysed polymerization of a series of cyanate monomers, albeit at relatively low temperatures, using both infrared and ultraviolet spectroscopy and postulate the formation of a complex nitrilium intermediate to mediate the reaction. The copper-catalysed polymerization is also noteworthy in producing a particularly broad exothermic peak spanning  $56\text{--}331^\circ\text{C}$ .

All catalysed cyanate homopolymerizations in this work display similar values of  $\Delta H_o$  (ca.  $180 \text{ kJ mol}^{-1}$  of difunctional monomer or  $90 \text{ kJ mol}^{-1}$  of cyanate groups) within the limits of the DSC analysis—which is generally accepted as containing a 5% error [20]. The catalysts in Table 1 gave rise to the following values (in  $\text{kJ mol}^{-1}$ ) of  $\Delta H_o$ , Ti = 178; Co = 182; Cu = 183; Zn = 178 (of difunctional monomer), with the aluminium-catalysed reaction being marginally higher ( $\Delta H_o = 192 \text{ kJ mol}^{-1}$  of difunctional monomer). These values are in agreement with Snow's review of polymerization enthalpies [21] for the uncatalysed polycyclotrimerization of L10 ( $\Delta H_o = 194\text{--}204 \text{ kJ mol}^{-1}$  of difunctional monomer, or  $97\text{--}102 \text{ kJ mol}^{-1}$  cyanate groups). A rescan of the same samples at the conclusion of the DSC experiments revealed no evidence of residual exotherms implying full reaction had taken place. The values of the onset of polymerization are interesting, for although the absolute values may be difficult to assign from the raw DSC data, it is clear that there are marked differences according to the catalyst used. Shimp and Craig [13,15] also compared the effect of different metal acetonates on the cure of bisphenol A dicyanate and the properties of the cured resin. They reported variations in gel time as a function of the metal ion (e.g., from 1 min at  $177^\circ\text{C}$  for  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  to 4 min for  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$ ), although the formulations incorporated metal ions at concentrations ranging from 65–435 ppm, making direct comparison difficult. In the present work,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  lead to relatively low onset temperatures (ca.  $50\text{--}60^\circ\text{C}$ ), whereas  $\text{Ti}^{4+}$  and  $\text{Co}^{2+}$  yield similar values of  $80\text{--}85^\circ\text{C}$ . Again,  $\text{Al}^{3+}$  appears to yield an anomalous result with a relatively high onset value (ca.  $114^\circ\text{C}$ ), but with a very narrow exothermic peak (the conclusion of the peak occurs at  $296^\circ\text{C}$ ). Overall, the trend observed for the onset of polymerization is  $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Co}^{2+} < \text{Ti}^{4+} < \text{Al}^{3+}$  (which incidentally follows the order of atomic weight and is generally in agreement with Shimp and Craig's study [15]). Hence, it is important to note that while the variety of molar masses of the metal ions leads to a variety of metal concentrations (by weight), the molar concentrations of the acetylacetonates used in the blends were carefully kept constant (Table 1). This should remove the effect of concentration and allow the influence of metal ion activity to predominate.

**3.2.1.2. Homopolymerization of XU366.** The DSC data for the homopolymerizations of the XU366 cyanate monomer

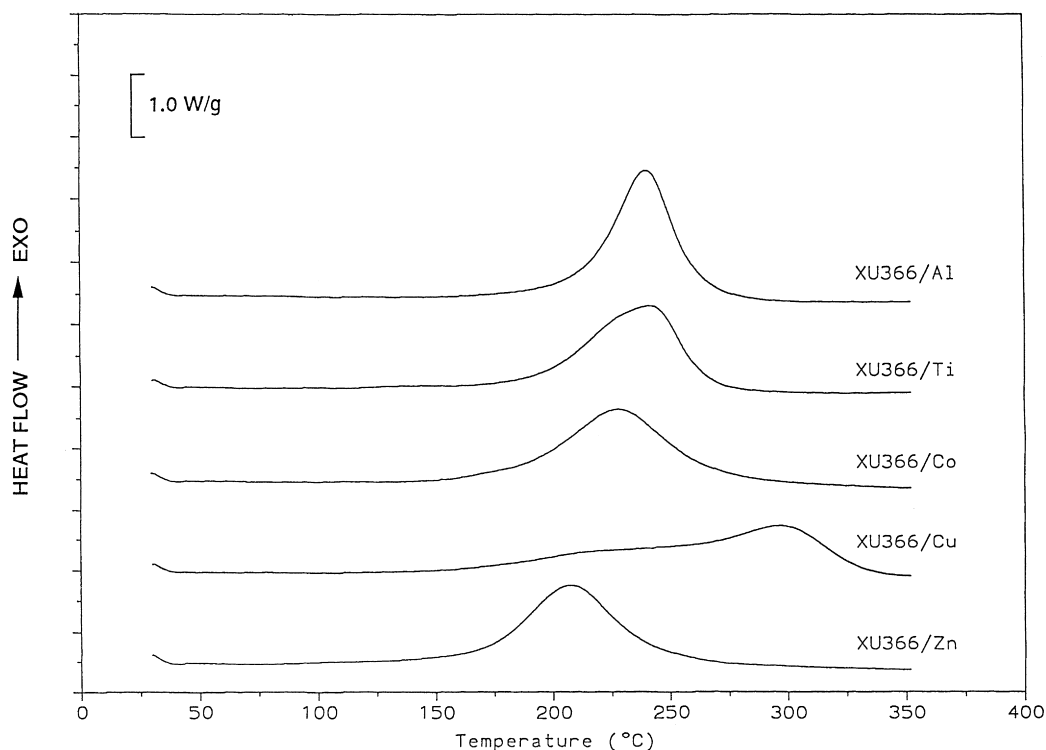


Fig. 3. DSC thermograms for catalyzed homopolymerizations of the XU366 cyanate monomer, showing the effect of metal species on the polycyclotrimerization.

are displayed in Fig. 3 which shows an overlay of the DSC thermograms on the same axes. The first point to note is that the polymerizations are occurring in a higher temperature regime than the corresponding L10 formulations. A comparison of the  $\Delta H_o$  value obtained in this work (164–175 kJ mol<sup>-1</sup> of difunctional monomer, or 82–88 kJ mol<sup>-1</sup> of cyanate groups) is a little lower than that reported in Snow's review of polymerization enthalpies [21–23] for the uncatalysed polycyclotrimerization of XU366 ( $\Delta H_o = 200$  kJ mol<sup>-1</sup> of difunctional monomer, or 100 kJ mol<sup>-1</sup> of cyanate groups). In a previous study of XU366 (previously known as RTX-366, reflecting its previous status as a 'research monomer'), AroCy B-10 and L10 [24,25] revealed that for a given formulation (2 phr nonylphenol and 0.15 phr zinc naphthenate) the RTX-366 monomer reached the highest degree of conversion of the three cyanates tested at each of three cure temperatures. While the data from the present work appear to be at odds with these findings, it is important to note that the previous literature formulations were based on a given weight of monomer (phr) rather than in terms of molar equivalents. The relative molar masses (RMM) are quite different for each monomer (particularly so in the case of RTX-366),  $RMM_{L10} = 264$ ,  $RMM_{B10} = 278$  and  $RMM_{RTX-366} = 396$ , and this leads to a higher degree of catalysis (loading of catalyst) in the latter case. This again underlines the need to observe molar equivalences when attempting to draw conclusions about the effect of various

catalysts—a point frequently absent in discussions of published data.

In general in the current work, the same DSC profiles are observed for XU366 as in the earlier L10 measurements. Again, the aluminium-catalysed reaction is the only one of those studied here to give rise to a Gaussian-type distribution, whereas the remainder display shoulders or other minor exotherms preceding the main peak. Furthermore, the copper-catalysed polymerization also yields a broad exothermic peak spanning 124–352°C, but in this case is bimodal.

As with the L10 formulations, all catalysed XU366 homopolymerizations display similar values of  $\Delta H_o$  (ca. 170 kJ mol<sup>-1</sup> of difunctional monomer, or 85 kJ mol<sup>-1</sup> of cyanate groups) within the limits of the DSC analysis. The catalysts in Table 1 gave rise to the following values (in kJ mol<sup>-1</sup>) of  $\Delta H_o$ , Ti = 164; Co = 169; Cu = 171; Al = 171, and Zn = 175 (of difunctional monomer). The onset values again show differences according to the catalyst used, but the trend differs from that observed for L10, although the zinc-catalysed reaction still displays the lowest onset value (82°C). However, now the order of polymerization onset is Zn<sup>2+</sup> < Ti<sup>4+</sup> < Cu<sup>2+</sup> < Co<sup>2+</sup> < Al<sup>3+</sup>. Again, aluminium yields the highest value (ca. 151°C), but with a very narrow exothermic peak (the peak is concluded by 301°C). It is worth noting that the copper-catalysed polymerization of XU-366 displays a markedly different profile to that in the L10 blend (Fig. 2). The broad exotherm is also

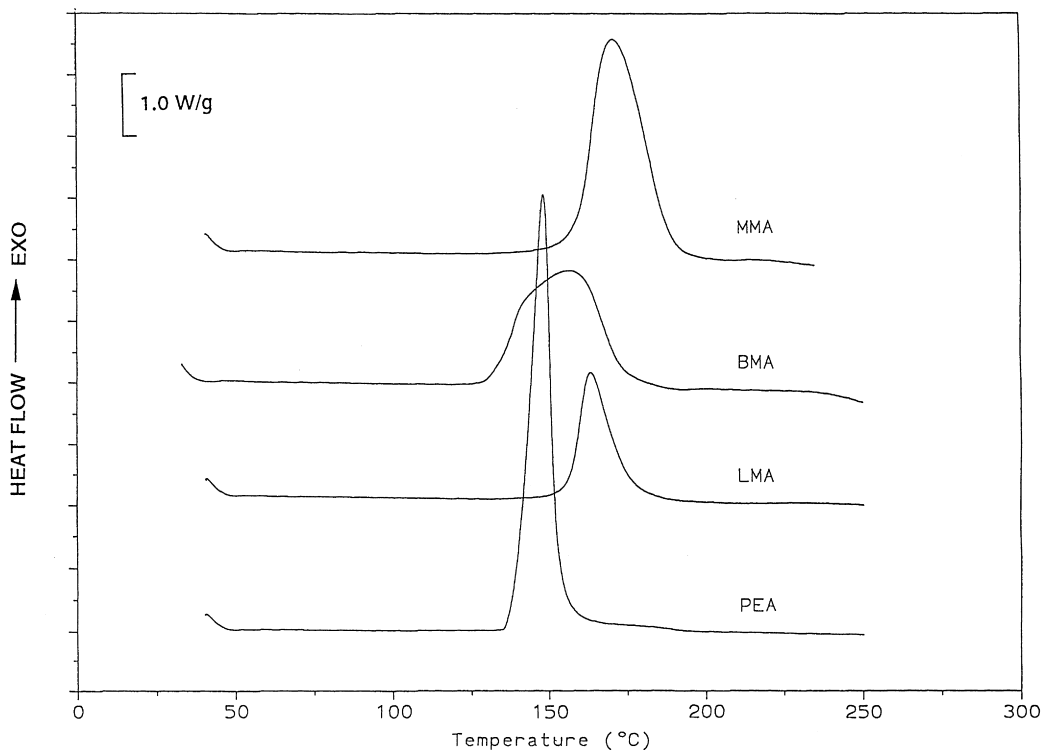


Fig. 4. DSC thermograms for catalyzed homopolymerizations of the acrylate monomers.

distinctly bimodal in nature with an extremely high value of  $T_{\max}$  (297°C).

### 3.2.2. Acrylate homopolymerizations

Each blend of acrylate together with PBZ (1 mol%) was analysed separately using DSC. The data for the thermal polymerizations of the acrylate monomers are displayed in Fig. 4 which shows an overlay of the DSC thermograms on the same axes. It is immediately apparent that the acrylates display a range of reactivities and exotherm profiles. For example, PEA appears to be the most reactive of the monomers tested, with a very narrow polymerization exotherm spanning 129–192°C. Otherwise, the order of peak maxima falls into the series: PEA < BMA < LMA < MMA. To complicate the analysis further, the relative purities of the acrylates should be taken into account in order to draw meaningful conclusions. Both MMA and BMA are stabilized with hydroquinone monomethyl ether (10 ppm), while LMA contains no stabilizer (the latter is also quoted as being 96% pure, although no indication of the nature of the impurities was given). However, the level of incorporation of PBZ (1 mol%) is believed to be sufficient to overcome the effect of the free radical inhibitor.

In general, despite the differences in the peak profiles, all methacrylates displayed a similar value (in  $\text{kJ mol}^{-1}$ ) of  $\Delta H_0$  (MMA = 41, LMA = 41, BMA = 47) for the polymerization exotherm. These data yield values of  $\Delta H_0$  which are somewhat lower than those published [26] for MMA (56  $\text{kJ mol}^{-1}$ ) and BMA (58  $\text{kJ mol}^{-1}$ ), although the

literature data were acquired under isothermal conditions using 'reaction calorimetry' rather than DSC. Furthermore, it is already well established [27] that the ceiling temperature is 135–160°C for MMA (at which point the free energy of polymerization becomes zero, rendering further polymerization impossible). During our DSC analysis the calorimeter reached a temperature of at least 160°C (indeed the peak temperature of the polymerization enthalpy is also above this temperature) and so this might account for the lower enthalpy observed during this work. In contrast, the polymerization of PEA yielded a somewhat higher value ( $\Delta H_0 = 68 \text{ kJ mol}^{-1}$ ) than the methacrylates (although no comparable published data could be found for the thermal polymerization of PEA). It should also be noted that MMA is a volatile monomer, which might make thermal analysis difficult. However, the analyses were carried out in hermetically-sealed/crimped aluminium pans to avoid the loss of monomer and the data appear to confirm that the analyses are reproducible.

A brief comparison of the thermal behaviour of the acrylates and the cyanates prompts the following consideration of the ensuing blends. In some cases (e.g. PEA and aluminium-catalysed XU366) the two thermal behaviours are markedly different with the PEA undergoing polymerization at a much lower temperature than the cyanate. In contrast, with other examples (e.g. MMA and cobalt-catalysed L10), the two species are undergoing polymerization at similar temperatures. While it is accepted that in the presence of one another the curing kinetics of both species may be

Table 2

Analysis of the heats of polymerization of the cyanate/acrylate blends (all blends contain a cyanate/Al(acac)<sub>3</sub> molar ratio of 1000:1; L10 cyanates contained 102 ppm Al<sup>3+</sup> and 2.09 phr nonylphenol XU366 cyanates contained 68.1 ppm Al<sup>3+</sup> and 1.39 phr nonylphenol; all acrylates contained 1 mol% PBZ; T<sub>1</sub>, temperature of onset of polymerization exotherm; T<sub>exo</sub>, temperature of peak maximum of polymerization exotherm; T<sub>2</sub>, temperature for completion of polymerization exotherm; ΔH<sub>o</sub>, observed heat of polymerization; ΔH<sub>c</sub>, calculated heat of polymerization; acac, acetylacetonate)

Blend	ΔH <sub>o</sub> (J g <sup>-1</sup> )	ΔH <sub>c</sub> (J g <sup>-1</sup> )	ΔH <sub>o</sub> /ΔH <sub>c</sub>
L10/MMA			
90/10	633	713	0.89
50/50	525	639	0.82
33/67	472	589	0.80
L10/BMA			
90/10	634	704	0.90
50/50	462	587	0.79
33/67	373	521	0.72
L10/LMA			
90/10	601	672	0.89
50/50	367	450	0.82
33/67	215	355	0.61
L10/PEA			
90/10	621	699	0.89
50/50	497	571	0.87
33/67	467	508	0.92
XU366/MMA			
50/50	326	427	0.76
33/67	295	424	0.70
XU366/BMA			
50/50	288	405	0.71
33/67	287	389	0.74
XU366/LMA			
50/50	267	326	0.82
33/67	207	280	0.74
XU366/PEA			
50/50	373	407	0.92
33/67	386	395	0.98

affected, the selection of both acrylate and cyanate (as a blend) may be crucial to facilitate the formation of either a co-curing (though not necessarily a co-reactive) network or a blend which undergoes 'sequential' reaction. Both routes might offer interesting processing opportunities and it is believed that this is a novel route to preparing such materials. Fyfe et al. [28] briefly mentioned the copolymerization of methyl methacrylate and tris-(2,4,6-allyloxyphenyl)-1,3,5-triazine (a species first reported [29,30] in connection with modified cyanate/bismaleimide networks) with a benzoyl peroxide initiator to yield a thermoset network, but offered no characterization data. However, in contrast with the current study, the monomers were believed to coreact directly via a radical mechanism (through the olefinic allyl and methacrylate groups).

### 3.2.3. Thermal behaviour of the acrylate/cyanate blends

All acrylate/cyanate blends contained PBZ (1 mol% with respect to the acrylate) and aluminium(III) acetylacetonate in the molar ratio 1000:1 (acetylacetonate:cyanate)—this

amounts to either 102 or 68.1 ppm Al<sup>3+</sup> for blends containing L10 or XU366 respectively. Nonylphenol contents were fixed at a molar ratio of 25:1 (nonyl phenol:acetylacetonate), resulting in 2.09 (L10) and 1.39 phr (XU366).

**3.2.3.1. L10/acrylate blends.** The DSC data for the acrylate/L10 blends are summarized in Table 2 and depicted in Fig. 5: the thermograms tend to be quite complex. In general, for all blends an increase in the concentration of the acrylate in the composition leads to the appearance of a small exothermic peak preceding the main exotherm. It is believed that this is due to acrylate polymerization and its appearance is accompanied by both (i) a reduction in the height of the second exothermic peak (T<sub>exo2</sub>) attributed to the polycyclotrimerization reaction and also (ii) a shift of T<sub>exo2</sub> to a higher temperature. Among the methacrylates, both features (i) and (ii) are most pronounced in blends containing LMA. Overall, however, the blends containing MMA (Fig. 5) are least sensitive to the presence of acrylate in terms of the reduction in the exothermic peak height. It appears from the DSC data that the presence of both components (L10 and the acrylates), the polymerizations of both become slightly retarded, as evidenced by the peak maxima (T<sub>exo1</sub> and T<sub>exo2</sub>) when compared with the homopolymerization data presented earlier in Figs. 2–4. It is also noticeable that the total integral (ΔH<sub>o</sub>) for both exotherms varies with changes in the blend composition (Table 2) again indicating a lower degree of conversion in blends containing high acrylate contents. The DSC data confirm that the bulk of the polymerizations of the two components in blends containing high acrylate contents are occurring concurrently with only a small degree of overlap.

**3.2.3.2. XU366/acrylate blends.** The DSC data for the acrylate/XU366 blends are given in Fig. 6. Again, the thermograms are quite complex, displaying similar profiles to the L10/acrylate blends—although, as expected, the value of T<sub>exo2</sub> (corresponding to the cyanate polycyclotrimerization reaction) is located in a higher temperature regime than L10. The shift in the position of T<sub>exo2</sub> for XU366 in the presence of the acrylates is less marked than the corresponding L10 blends, with the exception of the blend containing LMA which shows a shift in T<sub>exo1</sub> and T<sub>exo2</sub> of 11 and 22°C respectively (i.e. the T<sub>exo</sub> values for the homopolymerizations). The DSC data confirm that the polymerizations of the two components are discrete without any apparent overlap taking place: the homopolymerization of the acrylate having concluded before the polycyclotrimerization of the cyanate commences.

A further treatment of the thermal data involves a determination of the effective concentrations of the cyanate and acrylate in each composition. The thermal analyses of the individual cyanate and acrylate monomers presented in Figs. 2–4 yielded values of enthalpy relating to full

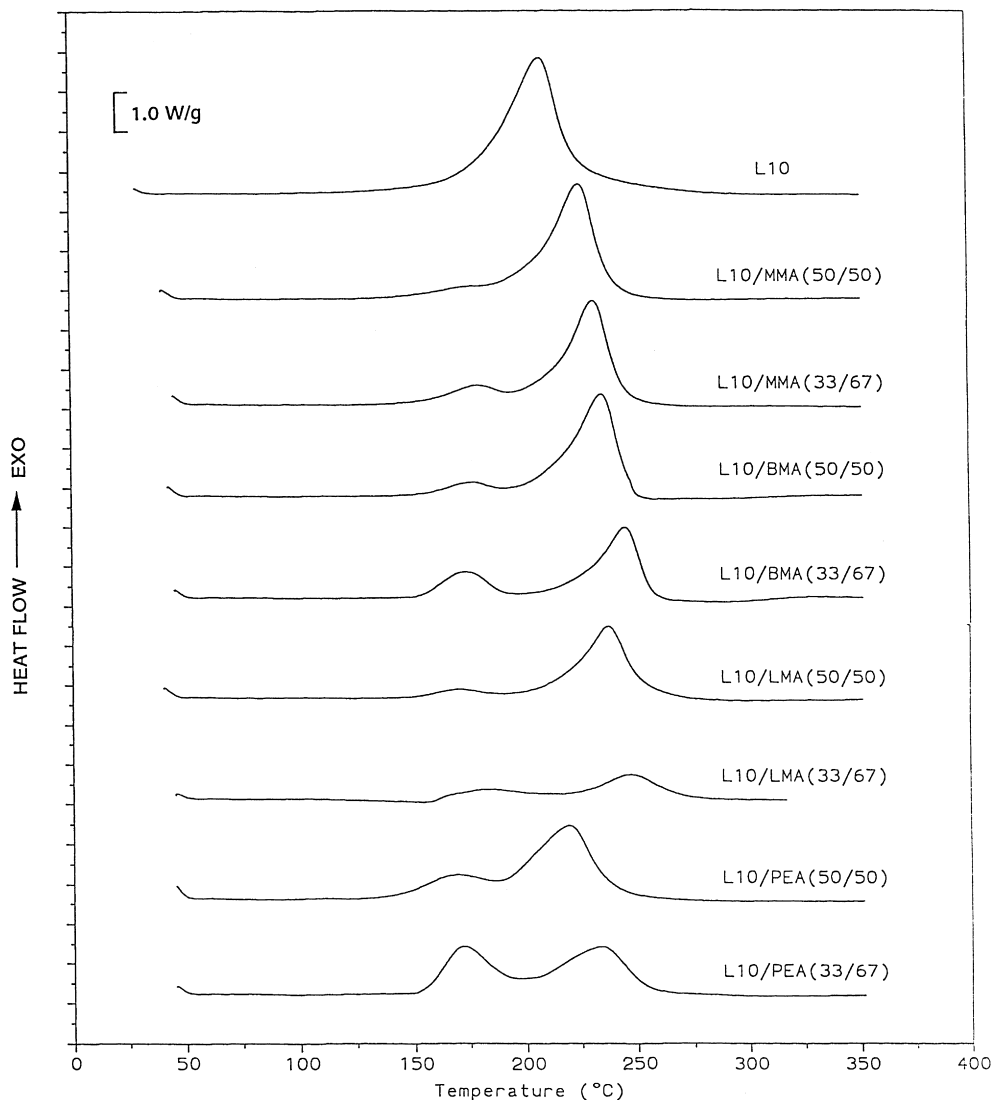


Fig. 5. DSC thermograms for the polymerization of the L10/acrylate blends.

conversion; these values agreed well with literature data. From a knowledge of the total number of polymerizable groups in each blend, it is possible to calculate a value of the theoretical polymerization enthalpy (denoted  $\Delta H_c$ ) which relates to the 'full' polymerization if all polymerizable groups are consumed. In order to determine the degree of polymerization for each blend, those experimental DSC enthalpies obtained for the blends ( $\Delta H_o$ ) are then ratioed with this theoretical value ( $\Delta H_o/\Delta H_c$ ) to provide the data shown in the last column of Table 2.

In fact, in all cases this ratio indicates that a lower  $\Delta H_o$  is observed for the blends than would be expected purely from a consideration of the concentrations of the polymerizable groups present in the blends. Table 2 shows the variation in  $\Delta H_c$  and  $\Delta H_o$  (expressed in  $\text{J g}^{-1}$  of blend) for both L10 and XU366 obtained from the DSC analysis of the cyanate monomer/acrylate blends. The values at the extreme ends of the range relate to 100% monomer (cyanate or acrylate,

respectively) obtained from DSC analysis of the pure monomers. The DSC rescan analyses (conducted after the conclusion of the polymerization exotherm), showed no residual exotherms indicating that the values of  $\Delta H_o$  obtained relate to the assumed 'full' conversions for L10 and XU366. These data show the deviation in the value of  $\Delta H_o$  away from the 'ideal'  $\Delta H_c$  as a function of blend composition. Clearly, as the amount of acrylate in the blend increases, so the deviation of  $\Delta H_o$  from  $\Delta H_c$  becomes larger. This finding, together with the observations of the shifts in  $T_{\text{exo}}$  to higher temperatures, suggests that the homopolymerization reaction of each component is being retarded in the presence of the other; a not unreasonable assumption. Lin and co-workers have already reported similar phenomena in compatible simultaneous interpenetrating networks formed from bisphenol A diglycidyl ether (BADGE) and acrylics [31,32]. In their studies they reported that hydrogen bonding between the components (evidenced by infrared



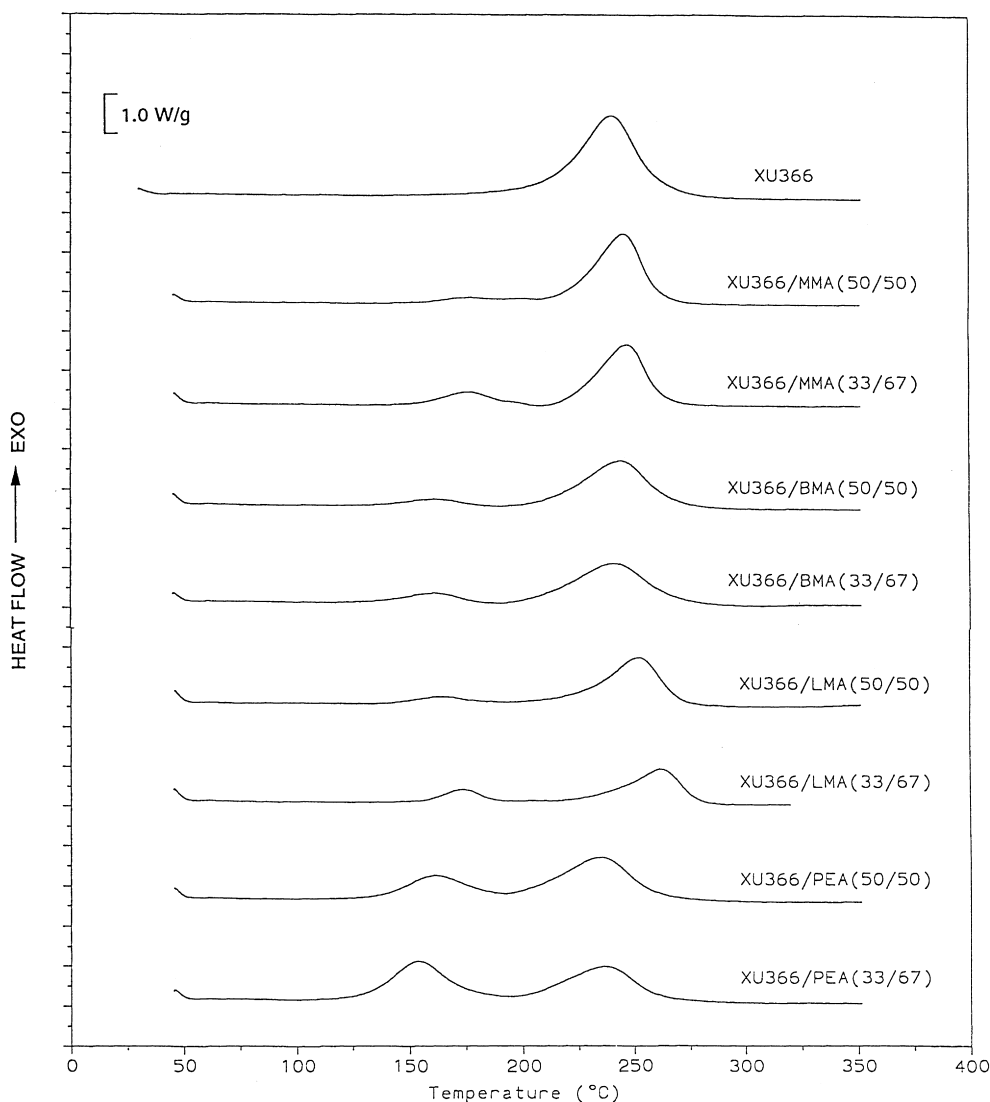


Fig. 6. DSC thermograms for the polymerization of the XU366/acrylate blends.

measurements) reduced BADGE chain mobility slightly leading to mutual entanglement between the two components. Lin et al. suggested that this network interlock effect provides a sterically hindered environment for the polymerization reactions and leads to lower rate constants and slightly higher activation energies than those observed during polymerization of each of the single components.

From the data presented in Table 2 it is possible to compare the relative effects of each acrylate on the cyanate homopolymerizations. It is apparent that LMA generally has the largest inhibitory effect on the L10 polymerization and PEA the smallest (there is a small reversal of the trend observed for LMA and BMA at compositions of 50/50 and 33/67). For XU366/acrylate blends, although the effect is less marked, it is clear that PEA again has much less of an inhibitory effect on the cyanate polymerization than the remaining acrylates (the same reversal is again observed for LMA and BMA). These data may be related to the

solubility calculations presented earlier as the compatibility of the acrylates falls neatly into the series  $PEA > MMA > BMA > LMA$  (where  $>$  indicates 'is more compatible with cyanate than').

The cyanate blends containing PEA are particularly interesting since not only are the calculated compatibilities the most favourable of those studied here (and, moreover,  $\delta$  for the polycyanurates decreases further during reaction to become even closer to the increasing  $\delta$  values for the polyacrylates), but the values of  $T_{\text{exo}}$  for both homopolymerizations (cyanates and PEA) are the most widely separated in terms of temperature. The DSC data confirm that the polymerizations of the two components are discrete and apparently proceed to complete conversion without any co-reaction taking place. This suggests that the XU366/acrylate blends (particularly those containing PEA) may tend towards the formation of sequential semi-IPNs [33] (although this definition is not completely accurate since

the monomers are essentially both polymerized in situ, rather than in two separate operations). Work continues to examine the thermo-mechanical and morphological aspects of these cyanate/acrylate blends.

#### 4. Conclusions

Initial screening of a series of blends containing one of two commercial cyanates, AroCy L-10 and AroCy XU-366 and acrylate monomers was based on an assessment of the compatibility of the blends' components. Fedors' method predicted that PEA would have the greatest degree of compatibility with both cyanates (and that this compatibility should initially increase as cure proceeds). DSC analysis of the cyanate homopolymerizations yielded values of  $\Delta H$  which were in agreement with published data. For catalysed L10 polymerizations the trend observed for the onset of polymerization was  $Zn^{2+} < Cu^{2+} < Co^{2+} < Ti^{4+} < Al^{3+}$  which is generally in agreement with published work. Homopolymerizations of XU366 occurred in a higher temperature regime than the corresponding L10 formulations, but the order of the onset of polymerization was  $Zn^{2+} < Ti^{4+} < Cu^{2+} < Co^{2+} < Al^{3+}$ . The PBZ-catalysed acrylate homopolymerizations revealed that PEA appears to be the most reactive of the monomers tested, otherwise, the order of exothermic peak maxima fell into the series: PEA < BMA < LMA < MMA. For L10/acrylate blends an increase in the concentration of the acrylate in the composition led to the appearance of a small exothermic peak preceding the main exotherm. In the presence of both cyanate and acrylate components, the polymerizations of both became slightly retarded. With XU366/acrylate blends the polymerizations of the two components were discrete without any overlap apparently taking place: the homopolymerization of the acrylate having concluded before the polycyclotrimerization of the cyanate commence. A consideration of a ratio of experimental to theoretical values of polymerization enthalpy as a function of blend composition made it possible to compare the relative effects of each acrylate on the cyanate homopolymerizations. PEA had the smallest inhibitory effect on the cyanate polymerizations. Thermal data suggest that the XU366/acrylate blends (particularly those containing PEA) may tend towards the formation of sequential networks and future work will address the thermo-mechanical and morphological properties of the blends.

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