

# Catalyst Effect on Cure Reactions in the Blend of Aromatic Dicyanate Ester and Bismaleimide

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**ABSTRACT:** Catalyst effects on cure reactions of a bismaleimide [4,4'-bismaleimidodiphenylmethane (BMI)] associated with a liquid aromatic dicyanate ester [1,1'-bis(4-cyanatophenyl)ethane (BEDCy)] and with a powder type of aromatic dicyanate ester [bisphenol A dicyanate (BADCy)] were thoroughly investigated by *in situ* FTIR and DSC dynamic scanning. In noncatalyzed blend systems, coreactions between the dicyanate ester and bismaleimide always occur, and thus the formation of the pyrimidine and/or pyridine structures occurs. The pyrimidine structure always predom-

inates. The use of a dicyanate-sensitive catalyst facilitates the formation of a sequential interpenetrating network (IPN). The extent of the sequential IPN depends on the level of catalyst and the type of matrix materials, and thus the extent of coreactions. Probable reaction paths were also proposed for various formulations of hybrid blends. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 345–354, 2004

**Key words:** interpenetrating networks; thermosets; polyimides; bismaleimide; dicyanate ester

## INTRODUCTION

Polycyanurates derived from the thermal cure of aromatic dicyanate esters possess many attractive physical, dielectric, and mechanical properties. However, the thermal characteristics are inferior to those of conventional bismaleimide systems. Blends of aromatic dicyanate esters and bismaleimide have been achieved to derive systems bearing good physicochemical attributes of the two components: the thermal characteristics of bismaleimide and the toughness of polycyanurates. Some blend systems were investigated by the addition polymerization of bisphenol A dicyanate (BADCy) and 4,4'-bismaleimido diphenylmethane (BMI),<sup>1,2</sup> and also BADCy and 2,2'-bis[4-(4-maleimidophenoxy)propane] (BMIP).<sup>3,4</sup> Commercial-blend formulations of bismaleimide–cyanate, known as B-T resins, are available.<sup>5,6</sup> Several patented B-T resin formulations find applications as engineering materials in aircrafts, reinforced plastics, and injection-molding powders, as well as materials in electric motor coil windings, for example.<sup>7,8</sup> Some novel allyl-functionalized aryl cyanate esters were developed to be incorporated into cyanate ester/bismaleimide blends.<sup>9–14</sup> The addition of a small amount of allyl-functionalized

aryl cyanate esters may increase the glass-transition temperature ( $T_g$ ) of the overall network by linking the polycyanurate network to the polybismaleimide network while maintaining levels of model I fracture toughness ( $G_{IC}$ ).

In the blend systems containing BADCy, it was postulated that the two components coreact during curing, but without much proof for the resulting pyrimidine or pyridine structures. It is believed that the resultant polymer matrix is an interpenetrating network (IPN), rather than a cocured matrix.<sup>13–15</sup> The IPNs formed in these cases have been found to exhibit two  $T_g$  values, resulting from the microphase separation.<sup>13–15</sup> It should be pointed out that the above-mentioned systems were cured by adding a BADCy-sensitive catalyst, such as copper (II) naphthenate with nonylphenol. Reghunadhan Nair et al.<sup>3,4</sup> examined the system containing BADCy and BMIP with dibutyl tin dilaurate as catalyst by DSC scanning. The near simultaneous cure of the blend could be transformed to a clear sequential peak by catalyzing the dicyanate cure to a lower temperature, suggesting that the resultant system has to be an IPN and not a cocured system. The catalyst was added for the early cure of the BADCy component. It helps gelation and consolidation of the blend system at lower temperature and facilitates its molding.

Various aromatic dicyanates were substantially investigated in our laboratory on the cure kinetics and mechanisms of polycyclotrimerization,<sup>16–18</sup> effect of intramolecular cycles on the polycyclotrimeriza-

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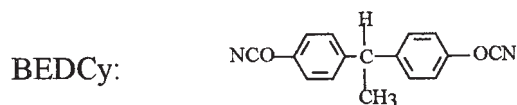
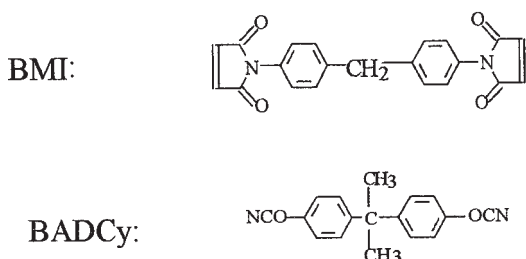
tion,<sup>19,20</sup> the  $T_g$ -conversion relationship in the polycyclotrimerization,<sup>21,22</sup> the cure reaction of aromatic dicyanate ester with different types of epoxy resins,<sup>23</sup> and the cure reaction of the dicyanate/diepoxide/diamine system.<sup>24</sup> The curing system of BMI/BADCy blend without a specific catalyst was investigated,<sup>17,25</sup> and the crosslinking reactions between BMI and BADCy were indeed detected in the FTIR spectra. No cyclotrimerization was observed in the blend BMI/BADCy without catalyst, suggesting that pyrimidine and/or pyridine structures were formed.<sup>17</sup> The reactions between two model compounds, *N*-phenylmaleimide (MI) and *p*-phenyl-phenylcyanate (S-Cy), were examined in our laboratory.<sup>25</sup> <sup>13</sup>C-NMR spectra of the model compounds demonstrated the formations of linkages of *sym*-triazine rings, pyrimidine structures, pyridine structures, and dioxazine structures. The reaction mechanism or linkage structures produced in the model compound system studied may be different from those of the real system as a result of a diffusion effect in real systems or of the different activation energy in both systems.

The objectives of this work were to illuminate the catalyst effect on the reaction between dicyanate and bismaleimide. We attempted to thoroughly explore the reactions of BMI with different types of aromatic dicyanate esters. In a first step, BMI/BADCy systems, with or without external BADCy-sensitive catalysts, were investigated by *in situ* FTIR and DSC dynamic scanning to illuminate the effect of catalyst on the reaction of the hybrid system. Then, BMI with a liquid type of aromatic dicyanate ester [1,1-bis(4-cyanatophenyl) ethane (BEDCy)] was cured with or without catalysts to evaluate the differences with the BMI/BADCy systems.

## EXPERIMENTAL

### Materials

4,4'-Bismaleimidodiphenylmethane (BMI; Aldrich Chemical Co., Milwaukee, WI), bisphenol A dicyanate (BADCy; TCI, Tokyo, Japan), 1,1'-bis(4-cyanatophenyl)ethane (BEDCy; Ciba-Geigy, Fluka, Buchs, Switzerland), copper-acetylacetonate (Merck, Darmstadt, Germany), and *p*-nonylphenol (TCI) were used as purchased.



All hybrid samples prepared for curing were homogeneously mixed by the use of dichloromethane, then vacuum-distilled to remove the residual solvent.

### Instrumentation

#### Differential scanning calorimetry (DSC)

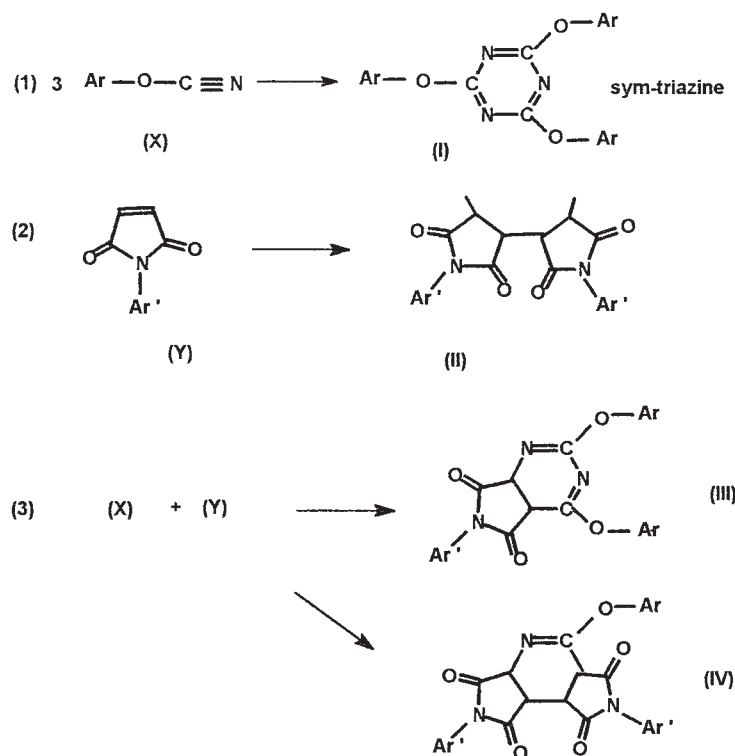
Samples, approximately 3–6 mg in weight, were sealed in hermetic pans and scanned in a differential scanning calorimeter (DSC-7; Perkin Elmer Cetus Instruments, Norwalk, CT) calibrated with an indium standard. A stream of nitrogen at a flow rate of 20 mL/min was used to purge the DSC cell.

#### FTIR spectroscopy

The sample was mixed with dried KBr powder and pressed into a pellet. An FTS-40 FTIR spectrometer (Digi-Lab, Singapore) equipped with a temperature-controlled sample holder in a N<sub>2</sub> atmosphere was used to study the cure reaction *in situ*. The cure reaction proceeded at a heating rate of 5°C/min in the FTIR cell. The FTIR scans were performed at each 10°C-increment sequence of progressively ascending temperatures during heating. Spectra were obtained in an optical range of 400 to 4000 cm<sup>-1</sup> by averaging six scans at a resolution of 8 cm<sup>-1</sup> to minimize the effect of dynamic scanning.

## RESULTS AND DISCUSSION

Before the hybrid cure systems were investigated, the cure reaction of the neat dicyanate ester and neat bismaleimide were preliminarily examined through a cross-reference between *in situ* FTIR and DSC dynamic scanning. To be able to compare the FTIR spectra and DSC thermograms, we took measurements with both instruments at the same heating rate (5°C/min). Although there is a slight uncertainty as to the exact heating rate used for the FTIR work, the progressive temperature increase between the FTIR spectra and the corresponding DSC thermograms is comparable. In our work, the FTIR scans were conducted at 10°C increments of progressively ascending temperature during the heating. The successive FTIR spectra of neat dicyanate showed that the disappearing absorption bands of the cyanate at 2267 and 2237 cm<sup>-1</sup> were accompanied by the emerging absorptions of triazine at 1565 and 1366 cm<sup>-1</sup> (see Lin<sup>23</sup>; not shown here for brevity). This suggests that polycyclotrimerization is the exclusive reaction in the neat aromatic dicyanate system and only one type of linkage (i.e., the



**Scheme 1** Pathways proposed for the reaction of bismaleimide with dicyanate ester.

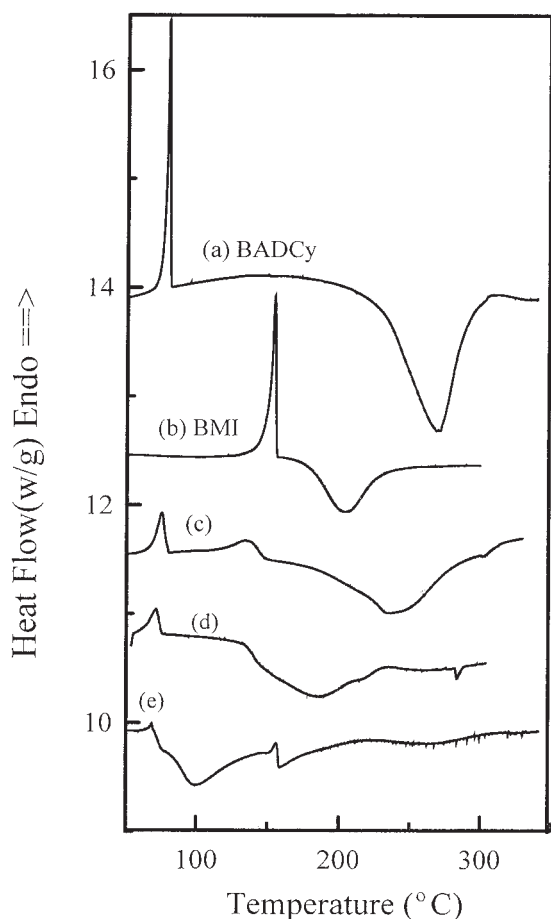
*sym*-triazine ring) is formed during the whole course of the reaction with or without external catalysts.<sup>7,16,18,23,26</sup> Polycyclotrimerization of aromatic dicyanates proceeds by a combination of three functional groups to form a triazine ring, as illustrated in path 1 of Scheme 1. Correspondingly, only one reaction exotherm was observed in the DSC thermogram when curing neat BADCy at a heating rate of 5°C/min, as shown in Figure 1(a). The peak temperature lies in the vicinity of 268°C.

The DSC thermogram for curing neat BMI is shown in Figure 1(b). Only one reaction exotherm was observed at the peak temperature of 200°C. Shown in Figure 2 are some crucial FTIR spectra of neat BMI during dynamic heating from room temperature to 300°C, at a heating rate of 5°C/min. The characteristic absorptions attributed to the =C—H bending vibrations of maleimide, which appeared at 689 cm<sup>-1</sup> in the monomer, gradually disappeared during the curing process, suggesting the homopolymerization of the vinyl moieties of bismaleimide. The absorption peak at 832 cm<sup>-1</sup>, attributable to the out-of-plane bending of the =CH group of the maleimide moiety, and the absorption at 689 cm<sup>-1</sup> disappeared simultaneously. However, these peaks did not disappear completely in the spectra of the cure polymer, most likely because of concomitant absorption resulting from the bending vibration of other C—H groups (aromatic) at the same frequency. Homopolymerization of bismaleimide is proposed as shown in path 2 of Scheme 1.

#### BADCy/BMI cure system

The DSC thermograms for curing hybrid BADCy/BMI systems at a heating rate of 5°C/min, with or without external catalysts, are shown in Figure 1(c)–(e). Figure 1(c) shows the DSC trace of the BADCy/BMI system in a molar ratio of 1 : 1 without catalyst, illustrating a broader exothermic peak, which lies between the peaks of its individual components [neat BADCy and neat BMI shown in Fig. 1(a) and (b), respectively]. The shift to a lower temperature suggests that the BADCy component was induced to undergo a reaction in the presence of BMI. The probable reactions in this blend were elucidated by the corresponding *in situ* FTIR spectra in a dynamic scanning. Shown in Figure 3 are some pertinent FTIR spectra of the BADCy/BMI blend during the dynamic heating from room temperature to 300°C, at a heating rate of 5°C/min. These FTIR spectra show that dynamic heating from room temperature to 280°C results in the complete consumption of the cyanate groups (2267 and 2237 cm<sup>-1</sup>). Nevertheless, we did not find the formation of the *sym*-triazine ring (1565 cm<sup>-1</sup>). The exclusive way is that BADCy does react with BMI, thereby forming a pyrimidine (III) and/or pyridine (IV) structure, as shown in path 3 of Scheme 1.

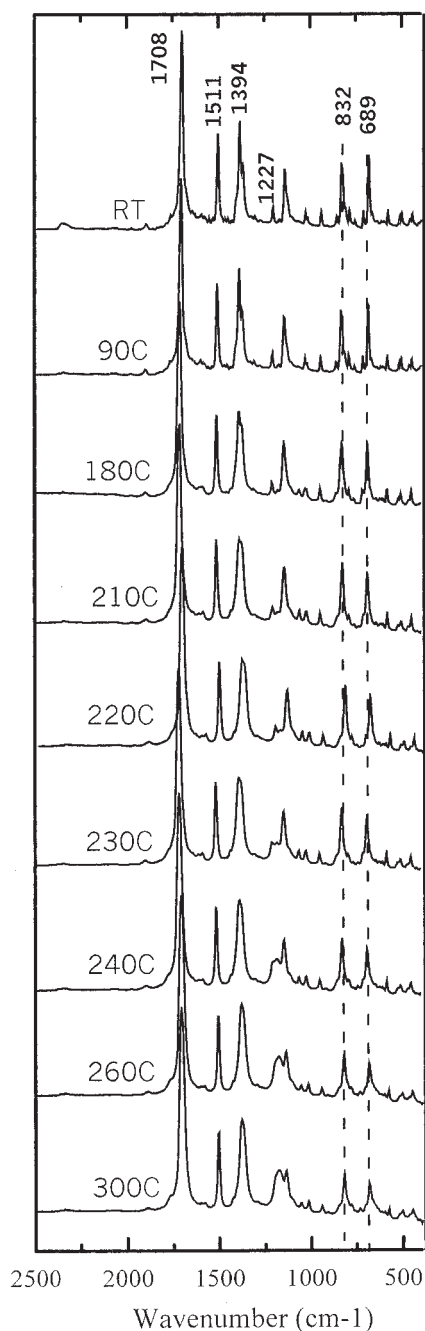
The formations of pyridine and pyrimidine structures were directly evidenced in our laboratory by the model compound method (*N*-phenylmaleimide and *p*-phenyl-phenylcyanate) using <sup>13</sup>C-NMR.<sup>25</sup> In the



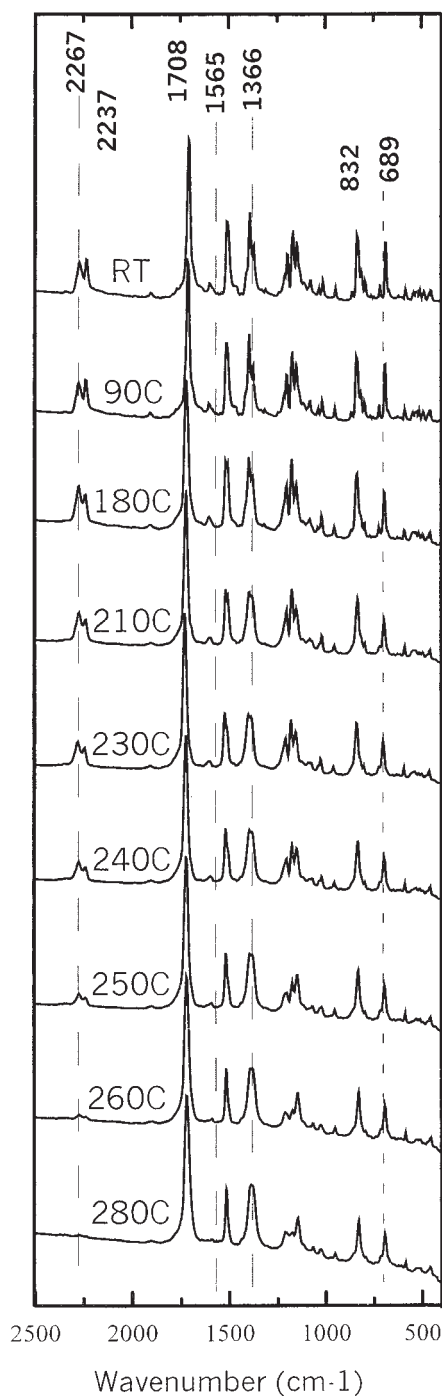
**Figure 1** DSC thermograms at a heating rate of 5°C/min: (a) neat BADCy, (b) neat BMI, (c) BADCy/BMI (1 : 1), (d) BADCy/BMI (1 : 1) with copper-AcAc 1000 ppm and *p*-nonylphenol 4 phr, (e) BADCy/BMI (1 : 1) with copper-AcAc 1.4 phr and *p*-nonylphenol 4 phr.

meantime, the characteristic absorptions of  $=C-H$  in the maleimide groups ( $832$  and  $689\text{ cm}^{-1}$ ) were gradually consumed by its homopolymerization or the coreaction with BADCy during dynamic heating. It is thus reasonable to expect that the reaction paths 2 and 3 in Scheme 1 are available for the noncatalyzed BADCy/BMI blend. The characteristic absorption at  $1365\text{ cm}^{-1}$  may be presumably attributable to the pyrimidine structures (III) and the pyridine structures (IV). This absorption gradually coincided with the absorptions of dicyanates at  $1366$  and  $1355\text{ cm}^{-1}$  when the reaction path 3 proceeded. Except for this possible absorption ( $1365\text{ cm}^{-1}$ ), no newly formed characteristic peaks for the other functional groups or linkages were found, implying that BADCy reacts with BMI to form the pyrimidine structure and the pyridine structure, as evidenced by the  $^{13}\text{C-NMR}$  spectra.<sup>25</sup> Quantitative analyses of the pyrimidine structures (III) and the pyridine structures (IV) formed in the reaction path 3 are not possible because of the serious overlapping of the characteristic bands in the FTIR spectra.

However, from mathematical logic of the stoichiometric relationship between the cyanate units and the maleimide units, we expect that the pyrimidine structures (III, two cyanate units combined together with one maleimide unit) predominate compared to the pyridine structures (IV, one cyanate unit combined with two maleimide units); otherwise, some BADCy monomers will be retained and proceed in a polycyclotrimerization to form *sym*-triazine rings for the system in a molar ratio of 1 : 1. Actually, we did not find



**Figure 2** Some crucial FTIR spectra for neat BMI during dynamic heating from room temperature to 300°C, at a heating rate of 5°C/min.



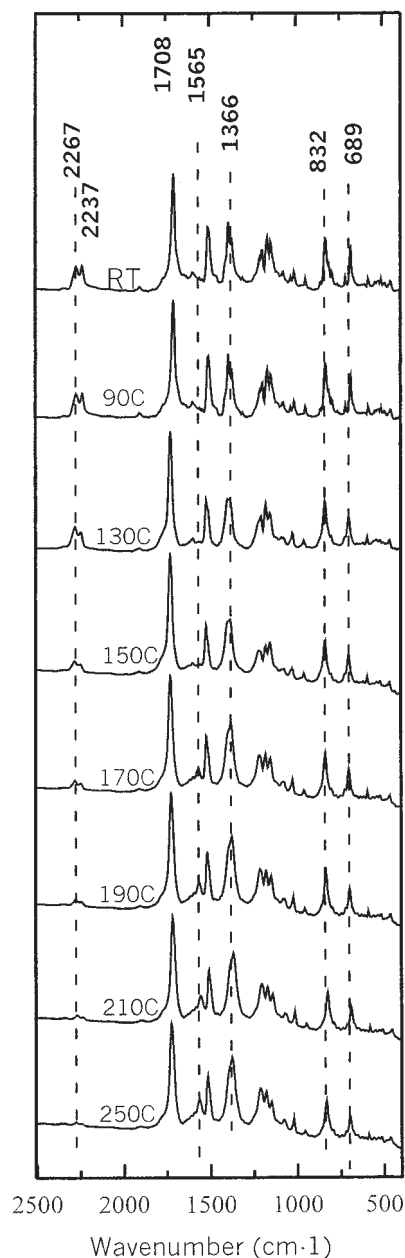
**Figure 3** Some crucial FTIR spectra for the BADCy/BMI (1 : 1) system during dynamic heating from room temperature to 300°C, at a heating rate of 5°C/min.

the *sym*-triazine rings, demonstrating that the pyrimidine structures must be predominant.

Relative amounts of reaction path 2 (homopolymerization of BMI) should be small; otherwise, an obvious exothermic peak should be observed in the DSC thermogram over the same temperature range as that for the neat BMI component [Fig. 1(b)]. Actually, no such exothermic peak was detected, implying homopoly-

merization of BMI was suppressed in the presence of BADCy. Homopolymerization of BMI always proceeds at a lower temperature compared with that of its hybrid system.

Figure 1(d) shows the DSC trace of a BADCy/BMI system in a molar ratio of 1 : 1 with copper-acetylacetonate (1000 ppm) associated with *p*-nonylphenol (4 phr) as catalyst, illustrating that a broader exothermic peak shifts to a lower temperature range compared with that of the noncatalyzed system [Fig. 1(c)]. The probable reactions in this blend are elucidated by the

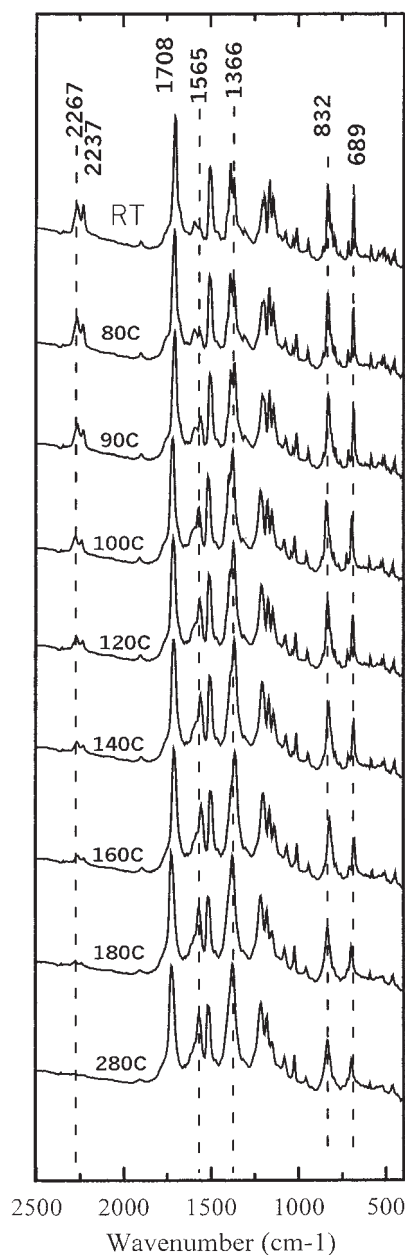


**Figure 4** Some crucial FTIR spectra for the BADCy/BMI (1 : 1) system with copper-AcAc 1000 ppm and *p*-nonylphenol 4 phr as cocatalyst during dynamic heating from room temperature to 250°C, at a heating rate of 5°C/min.



corresponding *in situ* FTIR spectra obtained by dynamic scanning. Shown in Figure 4 are some pertinent FTIR spectra of the catalyzed BADCy/BMI blend, which were obtained by dynamic heating from room temperature to 250°C, at a heating rate of 5°C/min. The progressive FTIR spectra of this system are basically the same as those of the noncatalyzed system, except for the fact that some characteristic absorptions of triazine rings (1565 cm<sup>-1</sup>) were detected enhancing at a lower temperature range, from 140 to 250°C, matching the observations from the DSC trace [Fig. 1(d)]. The cocatalyst of copper–acetylacetonate with *p*-nonylphenol is a dicyanate-sensitive catalyst, thereby reducing the activation energy of the polycyclotrimerization of BADCy and facilitating its reaction. Only a small amount of the triazine rings were detected in this blend, judging from the intensity of the characteristic absorptions of triazine rings (1565 cm<sup>-1</sup>). This suggests that not all cyanates were completely converted to triazine rings, and that the cure reactions in this blend included three paths, which are shown in Scheme 1. Only one broad exothermic peak in the DSC thermogram can be observed, implying that all reaction paths proceed simultaneously. The resulting polymer matrix may be crosslinked to some extent because of the coreaction between BADCy and BMI. Two  $T_g$  values in this matrix may be found depending on the domain size of the polycyanurates phase, matching the observations of some authors.<sup>13–15</sup>

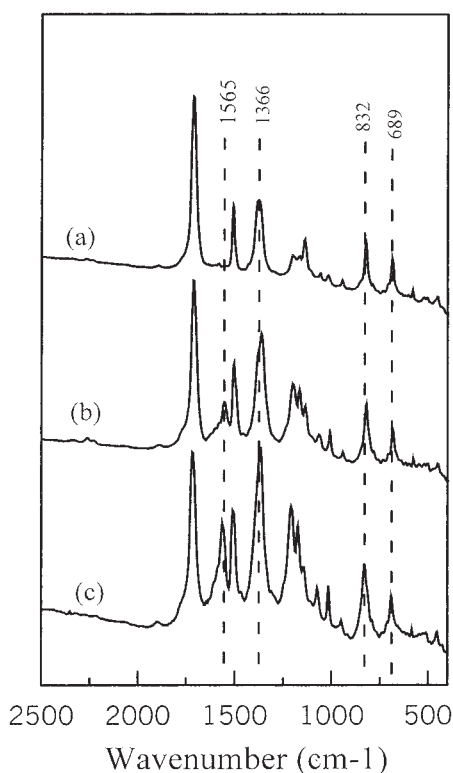
Figure 1(e) shows the DSC trace of a BADCy/BMI system in a molar ratio of 1 : 1 with greater amounts of copper–acetylacetonate (1.4 phr) associated with *p*-nonylphenol (4 phr) as cocatalyst. An exothermic peak exists before the melting peak of BMI (~ 155°C). This thermogram indicates that most of cyanate groups underwent polycyclotrimerizations before the BMI component melted. The BMI component was thus confined in the network matrix of polycyanurates, subsequently melted, and underwent homopolymerizations, thereby forming a sequential IPN. This is in line with the observation of some authors.<sup>3,4,15</sup> The reaction enthalpy ( $\Delta H$ ) of homopolymerization for the BMI component was not obviously observed in the DSC thermogram, probably because this component was tightly confined and the cure reaction consecutively went on for a long time. We rescanned the cured sample by DSC and did not find any melting peaks, implying that the confined BMI component was cured beyond the melting peak on the first scanning. Correspondingly, shown in Figure 5 are some pertinent FTIR spectra of this catalyzed BADCy/BMI blend conducted by dynamic heating from room temperature to 280°C, at a heating rate of 5°C/min. The triazine rings (1565 cm<sup>-1</sup>) were already formed before the melting temperature of BMI (155°C). Subsequently, the characteristic absorptions of =C–H in the maleimide



**Figure 5** Some crucial FTIR spectra for the BADCy/BMI (1 : 1) system with copper–AcAc 1.4 phr and *p*-nonylphenol 4 phr as cocatalyst during dynamic heating from room temperature to 280°C, at a heating rate of 5°C/min.

groups (832 and 689 cm<sup>-1</sup>) were gradually consumed by its homopolymerization beyond 150°C.

Figure 6 compares the FTIR spectra of the completely cured BADCy/BMI hybrid with different levels of catalyst. Figure 6(a) (the last spectrum in Fig. 3) is noncatalyzed, Figure 6(b) (the last spectrum in Fig. 4) is catalyzed with a lower level of catalyst, and Figure 6(c) (the last spectrum in Fig. 5) is catalyzed with an excess level of catalyst. The amount of the triazine rings (1565 cm<sup>-1</sup>) formed in this blend was considerably larger than that in the system with less



**Figure 6** Comparison of the FTIR spectra for the completely cured BADCy/BMI (1 : 1) hybrid with different levels of catalyst: (a) nuncatalyzed, (b) copper-AcAc 1000 ppm and *p*-nonylphenol 4 phr, (c) copper-AcAc 1.4 phr and *p*-nonylphenol 4 phr.

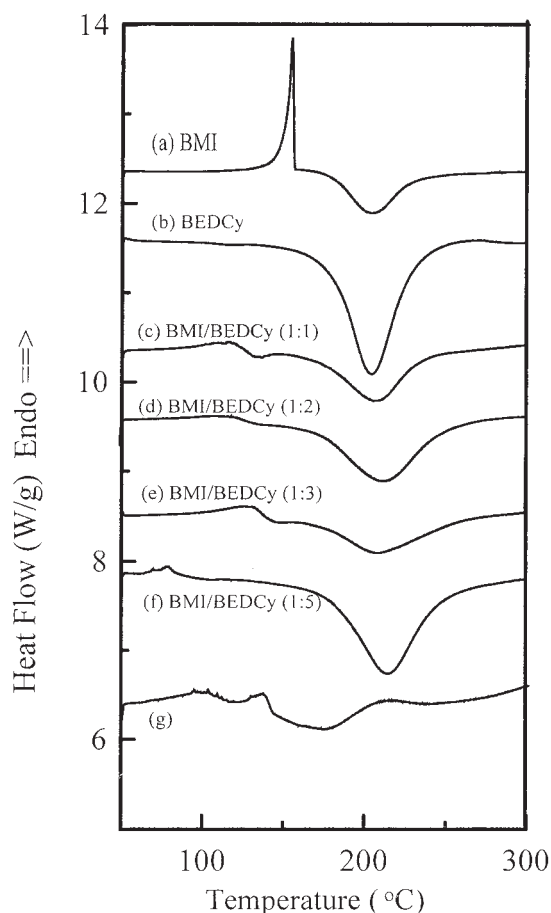
catalyst, suggesting that most of cyanates were converted to triazine rings. This indicates that the major cure reactions in this blend are paths 1 and 2 in Scheme 1 and a real sequential IPN is formed. Nevertheless, some negligible coreaction (path 3) could probably occur. In practice it is impossible to add this much catalyst (1.4 phr copper-acetylacetonate) in such a blend. An appropriate amount of catalyst added to such a blend usually exhibits an overlapping exothermic peak in the DSC thermogram, and coreactions always occur.

Incidentally, the cure system of BADCy/BMIP<sup>3,4</sup> should be especially noted. The reaction exotherm of neat BMIP, ranging from about 225 to 315°C, was observed in the DSC thermogram at a heating rate of 5°C/min. The exothermic temperature range of neat BMIP in the DSC thermogram is higher than that of neat BADCy component. The cure reaction of BADCy was promoted by adding a dicyanate-sensitive catalyst and its exothermic peak shifted to a lower temperature range, resulting in an obvious separation in the exothermic peak.<sup>3</sup> The independent curing therefore progressed. That is why IPN occurs more easily in the BADCy/BMIP cure system than in the BADCy/

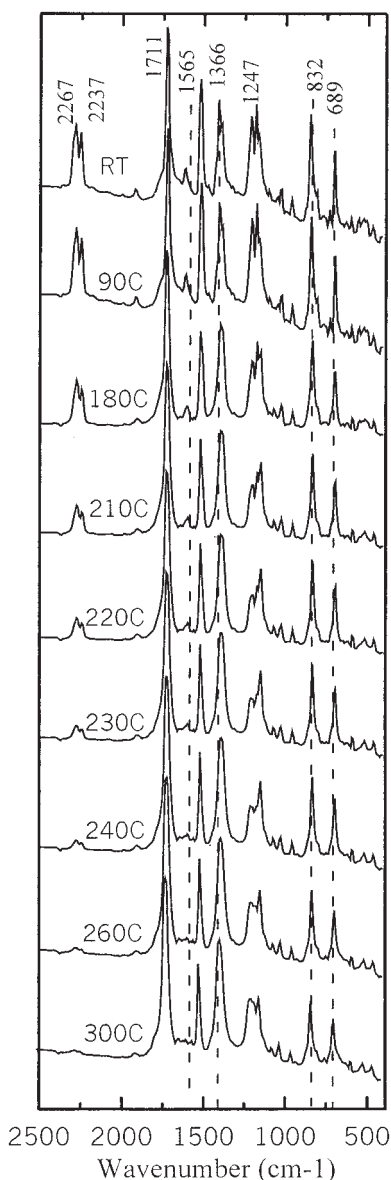
BMI system when an appropriate amount of catalyst was added in this blend.

### BEDCy/BMI cure system

Shown in Figure 7(a) and (b) are the DSC thermograms for curing neat BEDCy and neat BMI, respectively, at a heating rate of 5°C/min. Both components show an exclusive exothermic peak, located in the same temperature range from about 165 to 250°C. Figure 7(c) shows the DSC trace of the BEDCy/BMI system in a molar ratio of 1 : 1 without catalyst, illustrating merely one exothermic peak in the same temperature range as that of its individual components. The progressive FTIR spectra of this system are shown in Figure 8, obtained from dynamic heating *in situ* from room temperature to 300°C, at a heating rate of 5°C/min. These results illustrate that the complete consumption of the cyanate groups (2267 and 2237 cm<sup>-1</sup>) was not accompanied by the formation of a *sym*-triazine ring (1565 cm<sup>-1</sup>). This is virtually the



**Figure 7** DSC thermograms of various formulations at a heating rate of 5°C/min: (a) neat BMI, (b) neat BEDCy, (c) BEDCy/BMI (1 : 1), (d) BEDCy/BMI (2 : 1), (e) BEDCy/BMI (3 : 1), (f) BEDCy/BMI (5 : 1), (g) BEDCy/BMI (1 : 1) with copper-AcAc 1000 ppm and *p*-nonylphenol 4 phr.



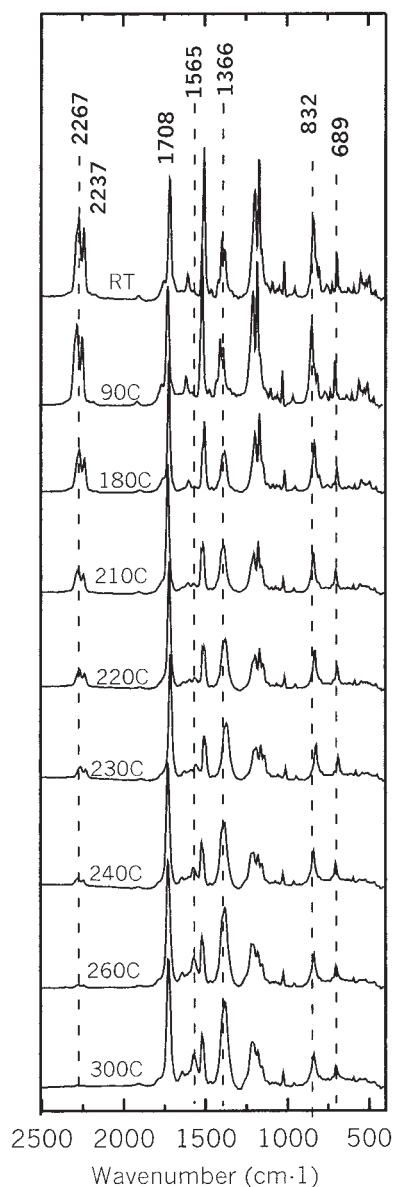
**Figure 8** Some crucial FTIR spectra for the BEDCy/BMI (1 : 1) system during dynamic heating from room temperature to 300°C, at a heating rate of 5°C/min.

same as in the BADCy/BMI cure system, indicating that BEDCy does react with BMI, thereby forming pyrimidine (III) and/or pyridine (IV) structures. We also expect that the pyrimidine structures predominated over the pyridine structures, as analyzed in the BADCy/BMI cure system. This fact was further evidenced by gradually enhancing the BEDCy component in the BEDCy/BMI hybrid system with molar ratios of 2/1, 3/1, and 5/1, respectively.

The corresponding DSC thermograms of these different levels of BEDCy are shown in Figure 7(d), (e), and (f), respectively. All of the exothermic peaks are located in the same temperature range. As expected, the characteristic absorption of the *sym*-triazine ring

(1565  $\text{cm}^{-1}$ ) was not detected in the progressive FTIR spectra of the BEDCy/BMI cure system with a molar ratio of 2/1 (not shown here for brevity), demonstrating that the pyrimidine structures (two  $-\text{OCN}$  units combined with one maleimide unit) predominated over the pyridine structures (one  $-\text{OCN}$  unit combined with two maleimide units).

Not surprisingly, the characteristic absorption of the *sym*-triazine ring (1565  $\text{cm}^{-1}$ ) was observed in the progressive FTIR spectra of the BEDCy/BMI cure system with a molar ratio of 3/1, as shown in Figure 9. In the early stage of curing process (dynamic curing from room temperature to 220°C), the majority of cyanate groups were consumed and coreacted with BMI to



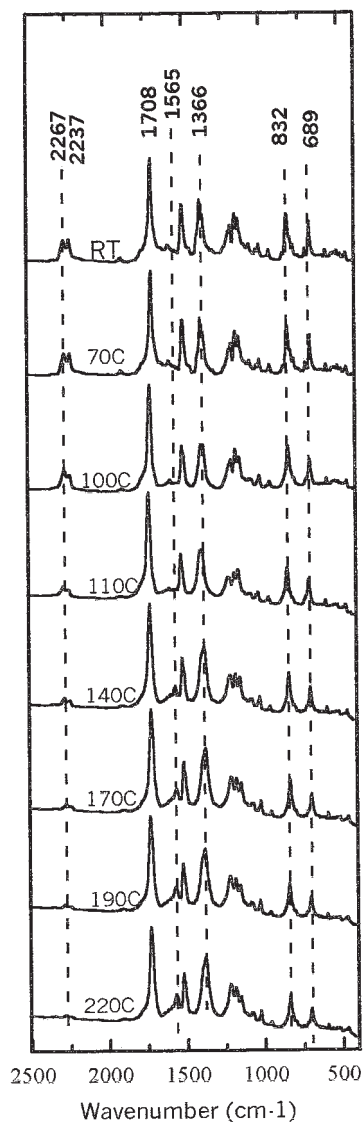
**Figure 9** Some crucial FTIR spectra for the BEDCy/BMI (3 : 1) system during dynamic heating from room temperature to 300°C, at a heating rate of 5°C/min.



form the pyrimidine structures with a composition ratio of 2/1 and no *sym*-triazine ring ( $1565\text{ cm}^{-1}$ ) was detected. Beyond  $220^\circ\text{C}$ , extra composition of the BEDCy monomers was retained; these then proceeded in a polycyclotrimerization to form *sym*-triazine rings. Meanwhile, the intensity of the peaks at  $832$  and  $689\text{ cm}^{-1}$  was kept unaltered beyond  $220^\circ\text{C}$ , indicating that polycyclotrimerization was the exclusive reaction in this stage, and that all of the active maleimide groups ( $832$  and  $689\text{ cm}^{-1}$ ) underwent homopolymerization or coreacted with BEDCy during the early stage.

The progressive FTIR spectra of the BEDCy/BMI cure system with a molar ratio of 5/1 were basically identical to those of the curing system with a molar ratio of 3/1, except for the bigger amount of *sym*-triazine rings formed in the latter stage of the curing process. Two parts of the BEDCy component were consumed to form the pyrimidine structures in the early stage, and three parts of BEDCy were retained and proceeded in a polycyclotrimerization to form *sym*-triazine rings in the latter stage. The BEDCy/BMI cure systems, without excess amounts of BEDCy and external catalysts, basically follow the reaction paths 2 and 3a in Scheme 1. Reaction path 1 takes place additionally if the molar ratio of BEDCy/BMI is more than 2/1, even without a catalyst.

Figure 7(g) shows the DSC trace of a BEDCy/BMI system in a molar ratio of 1 : 1 with copper-acetylacetonate (1000 ppm) associated with *p*-nonylphenol (4 phr) as catalyst. It illustrates that the onset temperature of reaction shifts to a temperature lower than the melting peak of BMI, and thus it appears as two separate exothermic peaks. Actually, there is only one broader exothermic peak, which overlaps with the melting peak of the BMI component. The progressive FTIR spectra (shown in Fig. 10) of this system showed that some characteristic absorptions of triazine rings ( $1565\text{ cm}^{-1}$ ) were detected enhancing at the lower temperature range before the melting peak of BMI ( $\sim 155^\circ\text{C}$ ). As analyzed in the BADCy/BMI cure system, the cocatalyst of copper-acetylacetonate with *p*-nonylphenol may reduce the activation energy of the polycyclotrimerization of BEDCy and facilitate its reaction. Although a moderate amount of polycyclotrimerization of BEDCy took place in this case, the resulting polymer matrix may be crosslinked to some extent because of the coreaction between BEDCy and BMI. In the BEDCy/BMI cure system it is not easy to find a sequential IPN because both of the exothermic reaction peaks of BEDCy and BMI in the DSC thermogram are located at a temperature lower than that of the BADCy and BMIP monomers. Although the cure reaction of BEDCy may be promoted by adding a dicyanate-sensitive catalyst, its exothermic peak cannot shift to a low enough temperature, and



**Figure 10** Some crucial FTIR spectra for the BEDCy/BMI (1 : 1) system with copper-AcAc 1000 ppm and *p*-nonylphenol 4 phr as cocatalyst during dynamic heating from room temperature to  $300^\circ\text{C}$ , at a heating rate of  $5^\circ\text{C}/\text{min}$ .

thus results in an obvious separation of the exothermic peaks.

## CONCLUSIONS

The melting temperature of neat BMI is located at  $155^\circ\text{C}$  and the cure reaction subsequently proceeds just beyond the melting temperature. Despite the use of BADCy or BEDCy, the curing temperature of BADCy/BMI or BEDCy/BMI blend systems is not less than the reaction exotherm of neat BMI in the case without catalyst or with a lower level of catalyst. Meanwhile, only one broad exothermic peak in the DSC thermogram can be observed, suggesting all reaction paths proceed simultaneously. The resulting

polymer matrix may be crosslinked to some extent because of the coreaction between the dicyanate ester and BMI, and thus the formations of pyrimidine and/or pyridine structures. Consequently, the use of BMI in the dicyanate ester/bismaleimide blends facilitates coreaction between its components without catalyst or with a lower level of catalyst. Unless a high level of catalyst is used, the cure reaction of the dicyanate ester cannot be encouraged to surpass the reaction exotherm of neat BMI and results in an obvious separation of the exothermic peak. Therefore, the complete sequential IPN cannot easily be found.

In contrast to the dicyanate ester/BMI blend systems, the dicyanate ester/BMIP blend systems form the sequential IPN more readily if a dicyanate-sensitive catalyst is properly used. The reaction exotherm of neat BMIP, ranging from about 225 to 315°C, was observed, higher than that of neat BMI. The exothermic temperature range of neat BADCy almost overlaps with that of the neat BMIP component, and the exothermic temperature range of neat BEDCy is much lower than that of the neat BMIP component. Consequently, when the cure reaction of dicyanate ester is encouraged by adding a dicyanate-sensitive catalyst, its exothermic peak shifts to a lower temperature range, resulting in an obvious separation of the exothermic peak. The independent curing thus progressed, thereby forming the sequential IPN.

Polycyclotrimerization of dicyanate ester is known to be slow in the absence of metal carboxylates, chelates, or Lewis acids. The presence of the BMI component in the BMI/cyanate blend system will tend to disrupt and retard the cyclotrimerization, and thus no *sym*-triazine ring was found. If the blend does not contain any specific catalyst to encourage the formation of polycyanurate, then the absence of a *sym*-triazine ring is perhaps not so surprising.

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