

Study on the Cure Behavior of 2,7-Dihydroxynaphthalene Dicyanate

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ABSTRACT: The cure behavior of 2,7-dihydroxynaphthalene dicyanate (DNCY) was studied by means of nonisothermal DSC, isothermal DSC, and FTIR. In nonisothermal DSC, the cure kinetics parameters of DNCY were calculated by the Coats–Redfern method and compared with those of biphenol A dicyanate (BACY). It was revealed that the activation energy of DNCY was enhanced compared with that of BACY because of the presence of naphthalene, and the gelation of DNCY occurred within the conversion range 50–55%, which is lower than that of BACY. In isothermal DSC, a good time–temperature superposition of the conversion profiles of DNCY was obtained during conversions below about 50%. These results

were consistent with those obtained by nonisothermal DSC. For the catalyzed system, the autocatalytic behavior prevailed at conversions below 30%, whereas the catalytic behavior occurred only at conversions above 30%. *In situ* FTIR spectra revealed that a triazine network was formed by cyclotrimerization of the OCN functional group during the cure process for systems with and without catalysts. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3927–3939, 2004

Key words: 2,7-dihydroxynaphthalene dicyanate (DNCY); curing of polymers; differential scanning calorimetry (DSC); FTIR; triazine network

INTRODUCTION

Cyanate ester resins have attracted increasing attention because of their highly desirable chemical, electrical, and mechanical properties for several applications, such as high-speed printed circuit boards and aerospace structural composites, for example.^{1–3} With good processability in most applications, they surpass the performance of the state-of-the-art formulations in structural composites like epoxies and bismaleimides.^{2,4} They exhibit good solubility in solvents and low moisture absorption compared with those of bismaleimides and epoxies.^{2,5,6} Because of their good miscibility and physicochemical attributes of epoxy and bismaleimide systems, cyanate ester resins are also blended with epoxies and bismaleimides to enhance their thermal characteristics and fracture toughness.^{7–10}

Although many kinds of cyanate ester resins have been investigated, to date few studies have been reported concerning cyanate ester resin containing a naphthalene structure [2,7-dihydroxynaphthalene dicyanate (DNCY)]. In our recent study,¹¹ DNCY resins exhibited higher glass-transition temperature, thermal stability, and modulus than those of commercial bisphenol A dicyanate resins (BACY) because naphthalene enhanced the rigidity of the molecule chain. Furthermore, the thermoset cure of DNCY may be quite different from that of BACY because of the electroat-

tracting difference between naphthalene and benzene, and many other properties of DNCY may also change because of the presence of naphthalene in the network structure. To fully understand and control the processing of this new thermoset cure to obtain superior properties, it is necessary for us to study the thermoset cure kinetics and their properties.

The purpose of this research was to study the thermoset cure of DNCY without and with catalysts. Different techniques based on DSC, FTIR, ¹³C-NMR, dynamic dielectric analysis, and their combination were used to trace the thermoset cure.^{12–17} In this study, nonisothermal DSC and isothermal DSC were used to determine the exothermic heat of cure and analyze the complex cure nature of DNCY. In view of catalyst choice, many kinds of catalysts were studied in detail for the cure reaction of dicyanate esters.^{18–21} Shimp²² found that transition metal acetylacetonates are preferable to carboxylates or naphthalene because the resulting networks have better thermal stability and less moisture absorption property during the dicyanate ester cure kinetics by the gel behavior of the resin. Therefore, cobalt acetylacetonate and nonylphenol (NP) were chosen as catalysts. In addition, *in situ* FTIR was chosen to provide more detailed information on the nature of the cure reaction.

EXPERIMENTAL

Materials

DNCY was synthesized by a two-step method.^{23,24} First, cyanogen bromide was synthesized by reaction

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of bromine and potassium cyanide in H_2O , while maintaining the temperature of the reaction mixture at -5 to $5^\circ C$ in an ice-salt bath. Second, DNCY was synthesized by 2,7-dihydroxynaphthalene and cyanogen bromide using acetone as solvent in the presence of triethylamine at a temperature from -5 to $10^\circ C$. Cobalt acetylacetonate was prepared by reacting cobaltous chloride with acetyl acetone. Technical-grade NP (99%) was used. All solvents used were of reagent grade.

Sample preparation

The required amount of cobalt acetylacetonate at 0.11 mmol/mol $[Co(AcAc)_2/dicyanate\ esters]$ was predissolved in NP at 2% of the total resin weight at $100^\circ C$ with continuous stirring until a homogeneous mixture was obtained, after which the mixture was cooled to room temperature. The catalytic mixture was added to the preselected weight of the cyanate resins dissolved in solvent at $60^\circ C$, stirred for 5 min, and the solvent was evaporated in vacuum at room temperature. The mixture was pulverized to obtain a homogeneous mixture.

Differential scanning calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) supported by a Perkin-Elmer computer for data acquisition. DSC was calibrated with a high-purity indium. A 7–10 mg amount of the dry, powdered sample was used for DSC analysis, and experiments were conducted under a nitrogen flow of $20\ cm^3/min$. In nonisothermal DSC experiments, all the samples were subjected to a dynamic DSC scan from 50 to $400^\circ C$ at different heating rates ($\beta = 10, 20, 30, 40^\circ C/min$). The conversion of each sample (α) under nonisothermal conditions can be calculated from

$$\alpha = \frac{(H_{noniso})_T}{H_{noniso}} \quad (1)$$

where $(\Delta H_{noniso})_T$ is the enthalpy of reaction at a temperature T calculated from the nonisothermal mode, and ΔH_{noniso} is the total enthalpy from the nonisothermal mode. Isothermal curing was carried out at different temperatures. All the sample were then subjected to a dynamic DSC scan from 50 to $400^\circ C$ at $10^\circ C/min$ to determine the residual heat of reaction (ΔH_{res}). The conversion of each sample (α) under isothermal conditions can be calculated from eq. (2) by assuming a single reaction mechanism:

$$\alpha = \frac{(\Delta H_{iso})_t}{\Delta H_{iso} + \Delta H_{res}} \quad (2)$$

where $(\Delta H_{iso})_t$ is the enthalpy of reaction at a time t calculated from the isothermal mode, and $(\Delta H_{iso} + \Delta H_{res})$ is the total enthalpy calculated from the isothermal mode (ΔH_{iso}) and the residual mode (ΔH_{res}).

FTIR

FTIR studies were performed using a Vector 22 FTIR spectrophotometer (Vector Laboratories, Burlingame, CA) equipped with a temperature-controlled sample holder that allowed for *in situ* analysis of the curing reaction. Thin films of the resins were prepared from the samples dissolved in solvent casting on NaCl cells. The samples were then seared in the sample holder that had been preheated to the desired isothermal temperature. The spectra were tested at different time intervals. Peak areas were calculated for 2264 (cyanate vibration), 1567.7, and $1360.5\ cm^{-1}$ (triazine vibration). The C—H vibration of the naphthalene ring at $1512.2\ cm^{-1}$ was used as the reference peak. Because the peak areas are directly proportional to concentration, the normalized concentration of cyanate or triazine at any time was calculated from

$$C(t) = \frac{A(t)/A(t)_{1512.2}}{A(0)/A(0)_{1512.2}} \quad (3)$$

where $A(t)$ is the absorbance of cyanate or triazine at time t ; $A(t)_{1512.2}$ is the absorbance of naphthalene ring at time t ; $A(0)$ is the initial absorbance of cyanate or triazine; $A(0)_{1512.2}$ is the initial absorbance of naphthalene ring; and $C(t)$ is the fraction of unreacted cyanate or the fraction of created triazine.

RESULTS AND DISCUSSION

Nonisothermal DSC

With respect to a pure parameter estimation, nonisothermal DSC offers potentially much more data with fewer experiments and would probably take less time.^{26,27} Therefore, nonisothermal DSC is a convenient tool for monitoring exothermic cure reactions.

Typical nonisothermal DSC thermograms of the cure for different systems are shown in Figure 1. The monomodel distribution confirms the homogeneous distribution of the catalysts in the resin. The cure characteristics and the enthalpy of cure reaction (ΔH) under different conditions are given in Table I. The relations of conversion versus temperature for cure reaction of DNCY are shown in Figure 2.

It is known that no reaction occurs if absolutely pure dicyanate ester is heated, and thereby the reaction is believed to be catalyzed by residual hydrogen-donating impurities present in the sample, such as phenol, moisture, and so forth.¹⁹ On addition of the

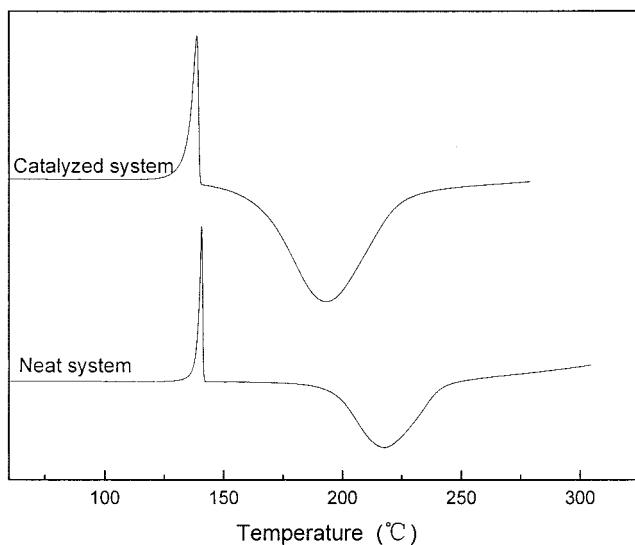


Figure 1 DSC thermograms of the cure reactions for neat and catalyzed systems at 10°C/min.

catalysts, the curing shifted to lower temperature as observed from a systematic drift of the cure characteristics, such as temperature of onset of cure (T_i), peak temperature in DSC (T_p), conversion at T_p (α_p), temperature corresponding to 50% conversion (T_{50}), and temperature corresponding to end of cure (T_f), as shown in Table I and Figure 2.

Kinetics of cure

The kinetics of uncatalyzed cure reaction of dicyanate ester has been established to follow a second-order autocatalytic model²⁷ as

$$\frac{d\alpha}{dt} = k_1(1 - \alpha)^2 + k_2(1 - \alpha)^2\alpha \quad (4)$$

However, in some cases, for both catalyzed and uncatalyzed systems an n th-order reaction has been found to explain the cure profile satisfactorily.^{21,28}

Under nonisothermal conditions, this rate expression takes the form

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (5)$$

where $f(\alpha)$ is the mathematical expression of the kinetics model, β is the heating rate, E is the activation energy, and A is the Arrhenius frequency factor.

Different methods are available in the literature for calculating the activation energy values. In the present case, the Coats–Redfern method was applied to derive the kinetic parameters.

Coats–Redfern method^{21,28,33}

In view of the high propensity of cyanate esters for externally added catalysts, the autocatalysis can be neglected in catalyzed systems and $f(\alpha)$ can be considered to follow the classical n th order model as

$$f(\alpha) = (1 - \alpha)^n \quad (6)$$

Under nonisothermal conditions, eq. (2) takes the form

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) (1 - \alpha)^n \quad (7)$$

where n is the order of reaction.

Several integral forms of the above equation have been used to evaluate the kinetics parameters. The most versatile one is the Coats–Redfern equation (C-R), given as

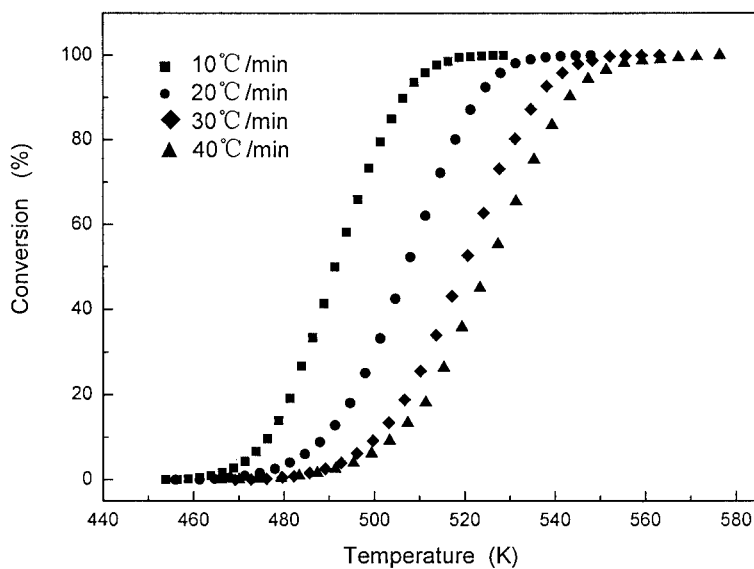
$$\ln[g(\alpha)/T^2] = \ln[(AR/\beta E)(1 - 2RT/E)] - E/RT \quad (8)$$

where $g(\alpha) = [1 - (1 - \alpha)^{1-n}]/(1 - n)$; for $n = 1$, $g(\alpha) = -\ln(1 - \alpha)$; R is the gas constant.

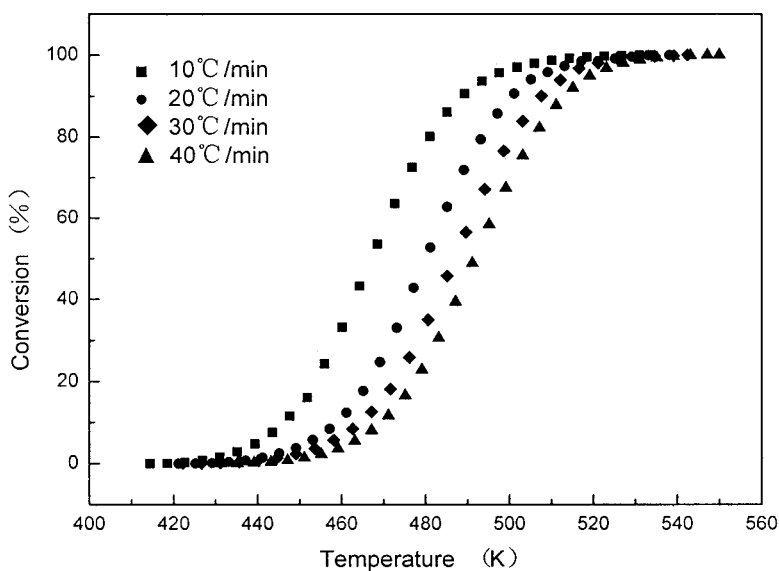
The order of reaction was estimated by the degree of fitness in plots of $\ln[g(\alpha)/T^2]$ against $1/T$ for different values of n . A typical kinetics plot for determination of

TABLE I
Thermal Cure Characteristics of DNCY

System	β (°C/min)	T_i (°C)	T_p (°C)	α_p (%)	T_{50} (°C)	T_f (°C)	ΔH (J/g)
Neat system	10	196.4	227.8	48.0	218.3	254.4	-794.7
	20	208.5	234.7	52.1	234.0	274.1	-805.4
	30	218.7	247.8	53.8	246.6	287.3	-848.3
	40	222.4	253.4	53.0	252.6	296.9	-836.2
Catalyzed system	10	164.2	193.0	48.6	193.7	249.5	-734.7
	20	177.4	206.3	49.0	207.2	261.0	-804.9
	30	183.7	213.8	52.5	214.1	271.1	-785.6
	40	186.9	218.4	50.4	218.9	277.5	-816.7



(a)



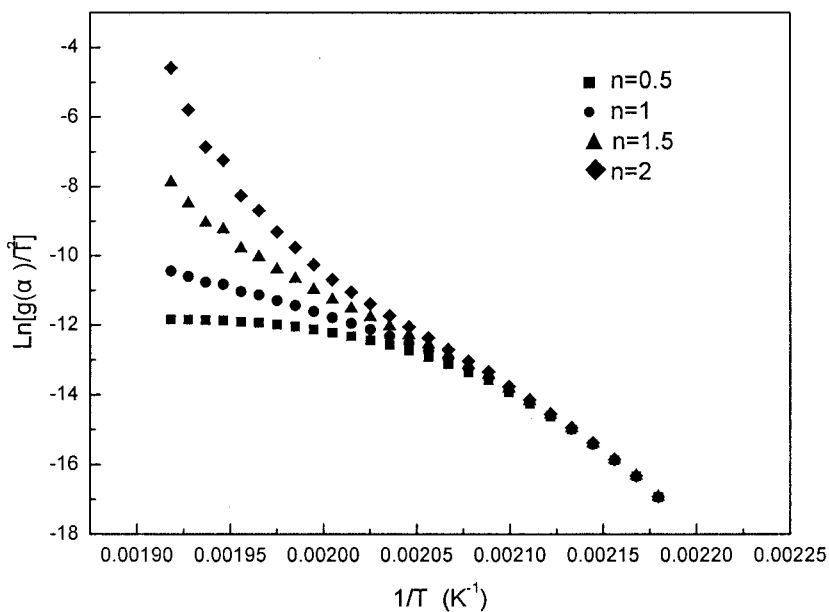
(b)

Figure 2 Conversion versus temperature for cure reaction of DNCY by nonisothermal DSC: (a) neat system; (b) catalyzed system.

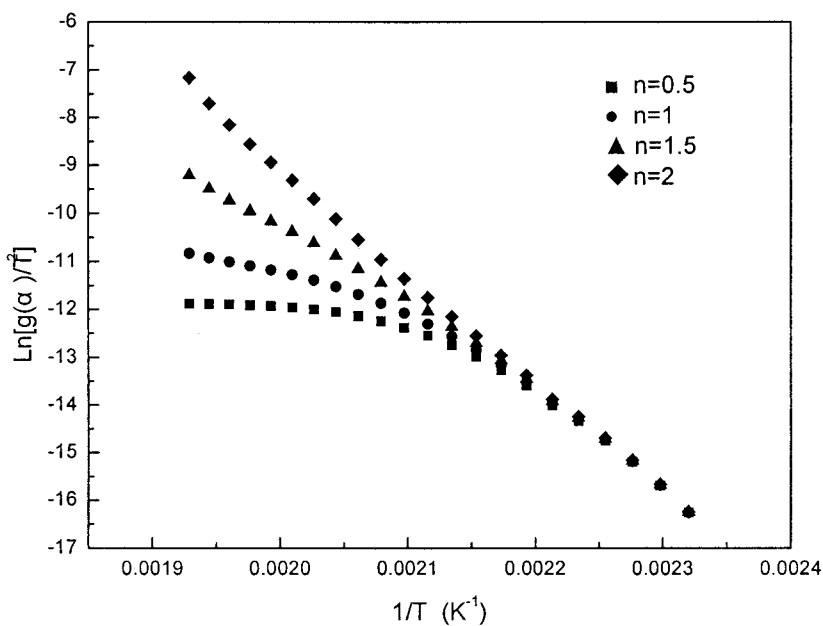
n is given in Figure 3. In most cases the values of n were found to be very close to 1.5 within most of the conversion range for neat and catalyzed systems, which was the same as that observed by Mathew for BACY resin.²⁹ The kinetics parameters (E and A) were determined from the linear plots of $\ln[g(\alpha)/T^2]$ against $1/T$ for $n = 1.5$ for different systems and different heating rates.

Calculation of the activation energy and analysis of the thermoset behavior

The E values of the neat and catalyzed system calculated by the C-R method are shown in Table II. The E values of two systems calculated by the C-R method were found to vary with different heating rates (β). The variation of E is only apparent and its effect can be compensated by a corresponding variation in the



(a)



(b)

Figure 3 Coats-Redfern plot for determination of n : (a) neat system; (b) catalyzed system.

value of A , that is, kinetics compensation (KC) correction. Because the reaction manifested a KC effect, the E values should be normalized for the average preexponential factor A of the neat system using the KC

plot. The E values of the catalyzed system normalized by KC correction was 205.1 kJ/mol, and the E value of the neat system was 187.6 kJ/mol. Obviously, the E value of the catalyzed system is lower than that of the

TABLE II
Computation Results of Two Systems Computed by Coats–Redfern Method by Nonisothermal DSC

System	β (°C/min)	E (kJ/mol)	A (s ⁻¹)	Correlation coefficient	E for $A = 1.74 \times 10^{20}$
Neat system	10	205.1	1.74×10^{20}	0.99677	205.1
	20	238.1	6.61×10^{24}	0.99886	
	30	245.1	1.28×10^{25}	0.99649	
	40	258.0	9.91×10^{27}	0.9991	
Catalyzed system	10	144.7	8.11×10^{15}	0.99647	187.6
	20	160.3	3.31×10^{17}	0.99763	
	30	162.9	5.85×10^{17}	0.99965	
	40	166.5	1.23×10^{18}	0.99888	

neat system, which illustrates that the E value is reduced in the presence of catalysts. For the neat system, the E value calculated by C-R was 205.1 kJ/mol, which was about 30 kJ/mol higher than that of BACY (the activation energy value of BACY calculated by C-R was 174.8 kJ/mol by Mathew²⁹). It was revealed that the existence of naphthalene in the structure enhances the E value, of which the electroattracting ability is stronger than that of benzene and affects the cure reaction activity of dicyanate ester.

Detailed sector-wise analysis using the Coats–Redfern method showed that cure kinetics depended on the conversion, although the entire reaction could be described satisfactorily by an overall n th-order reaction. Examination of the kinetics plot showed the optimum value of n for two major sectors for the cure reaction, as evidenced from a difference in the slopes of the cure setting at the conversion range 50–55%, as shown in Figure 4(a) and (b) for two cases. This means that the cure kinetics differs below and above this conversion range. This difference arises from the gelation of the cyanate ester, which is known to occur at this conversion level (α_{gel}). Obviously, the catalysts have no effect on α_{gel} according to Figure 4. α_{gel} of DNCY at which the gelation occurred is lower than that of BACY, whose α_{gel} was within the conversion range 58–65% (by Mathew et al.²⁸), because the introduction of naphthalene in the DNCY structure enhanced the rigidity of molecule chains. These results confirmed that α_{gel} was not affected by the catalysts and was influenced only by the structure.

Isothermal DSC^{19,26,31,34–36}

Isothermal DSC is a basic method for computing thermoset cure kinetics, which proved to be a more precise method than nonisothermal DSC method by MacCallum and Tanner.³⁴

For isothermal DSC cures, the values of $\ln k(T)$ and n were determined from eq. (6):

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k(T) + n \ln(1 - \alpha) \quad (9)$$

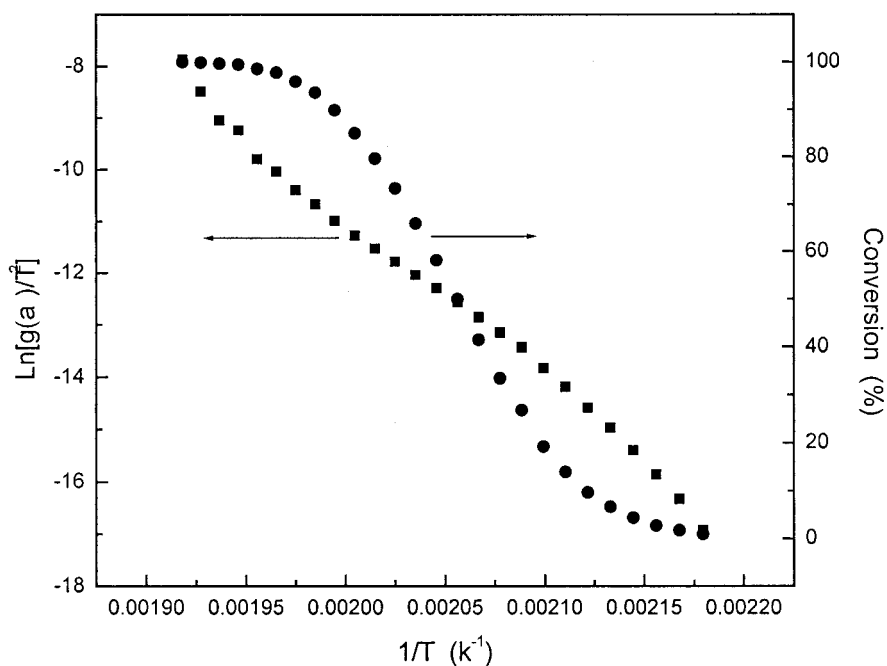
for each temperature. Then, the values of E and $\ln A$ were estimated by plotting $\ln k(T)$ versus T^{-1} from eq. (7):

$$\ln k(T) = \ln A - \frac{E}{RT} \quad (10)$$

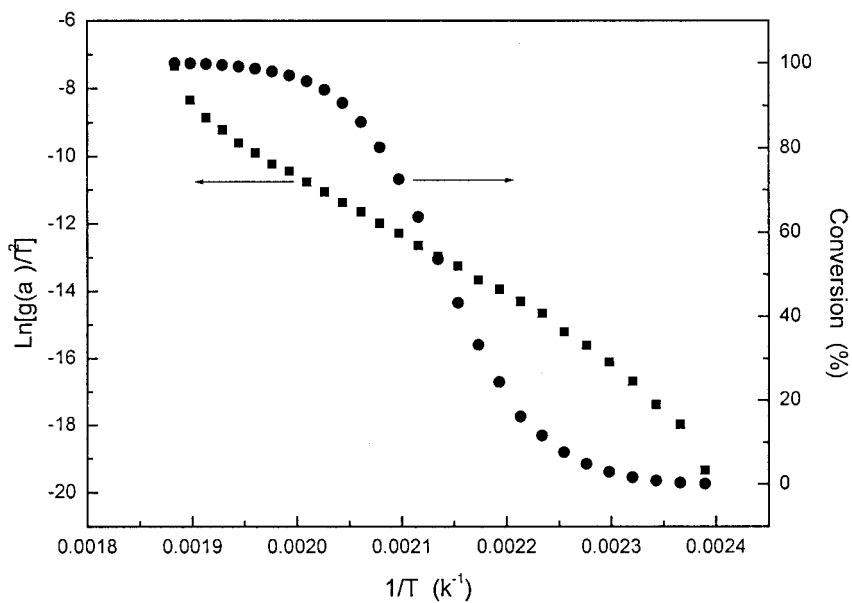
The relations of conversion versus time for cure reaction of DNCY by isothermal DSC are shown in Figure 5. With an increase in cure temperature, the conversion increased and the reaction time shortened for both of the two systems. On addition of the catalysts, the cure temperature obviously decreased and the reaction conversion increased. The E and A values computed by isothermal DSC are shown in Table III.

The plots of experimental rate of reaction against conversion for the neat and catalyzed system are shown in the Figure 6. The typical autocatalytic behavior (increase of the reaction rate with conversion) is shown in Figure 6(a). This confirms that the cure reaction of the neat system is autocatalytic behavior. In contrast with results in the literature, it was found that autocatalytic behavior also occurs at conversion below 30% for the catalyzed system from Figure 6(b). The catalytic behavior (decrease of the reaction rate with conversion and fit of the linear relation for the reaction rate against conversion) occurs only at conversion above 30% for the catalyzed system. This result illustrates that there are two contributions (autocatalytic and catalytic) to the rate of reaction for the catalyzed system.

Cyanate conversions at different temperatures can be horizontally shifted along the logarithmic time axis to form a master curve by overlapping the corresponding curves according to an arbitrarily selected reference temperature (T_r). As shown in Figure 7(a) and (b), a good overlay is evident for



(a)

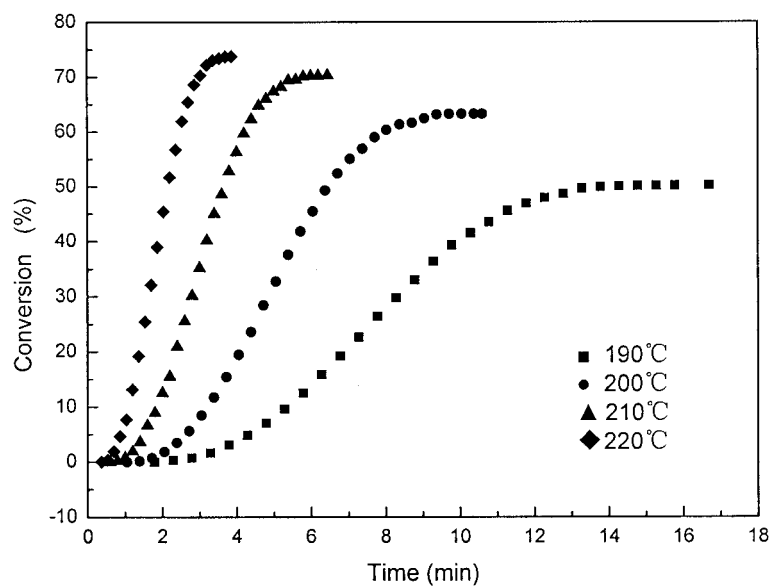


(b)

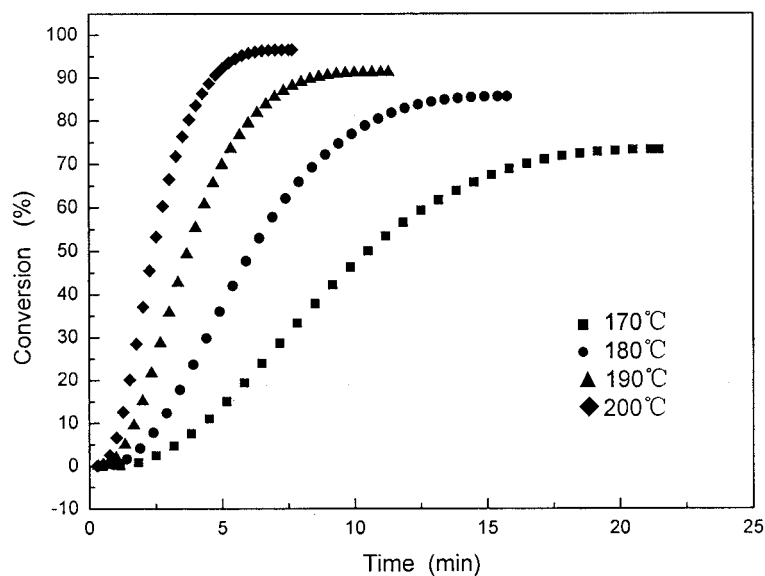
Figure 4 Kinetic plot of optimum value of n versus conversion for cure reaction of DNCY at 10°C/min. (■) C-R plot for $n = 1.5$; (●) variation of α as a function of temperature: (a) neat system; (b) catalyzed system.

conversions lower than about 50%, independent of the cure temperature (except for 190°C for the neat system, under which the cure reaction does not

occur sufficiently because of too low temperature). Below this conversion the experimental data for all cure temperature form a single curve, whereas



(a)



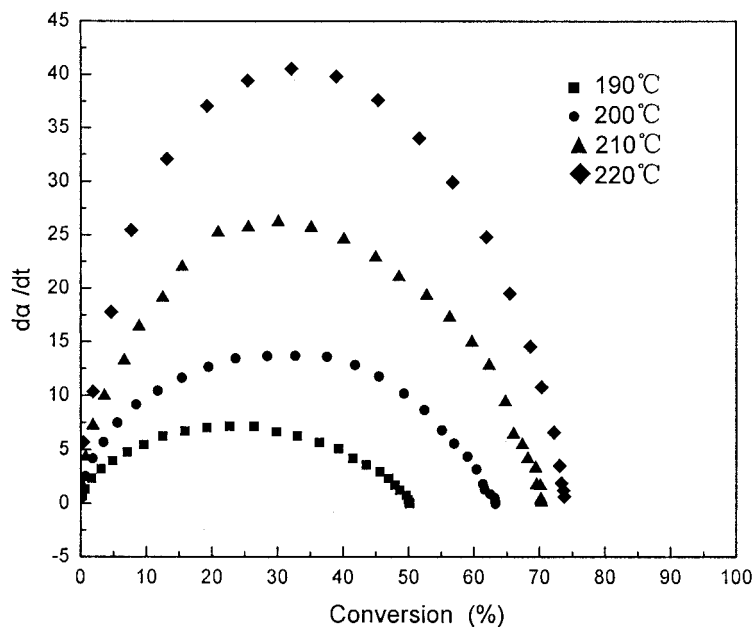
(b)

Figure 5 Conversion versus time for cure reaction of DNCY isothermal DSC: (a) neat system; (b) catalyzed system.

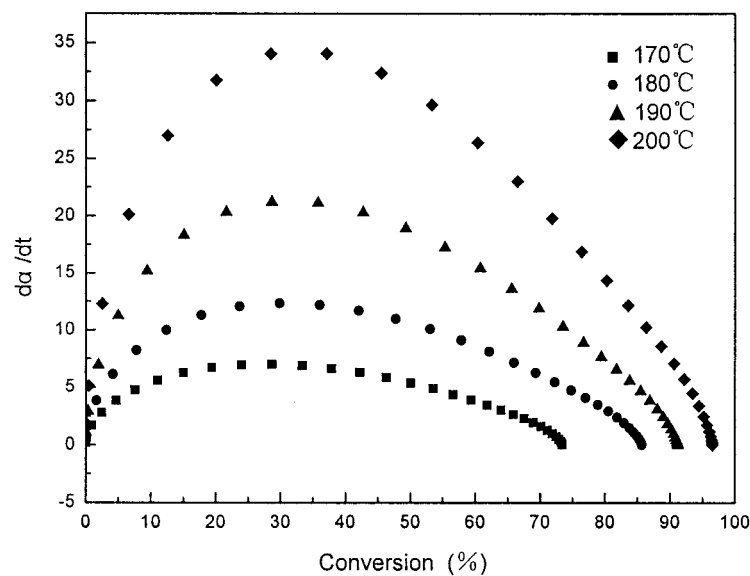
above this conversion the curve starts to diverge and the conversion distinctly increases as the curing temperature increases. This verified that the reaction was kinetically controlled and the effect of diffusion on the cure kinetics was not evident below about 50%, whereas the cure kinetics becomes increasingly diffusion-controlled above this conver-

TABLE III
Computation Results of Two Systems Using Isothermal DSC

System	E (kJ/mol)	A (s^{-1})
Neat system	102.6	8.5×10^9
Catalyzed system	76.7	1.8×10^{10}



(a)

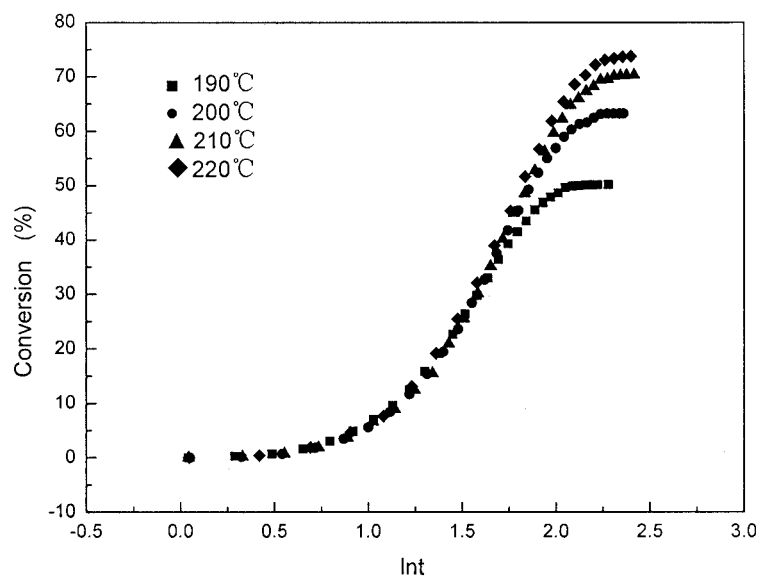


(b)

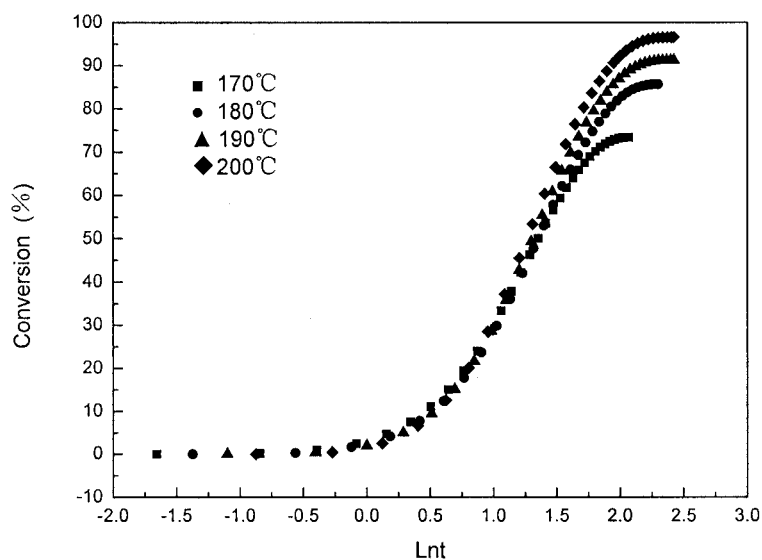
Figure 6 Reaction rate versus conversion degree in isothermal DSC experiments at different temperatures: (a) neat system; (b) catalyzed system.

sion. These results confirm that the reaction was kinetically controlled before the gelation, whereas the reaction was diffusion-controlled after the gelation. Compared with BACY, α_{gel} decreases because

of the effect of naphthalene in the structure on the rigidity of molecule chains (this conversion range is about 60% for BACY), a result that agrees perfectly with that obtained by nonisothermal DSC analysis.



(a)



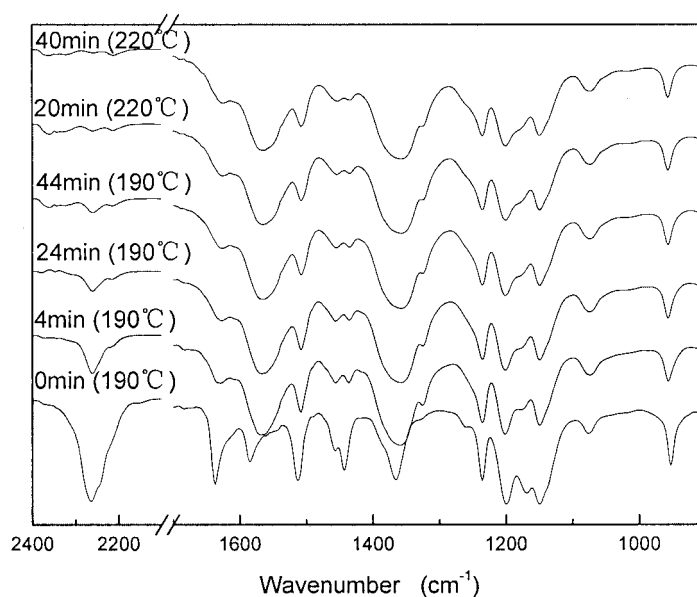
(b)

Figure 7 Superposition at the reference temperature (T_r) of cyanate conversion profiles in isothermal DSC experiments: (a) neat system, T_r : 190°C; (b) catalyzed system, T_r : 180°C.

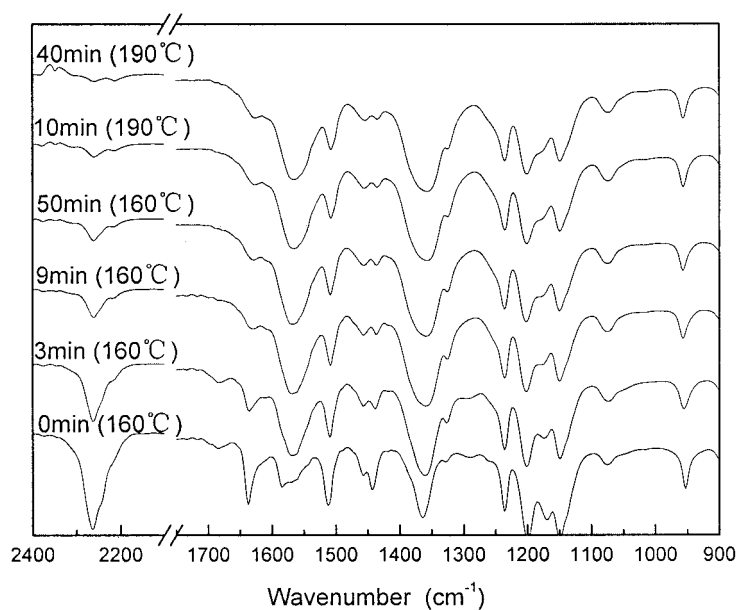
FTIR analysis

The systems with and without catalysts were analyzed by *in situ* FTIR. Spectra of the two systems are shown in Figure 8. The absorption of the OCN group appears at 2264 cm^{-1} and the absorption of the triazine ring appears at 1568.7 and 1360.5 cm^{-1} , which formed by

the cyclotrimerization reaction involving the cyanate group. Triazine groups were reported at 1568.7 and 1360.5 cm^{-1} in the spectrum of uncured monomer, which confirms that some DNCY had been cyclotrimerized during the synthetic process in the presence of triethylamine. The typical infrared spectra of DNCY



(a)

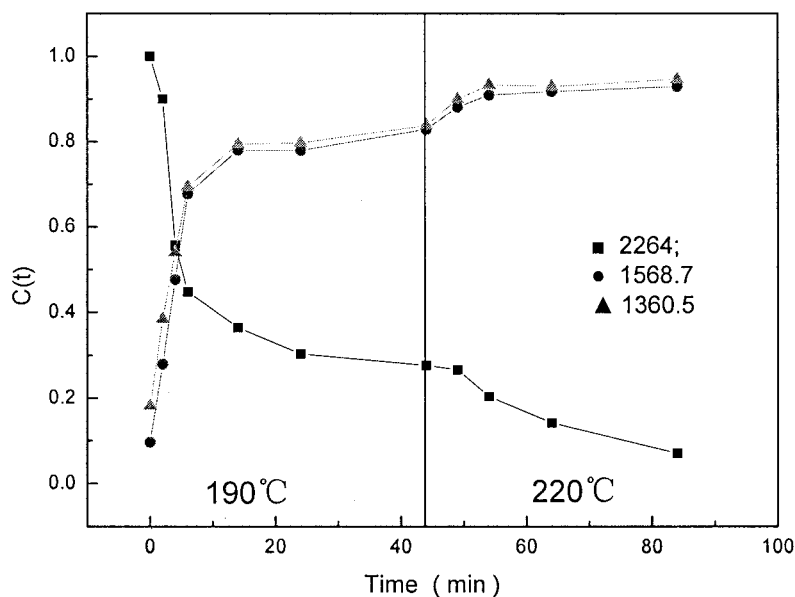


(b)

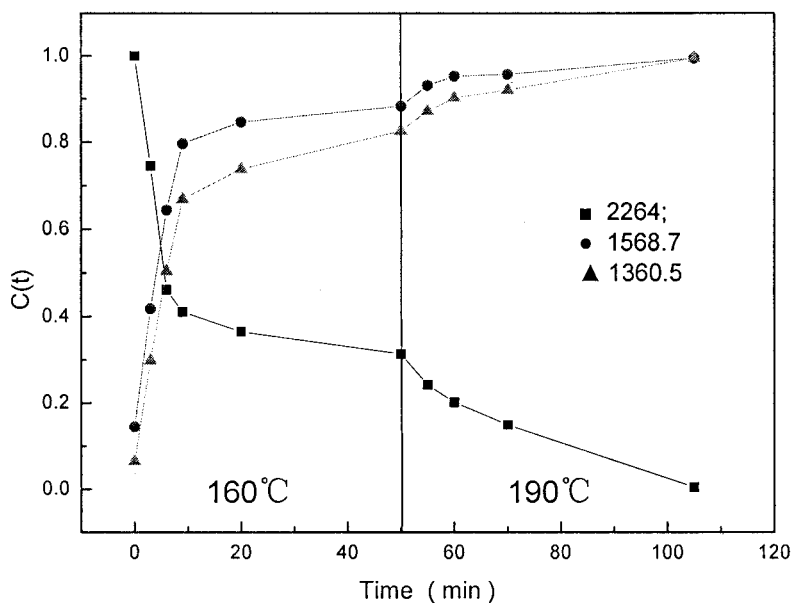
Figure 8 FTIR spectra of different cure times and temperatures of DNCY: (a) neat system; (b) catalyzed system.

ester that had been cured at different temperatures for different times are shown in Figure 8. As shown in Figure 8, the absorption of the OCN group was gradually being minimized and finally disappeared; simultaneously the absorption of the triazine group was gradually being strengthened, which confirmed that

the triazine network was formed by cyclotrimerization of the OCN functional group for systems with and without catalysts during the cure process. The $C(t)$ of the OCN group and the triazine are shown in Figure 9. It is obvious that the $C(t)$ variations of the two groups were quicker for the catalyzed system than for the neat



(a)



(b)

Figure 9 $C(t)$ variations of the two groups during the cure by *in situ* FTIR: (a) neat system; (b) catalyzed system.

system, and the cure temperature was also lower. This verifies that the cure reaction rate evidently sped up as a result of the presence of the catalysts.

CONCLUSIONS

The cure kinetics of DNCY was studied by DSC and FTIR. The variations of activation energy were ob-

tained from the analysis of nonisothermal DSC and isothermal DSC. The E values of systems without and with catalysts calculated by Coats-Redfern method were 205.1 and 187.6 kJ/mol, respectively. The E value of DNCY for the neat system was >30 kJ/mol higher than that of BACY for the neat system because of the presence of naphthalene in the structure. The gelation

of DNCY occurred at the conversion range of 50–55%, which was lower than that of BACY. This conversion level was not affected by the catalysts and influenced only by the structure. These results were also obtained from isothermal DSC. In isothermal DSC, a good time–temperature superposition of the conversion profiles of DNCY was obtained during conversions lower than about 50%, whereas the curve started to diverge and the conversion distinctly increased as the curing temperature increased above this conversion. From isothermal DSC, it was found that the autocatalytic behavior occurred at conversion < 30% and the catalytic behavior occurred only at conversion > 30% for the catalyzed system. There were two contributions (autocatalytic and catalytic terms) to reaction in the catalyzed system. By FTIR analysis, DNCY cured and formed a triazine network by thermal/catalytic cyclotrimerization, which was the same as that of BACY.

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