Cure Kinetics of Different Molar Ratios of 4,4'-Bismaleimidodiphenylmethane and Bisphenol A Dicyanate

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SYNOPSIS

Bismaleimide–triazine (BT) resins are thermosets derived from the addition polymerization of different molar ratios of 4,4'-bismaleimidodiphenylmethane (BM) and bisphenol A dicyanate (BA). The possible cross-linking reactions involved in the formation of BT resins are addition polymerization of BM, cyclotrimerization of BA, and heteropolymerization between BM and BA. Fourier-transform infrared spectroscopy reveals that cyclotrimerization of BA occurs during the cure of a 1 : 2 molar ratio of BM to BA (as 1M2A). No sign of cyclotrimerization is observed for the case of the 1 : 1 molar ratio of BM to BA (as 1M1A). A dynamic differential scanning calorimeter (DSC) is employed to study the cure kinetics. The apparent activation energy evaluated from the Prime method is increased with the content of the BM component in the starting mixture. The different pattern of activation energy with fractional conversion (α) indicates the different chemical nature for the cure reactions of 1M1A and 1M2A. The empirical rate functions thus evaluated are $2.32 \times 10^5 + 5.62 \times 10^5 \alpha - 8.61 \times 10^5 \alpha^2$ and $6.07 \times 10^5 + 1.06 \times 10^6 \alpha - 1.66 \times 10^6 \alpha^2 \text{ s}^{-1}$ for the cure reactions of 1M1A and 1M2A, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Bismaleimide–triazine (BT) resins are thermosets derived from the addition polymerization of 4,4'-bismaleimidodiphenylmethane (BM) and bisphenol A dicyanate (BA).[1-4] Dependent on the molar ratios between the two components, a variety of liquid or solid prepolymers can be generated. Due to the ease of dissolution of prepolymers in many organic solvents, BT resins can be readily used as impregnating resins. Also, the substantially better resistance to the catastrophic loss of insulation resistance, increasing resistance to moisture absorption, excellent chemical resistance, good dimensional stability, low dielectric constant, and low dielectric loss make BT resins attractive for circuit-board applications where high reliability is critical.

The processing of thermosetting polymers involves the exposure of these materials to varying levels of heat treatment. The temperature variation in a thermosetting material during cure depends to a large extent on the heat of reaction and thermal conductivity of the material at different stages of the cure cycle. Therefore, knowledge of these properties and the manner in which they vary with temperature and degree of cure would be useful in the analysis, control, and design of processing conditions. The processing of thermosetting BT resins is interesting in considering the complex nature of the cross-linking reactions involved in the cure of BM and BA. Several reactions, such as the cyclotrimerization of aromatic dicyanate,[5-10] the addition polymerization of bismaleimide,[11] and the cyclization reactions between the two components (Fig. 1), are responsible for the formation of network structures. Also, the molar ratio between BM and BA adds complexity to the cure conditions. Therefore, the purpose of this research is to study the cure kinetics of different molar ratios of BM and BA. Differential scanning calorimetry was used by a number of workers to determine the exothermic heat of cure and the kinetics of cure of thermosetting materi-
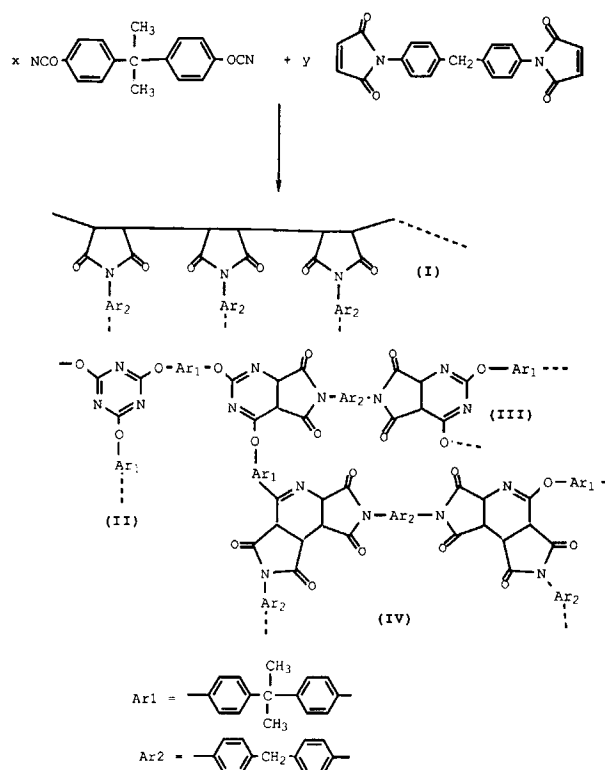
Figure 1 Formation of BT resins from the cure reactions of the mixture of BM and BA.

als.[12-14] A comprehensive review on the kinetic study of cure reactions using DSC has been given by Prime.[12] In view of the complex nature, dynamic techniques were employed by scanning samples with different heating rates in a differential scanning calorimeter (DSC). In addition, Fourier-transform infrared spectroscopy (FTIR) was chosen to provide more detailed information on the nature of cure reactions.

EXPERIMENTAL

Materials and Instrumentation

Bisphenol A dicyanate (BA) was synthesized according to the Grigat's procedures.[5] The crude product was further purified by consecutive precipitations with distilled water. 4,4'-Bismaleimidodiphenylmethane (BM; TCI Chem.) was used as received.

Different molar ratios of BM and BA were homogeneously mixed by the use of chloroform and cast on a KBr disc. The sample disc was then vacuum-distilled to remove the residual solvent and sent to an air-circulating oven set at a given temperature

(160, 200, and 220°C). Before the isothermal cure and periodically during the isothermal cure, the sample disc was removed from the oven for FTIR measurements at room temperature. Separate measurements were made for the specimen prepared by directly heating the sample disc from room temperature to 320°C. A Digilab FTS-40 Fourier-transform infrared spectrometer was used. Spectra in the optical range of 4000–400 cm⁻¹ were obtained by averaging 64 scans at a resolution of 2 cm⁻¹.

A DuPont DSC 910 cell connected to a DuPont 9900 data station was used in this study. Samples approximately 10 mg in weight were sealed in hermetic aluminum pans and scanned in the calorimeter with a heating rate of 10, 20, 30, or 40°C/min in the range of 50–350°C. The carrier gas was nitrogen at a flow rate of ca. 10 mL/min. Calibration of the calorimeter was conducted for each heating rate using an indium standard.

RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy (FTIR) was used to characterize the chemical nature of the cure reactions of different molar ratios of BM and BA. DSC was further employed to study the cure kinetics. The cure systems of 1 : 1, 1 : 2, and 2 : 1 molar ratios of BM and BA are designated as 1M1A, 1M2A, and 2M1A, respectively.

Fourier Transform Infrared Spectroscopy

The infrared study for cure of BM has been previously reported by Jasse et al.[15] Quantitative analysis is not possible due to the serious overlapping of the characteristic bands. Isothermal reactions of 1M1A and 1M2A at 160 (Fig. 2), 200, and 220°C result in the consumption of maleimide and cyanate groups. This can be demonstrated by the gradual shift of the absorption at 1714 cm⁻¹ (C=O, maleimide) to 1700 cm⁻¹ (C=O, succinimide) and the disappearance of 2236 and 2270 cm⁻¹ (O—C≡N, cyanate) absorptions in the infrared spectra. The decrease of cyanate absorption is accompanied by the appearance of a new absorption peak at 1507 cm⁻¹. Presumably, this peak may be attributed to the ring structure of III or IV in Figure 1 derived from the proposed cyclization reactions between maleimide and cyanate units (heteropolymerization is used for this reaction in the following discussion). This absorption gradually coincides with the absorptions at 1514 and 1500 cm⁻¹. The cyclotrimerization of the
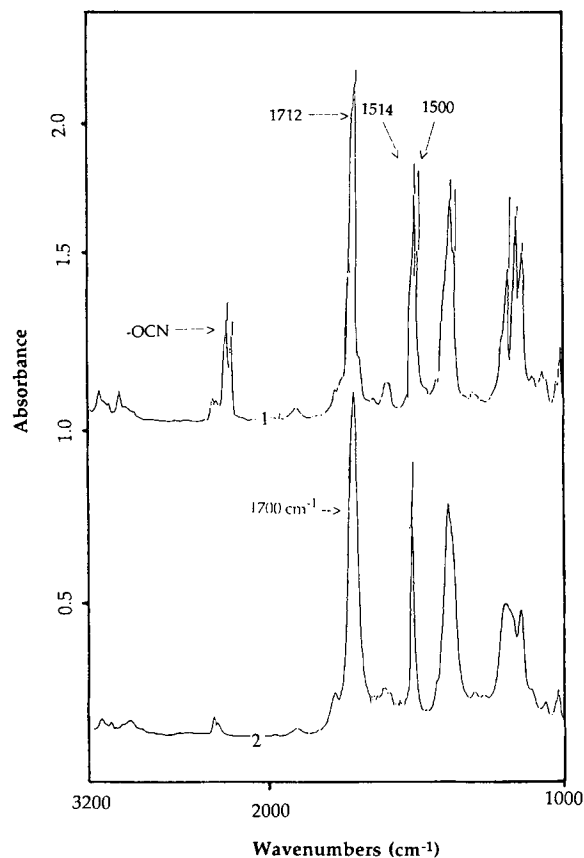
Figure 2   Infrared spectra of (1) 1M1A and (2) 1M1A after isothermal heating at 160°C for 64 h.

cyanate group can be easily detected by the appearance of triazine absorption (1565 cm^{-1}). After isothermal cure at 200°C for 24 h, neither 1M1A nor 1M2A exhibits the characteristic triazine absorption in the corresponding spectra. In any event, cure of 1M2A at 220°C for 25 min results in the triazine formation as evidenced by the appearance of 1565 cm^{-1} absorption. Also, dynamic heating of 1M2A from room temperature to 320°C provides the same observation (Fig. 3). Under identical experimental conditions, there is no triazine formation for cure of 1M1A. Addition polymerization of BM and heteropolymerization between BM and BA seem to be the predominant reactions at the initial stage. For cure of 1M2A, the cyclotrimerization of the extra BA progresses at the later stage. The absence of triazine formation in cure of 1M1A deserves further comment. The ring structures of I, II, III, or IV in Figure 1 are primarily assumed to be the major linking units derived from the various reactions mentioned above. Formation of structure IV requires a reaction stoichiometry of a 2 : 1 molar ratio of BM to BA. For the cure of 1M1A, this reaction stoichi-

ometry should result in at least half of the original amounts of BA unreacted at the initial stage and the inevitable formation of the triazine structure at the later stage. This rationale is contrary to our experimental result. Therefore, formation of structure III instead of IV can be proposed on the premise of the completeness of all the cross-linking reactions and the formation of a single-ring structure from heteropolymerization.

Differential Scanning Calorimetry

Qualitative Observation

Dynamic scans of BM, BA, 2M1A, 1M1A, and 1M2A were performed with heating rates of 10, 20, 30, and 40°C/min. Figure 4 shows the selected DSC thermograms at a heating rate of 10°C/min. Melting of BM or BA occurs before its corresponding curing exotherm. For the cure reactions of 2M1A, 1M1A, and 1M2A, the respective melting endotherm of BA shifts slightly to lower temperatures with increasing content of BM. The melting transitions of the BM component in these cure systems are broad, which is in contrast with the sharp melting of pure BM. Experimental and theoretical heat (calculated by multiplying the heat of melting for pure BM with the weight percentages of the BM component in the corresponding cure systems) for the melting of the BM component are well correlated for all the three
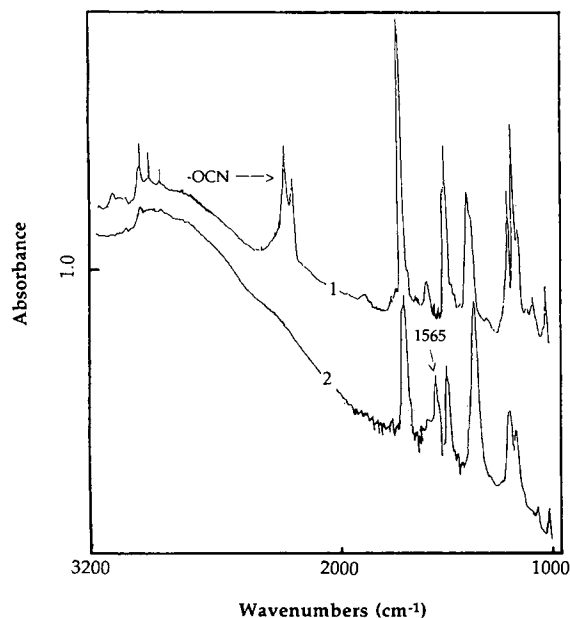

Figure 3   Infrared spectra of (1) 1M2A and (2) 1M2A after dynamic scan from room temperature to 320°C.
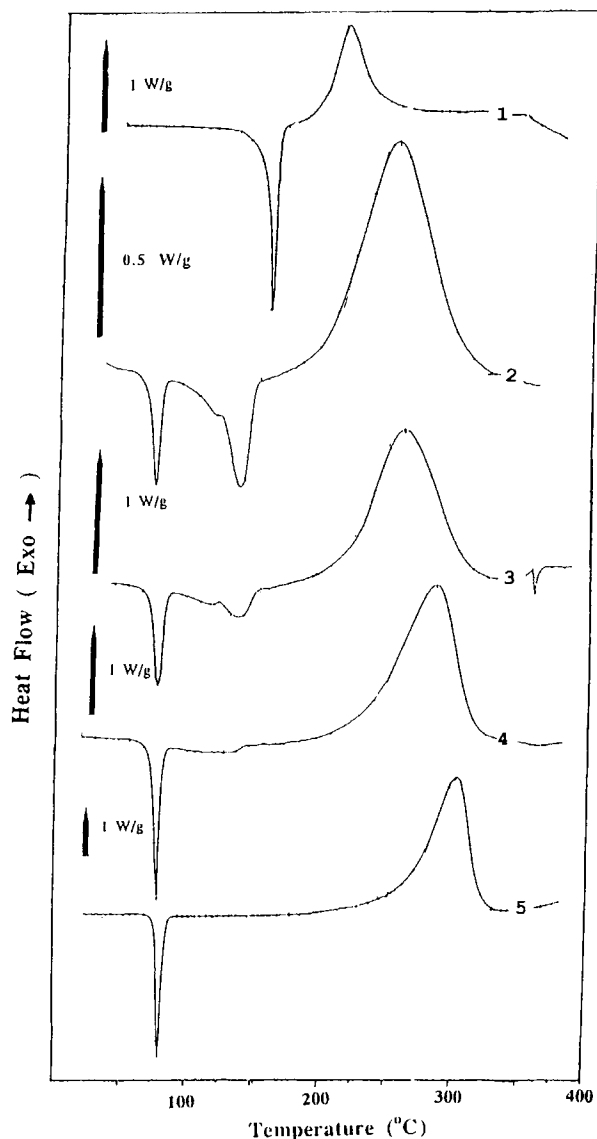
Figure 4 DSC thermograms for the cure reactions of (1) BM, (2) 2M1A, (3) 1M1A, (4) 1M2A, and (5) BA at 10°C/min.

cure systems. Therefore, only small amounts of cure or no cure reactions take place during the melting of the BM component. Cross-linking of BA occurs at the highest temperatures among all the cure systems. The participation of cyclotrimerization of BA in the cure of 1M2A contributes to the higher curing exotherm as compared with 1M1A or 2M1A.

Cure Kinetics

The specific heat of the cure reaction (ΔH_{rxn}, cal/g) corresponds to the total area under the peak divided by the heating rate. The specific heat for dif-

ferent systems is summarized in Table I. For each system, specific heat remains relatively constant despite the difference in the heating rate. Values of ΔH_{rxn} for the cure reactions of 1M1A, 1M2A, and 2M1A are between those of BA and BM. The specific heat is clearly decreased with the increasing content of the BM component from 1M2A to 1M1A and to 2M1A. The low value of ΔH_{rxn} (55.0 cal/g) for the cure of BM is responsible for this tendency. The extent of the addition polymerization of BM is presumably increased from 1M2A to 2M1A.

Apparent activation energy can be revealed by the dynamic DSC method.[12] The fractional conversion (α) is the ratio between the heat evolved up to a given moment and the corresponding specific heat. The rate of reaction ($d\alpha/dt$) corresponds to the height (with respect to the base line) of the thermogram at a given temperature. In view of the complex nature of the cure reactions, all the rate expressions should be considered empirical. The general way to express the rate of reaction is to start with

$$d\alpha/dt = kf(\alpha) = Af(\alpha)\exp(-Ea/RT) \quad (1)$$

where $k = A \exp(-Ea/RT)$ is the apparent rate constant; A, the preexponential factor; and $f(\alpha)$, an empirical function representing the conversion-dependent part of the rate expression. From eq. (1), a simple, usable yet accurate relationship between activation energy (Ea), heating rate (Φ), and peak temperature (T_p; temperature at maximum rate of reaction $[d\alpha/dt]$) can be deduced. It has been observed that the extent of reaction at the peak temperature is constant and independent of the heating rate for many thermosetting systems.[16-19] Integration of $1/f(\alpha)$ from $\alpha = 0$ to α_p (peak conversion; the corresponding conversion at peak temperature) should yield a constant value and the following relationship was therefore deduced by Prime[16]:

Table I Variations of Specific Heat (ΔH_{rxn}) with Heating Rates

Heating Rate (°C/min)	ΔH_{rxn}[a] for				
	BA	1M2A	1M1A	2M1A	BM
10	167.3	135.0	105.4	83.6	55.0
20	178.3	136.2	111.7	89.2	55.3
30	170.0	127.0	104.7	89.6	57.3
40	171.0	132.1	103.7	92.0	57.5

[a] Specific heat (cal/g) evolved during cure of the corresponding system.

Table II   Peak Temperatuers (T_p, °C) and Peak Conversions (α_p) at Different Heating Rates

Heating Rate (°C/min)	$T_p{}^a(\alpha_p)^b$ for				
	BA	1M2A	1M1A	2M1A	BM
10	302.0 (0.686)	285.9 (0.654)	260.5 (0.528)	256.1 (0.530)	213.3 (0.384)
20	323.3 (0.679)	304.4 (0.628)	284.1 (0.540)	272.6 (0.536)	224.0 (0.385)
30	331.7 (0.686)	314.2 (0.640)	293.3 (0.546)	280.9 (0.555)	231.2 (0.373)
40	342.0 (0.657)	326.1 (0.651)	303.8 (0.575)	289.3 (0.540)	236.7 (0.358)

[a] Peak temperature (°C): temperature at maximum rate of reaction.
[b] Peak conversion: conversion at peak temperature.

$$Ea = -0.951R[d \ln \Phi / d(1/T_p)] \qquad (2)$$

As suggested from eq. (2), the apparent activation energy can be estimated through the dependence of the activation energy on the heating rate (Φ) and peak temperature (T_p). Table II summarizes the peak temperature and peak conversion (α_p) for the cure reactions of BM, 1M2A, 1M1A, 2M1A, and BA. The peak conversion is nearly independent of heating rate. The plot of ln Φ vs. reciprocal peak temperature ($1/T_p$) is given in Figure 5. The apparent activation energy can be obtained by multiplying the slopes of the straight lines with -0.951 according to eq. (2) (Table III). The resulting value of 23.14 kcal/mol for cure of BA is close to the published value of 22.13 kcal/mol for cyclotrimerization of 4,4'-thiophenylcyanate.[20] The value of 27.42 kcal/mol for BM is lower than 31.07 kcal/mol, the published result for the addition polymerization of a flexible bismaleimide.[21] In any case, the apparent activation energies for the cure reactions of 1M1A, 1M2A, and 2M1A are between those for the cure reactions of BA and BM. Cure of BM has the highest apparent activation energy among all. The higher apparent
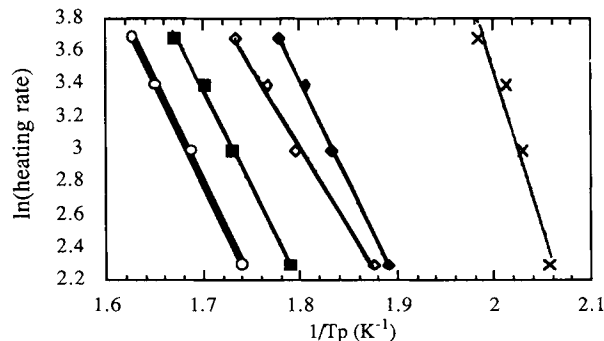
activation energy for cure of 2M1A is therefore attributed to the higher degree of addition polymerization of BM involved in the cure cycle as compared with 1M1A and 1M2A.

A more complete access of activation energy throughout the entire conversion range may be obtained by using Friedman's method.[22] When the apparent activation energy is taken as a constant, eq. (1) may be rewritten as

$$\ln[d\alpha/dt] = \ln[Af(\alpha)] - Ea/RT \qquad (3)$$

According to eq. (3), the plot of $\ln(d\alpha/dt)$ against reciprocal temperature at a selected conversion should yield a straight line with its slope equal to $-Ea/R$. Given in Figure 6 are Friedman plots for 1M1A from conversion 0.1 to 0.9. Values of Ea obtained in this manner for 1M1A and 1M2A are shown in Figure 7. The average values of 19.6 kcal/mol for 1M1A and 21.6 kcal/mol for 1M2A are close to the apparent activation energy obtained from Prime's method and used for the further evaluation of the kinetic expression. The Ea values for cure of 1M2A increase monotonically with α, whereas those for 1M1A have a minimum at α = ca. 0.4. The complex nature of the cure system is revealed by the scattered Ea values. The participation of cyclotrimerization of BA in the cure of 1M2A results in a different Ea pattern from 1M1A.

The Ea values for the present systems have been observed to fluctuate with conversion. Direct adoption of Friedman's original method would then result in unacceptable $\ln[Af(\alpha)]$ values. Therefore, eq. (3) can be rewritten as

$$\ln[Af(\alpha)] = \ln[d\alpha/dt] + Ea/RT \qquad (4)$$

The $\ln[Af(\alpha)]$ values can be calculated from experimentally determined $d\alpha/dt$ and Ea/RT, where the average values of Ea (19.6 kcal/mol for 1M1A

Figure 5   Linear relationship between ln(heating rate) and reciprocal peak temperature ($1/T_p$) for cure of ($\times$) BM, ($\Diamond$) 1M1A, ($\blacksquare$), 1M2A, ($\blacklozenge$) 2M1A, and ($\bigcirc$) BA.

Table III Apparent Activation Energy for Different Cure Reactions

	Cure System				
	BA	1M2A	1M1A	2M1A	BM
Apparent activation energy (kcal/mol)	23.14	21.03	19.42	22.56	27.42

and 21.6 kcal/mol for 1M2A) were used. For simple n-th-order reactions, the relationship, $\ln[Af(\alpha)]$ $= \ln A + n \ln(1 - \alpha)$, should hold and the plot of $\ln[Af(\alpha)]$ vs. $\ln(1 - \alpha)$ should yield a straight line with its slope equal to n. The resulting $\ln[Af(\alpha)]$ and $\ln(1 - \alpha)$ are not linearly related for both 1M1A (Fig. 8) and 1M2A systems. Therefore, a simple n-th order kinetics is not appropriate for these systems. The existence of the maximum rate of reaction at $\alpha = $ ca. 0.33 for 1M1A and $\alpha = $ ca. 0.32 for 1M2A indicates that these cure reactions are autocatalytic in nature.

A further attempt was made to express $Af(\alpha)$ in term of fractional conversion. This fitting was operated without presuming any particular kinetic equation such as the general kinetic expression for the autocatalytic reaction, $A(\alpha) = (k_1 + k_2\alpha^m)(1 - \alpha)^n$.[23] The resulting equations are

$$Af(\alpha) = 2.32 \times 10^5 + 5.62 \times 10^5\alpha$$
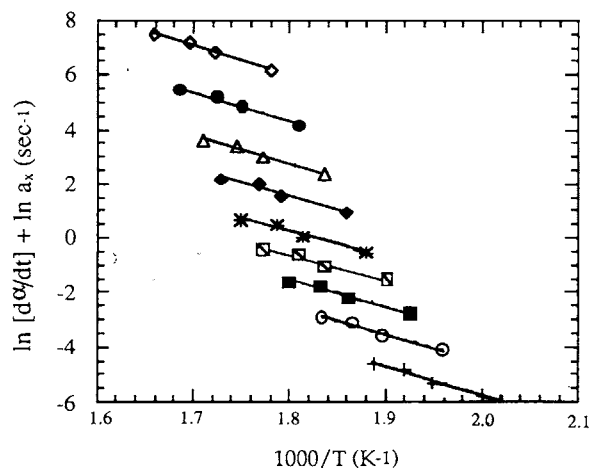$$- 8.61 \times 10^5\alpha^2 \text{ s}^{-1} \quad (5)$$

Figure 6 Friedman plots for cure of 1M1A at various conversions. Data points have been vertically shifted for the sake of clarity. Lines are corresponding least-square fits: (+) $\alpha = 0.1$; (O) $\alpha = 0.2$, shift factor $\ln a_x = 1$; (■) $\alpha = 0.3$, $\ln a_x = 2$; (□), $\alpha = 0.4$, $\ln a_x = 3$; (*) $\alpha = 0.5$, $\ln a_x = 4$; (◆) $\alpha = 0.6$, $\ln a_x = 4.5$; (△) $\alpha = 0.7$, $\ln a_x = 6$; (●) $\alpha = 0.8$, $\ln a_x = 9$; (◇) $\alpha = 0.9$, $\ln a_x = 11$.

and

$$Af(\alpha) = 6.07 \times 10^5 + 1.06 \times 10^6\alpha$$
$$- 1.66 \times 10^6\alpha^2 \text{ s}^{-1} \quad (6)$$

for 1M1A and 1M2A, respectively. Calculated curves are compared to the experimental results in Figures 9 and 10. Both cases appear to follow satisfactorily with the experimental results. Use of third-order polynomials ($1.98 \times 10^5 + 1.14 \times 10^6\alpha - 2.48 \times 10^6\alpha^2 + 1.15 \times 10^6\alpha^3$ s^{-1} for 1M1A and $6.46 \times 10^5 + 7.03 \times 10^5\alpha - 8.33 \times 10^5\alpha^2 + 5.48 \times 10^5\alpha^3$ s^{-1} for 1M2A) results in the same as with second-order polynomials except at the high conversion end of $\alpha > 0.93$. As mentioned above, the possible reactions involved in the cure of 1M1A are addition polymerization of BM and heteropolymerization between BM and BA. According to the discussion on infrared spectroscopy, we proposed that heteropolymerization involved the additions of two cyanates to one maleimide unit. In our opinion, heteropolymerization may proceed with a mechanism similar to cyclotrimerization of aromatic dicyanates as previously suggested by Bauer et al.[6] Heteropolymerization can be initiated by the attacking of impure phenolic OH to aromatic OCN, then followed by the additions of another aromatic OCN and a
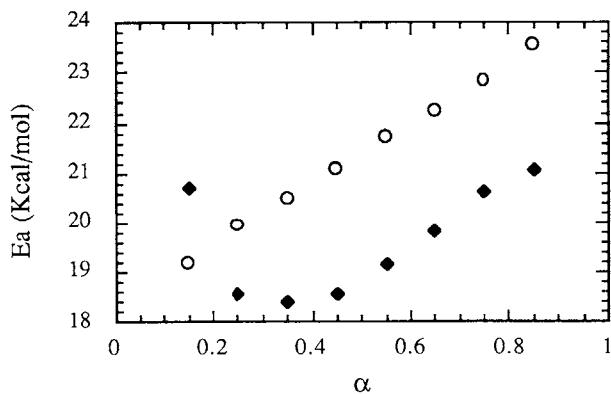
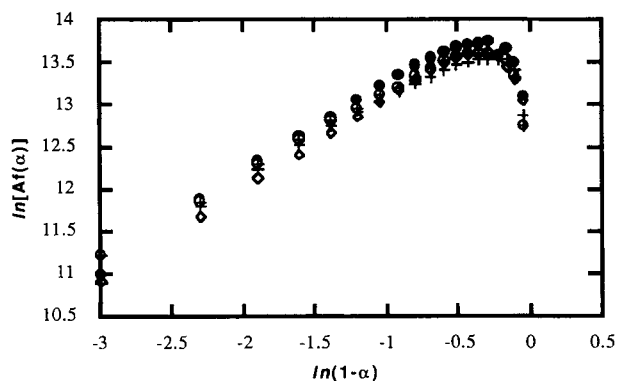**Figure 7** Variation of activation energy (Ea) with conversion for cure of (O) 1M1A and (◆) 1M2A.

Figure 8 Relationship between $\ln[Af(\alpha)]$ and $\ln(1 - \alpha)$ for cure of 1M1A. Data points are extracted from DSC dynamic scans at heating rates of (●) 10, (⊕) 20, (◇) 30, and (+) 40°C/min.

double bond on the maleimide (in the case of cyclotrimerization of aromatic dicyanate, additions of two aromatic OCN followed). The study on 4,4'-thiodiphenylcyanate in my laboratory revealed a second-order empirical function of the rate, $Af(\alpha) = k(C + \alpha)(1 - \alpha)$, for the cyclotrimerization reaction. Presumably, heteropolymerization may follow a similar second-order kinetic as cyclotrimerization of aromatic dicyanate. The resulting second-order kinetics for the cure of 1M1A may reflect the combined reaction orders of polymerization of BM and heteropolymerization. Nevertheless, the contribution of each reaction varied differently with the gross conversion and it is difficult to resolve the individual kinetic data. The cure kinetics of 1M2A is more complicated than that of 1M1A since cyclotrimerization of MA is also involved in the cure. At the
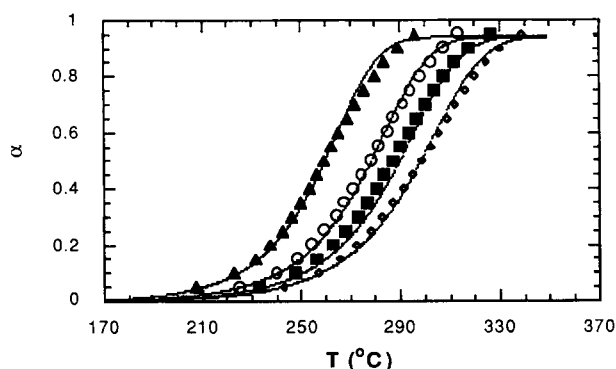

Figure 9 Comparison between experimental and calculated conversion for cure of 1M1A at different heating rates: (▲) 10°C/min; (○) 20°C/min; (■) 30°C/min; (△) 40°C/min. The corresponding solid curves are predictions from eq. (7).
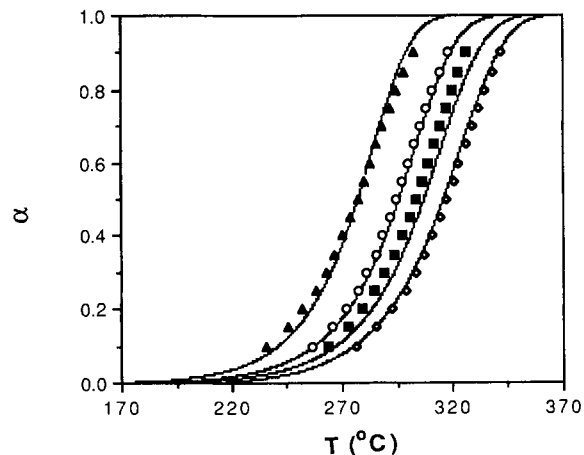

Figure 10 Comparison between experimental and calculated conversion for cure of 1M2A at different heating rates: (▲) 10°C/min; (○) 20°C/min; (■) 30°C/min; (△) 40°C/min. The corresponding solid curves are predictions from eq. (8).

present time, we may treat the kinetic data as phenomenological results in view of the complex nature of the cure reactions.

CONCLUSIONS

Several reactions such as addition polymerization of BM, cyclotrimerization of BA, and heteropolymerization between BM and BA are involved in the cure reactions of the mixture of BM and BA. The addition polymerization of BM and the heteropolymerization are probably the main reactions involved in the initial cure stage. FTIR reveals that cyclotrimerization of BA occurs in cure of 1M2A. This is not observed for the cure of 1M1A.

DSC is employed to study the cure kinetics of 1M1A and 1M2A. The apparent activation energy evaluated from the Prime method is increased with the content of the BM component in the starting mixture. The plot of Ea vs. α suggests the different chemical nature of the cure reactions of 1M1A and 1M2A. Also, the existence of the maximum rate of reaction at conversion of 0.32–0.33 suggests the autocatalytic nature of these cure reactions. The empirical functions of rate, $[Af(\alpha)]$, thus evaluated are $2.32 \times 10^5 + 5.62 \times 10^5\alpha - 8.61 \times 10^5\alpha^2$ and $6.07 \times 10^5 + 1.06 \times 10^6\alpha - 1.66 \times 10^6\alpha^2$ s^{-1} for 1M1A and 1M2A, respectively.

REFERENCES

1. S. Ayano, *Chem. Econ. Eng. Rev.*, **10**, 1 (1978).
2. D. Landman, in *Advances in the Chemistry and Applications of Bismaleimides*, G. Pritchurd, Ed., Development in Reinforced Plastics-5, Elsevier, New York, 1986, pp. 57-59.
3. D. A. Scola, in *Engineered Materials Handbook, composites*, C. A. Dostal, M. S. Woods, and H. J. Frissell, Eds., ASM International, Metals Park, OH, Vol. 1, 1987, pp. 82-83.
4. S. Ayano, *Proceed. ACS, Polym. Mater. Sci. Eng.*, **54**, 107 (1986).
5. E. Grigat, and R. Putter, *Chem. Ber.*, **97**, 3012 (1964).
6. M. Bauer, J. Bauer, and G. Kuhn, *Acta Polym.*, **37**, 715 (1986).
7. R. F. Cozzen, and P. Walter, *J. Appl. Polym. Sci.*, **34**, 601 (1987).
8. S. L. Simon, J. K. Gillham, and D. A. Shimp, *Proceed. ACS Polym. Mater. Sci. Eng.*, **62**, 96 (1990).
9. S. L. Gillham, and J. K. Gillham, in *Proceedings of the Annual Technical Conference (ANTEC), Society of Plastics Engineering*, 1991, p. 1554.
10. A. Osei-Owusu and G. C. Martin, *Polym. Eng. Sci.*, **31**, 1604 (1991).
11. K. N. Nonan, K. Krishnan, and J. Mathew, *J. Appl. Polym. Sci.*, **32**, 6033 (1986).
12. R. B. Prime, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981, pp. 435-569.
13. K. Horie, H. Hiura, M. Souvada, I. Mita, and H. Kambe, *J. Polym. Sci. Polym. Chem. Ed.*, **8**, 1357 (1970).
14. D. W. Sundstrom, and M. F. English, *Polym. Eng. Sci.*, **18**, 728 (1978).
15. C. Di Giulio, M. Gautier, and B. Jasse, *J. Appl. Polym. Sci.*, **29**, 1771 (1984).
16. R. B. Prime, *Polym. Eng. Sci.*, **13**, 365 (1973).
17. N. H. Horowitz, and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
18. P. Pryser and W. D. Bascom, *Anal. Calorim.*, **3**, 537 (1974).
19. T. H. Hsieh, and A. C. Su, *J. Appl. Polym. Sci.*, **41**, 1271 (1990).
20. R. H. Lin, J. L. Hong, and A. C. Su, *Proceedings of ACS Polym. Mater. Sci. Eng.*, **66**, 464 (1992).
21. M. Acevedo, J. de Abajo, and J. G. de la Campa, *Polymer*, **31**, 1955 (1990).
22. H. L. Friedman, *J. Polym. Sci. C*, **6**, 183 (1965).
23. M. R. Kamal, and S. Sourour, *Polym. Eng. Sci.*, **13**, 59 (1973).