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Analysis of the kinetics and mechanism of the cure of a bismaleimide–diamine thermoset

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Abstract

The polymerisation kinetics of 1,1′-(methylenedi-1,4-phenylene)bismaleimide (MDP-BMI) with the aromatic diamine 4,4′-diaminodiphenylmethane (DDM) has been investigated. Fourier-transform near infrared (FT-NIR) spectroscopy was used to obtain quantitative data for the various functional groups in BMI/DDM mixtures with respect to time during isothermal cure over the temperature range 160–180°C. Quantitative rate data were obtained for all the functional groups in the resins by mathematical differentiation of the time dependence of the concentrations. A mechanism for the polymerisation has been deduced from this rate data, in which the rate-determining step was found to involve a reaction between the primary or secondary amine and a hydrogen bonded complex formed between the maleimide and amine groups. The rate coefficients for the reaction of the amines with the complex were found to be four times larger for the primary amine than that for the secondary amine. The activation energy for the cure over this temperature range was found to be 43 kJ mol^{-1}. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bismaleimide–amine; Thermosets; Polymerisation kinetics

1. Introduction

The major reaction in bismaleimide, BMI, thermosets that are cured with primary amine, PA, is the nucleophilic addition of the amine to the maleimide, MI, double bond. This reaction is an example of the common Michael addition reaction [1]. Nucleophilic addition reactions generally fit second-order kinetics, at least in the presence of solvent. Crivello [2] performed a study of the nucleophilic addition reaction of *N*-phenylmaleimide and aniline in different solvents and found a good fit to second order kinetics. A marked rate enhancement was found with increasing polarity of the solvent. This suggested the presence of a charged intermediate or transition state that is stabilised by the medium, as shown in Fig. 1. Second-order kinetics were also reported for the polymerisation of 1,1′-(methylenedi-1,4-phenylene)bismaleimide with 4,4′-diphenyldiaminomethane, MDP-BMI/DDM, based upon results obtained using size exclusion chromatography [3] and FTIR [4] analyses.

A mechanism of the type shown in Fig. 1 allows the possibility of both acid or base catalysis for the MI-amine reaction, and indeed weak protonic acids are well known to have a marked catalytic effect on the reaction, which has been utilised in the synthesis of poly(aspartimide)s [2,5,6] for example. White et al. [7] came to a similar conclusion regarding the mechanism for nucleophilic addition of amine to a maleimide double bond.

A side reaction has been reported for maleimides and primary amines, the so-called amidisation reaction, which results in opening of the maleimide ring and formation of an amide group [8], as shown in Fig. 2. In a study of the addition of diamines to bismaleimides [1], the primary product was reported to be aspartimide, formed by the Michael addition reaction, except for some aliphatic diamines. However, Donnellan [9] did not observe any amide groups for the MDP-BMI/DDM systems, and an ^{15}N NMR investigation also found no evidence for substantial amounts of amidisation [10]. In the latter work, a small peak was observed at 162 ppm in the solution ^{13}C NMR spectra of un-gelled samples of MDP-BMI/DDM, which could be assigned to a carbonyl carbon formed through amidisation [8]. However, this peak represented only about 5% of the

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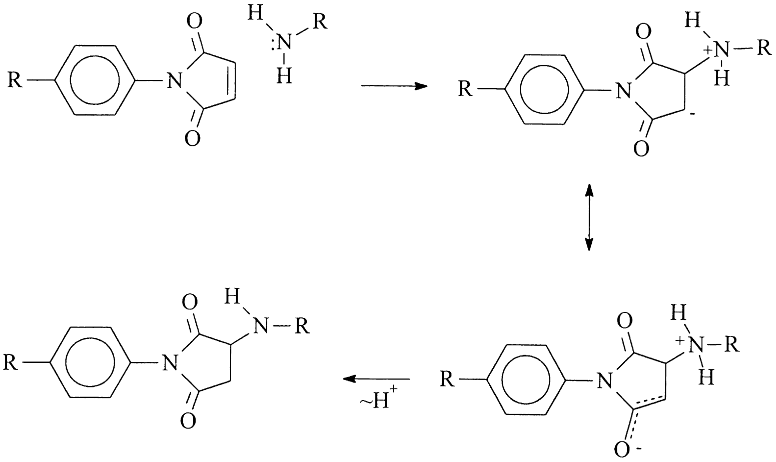

Fig. 1. Proposed mechanism for the reaction of a BMI with an aromatic amine.

maleimide groups for the model system of *N*-phenylmaleimide/aniline. Therefore, notwithstanding that one previous study [1] has reported considerable amidisation, this ring-opening reaction does not appear to play a significant role in the chemistry of the aromatic BMI/diamine system.

In the present study, the kinetics and mechanism of the polymerisation of the MDP-BMI/DDM system have been investigated over the temperature range 160–180°C using FT-IR, as described in our previous paper [11], to monitor the changing concentrations of the reacting groups. Substitution effects are not expected to play a significant role for these monomers because the diphenylmethane structural unit is large enough to ensure that the reactivities of the two functional groups are independent of one another. However, the secondary amine group formed after reaction may have a different reactivity to that of the primary amine, as has previously been reported for some epoxy systems [12].

2. Experimental

1,1′-(methylenedi-1,4-phenylene)bismaleimide (MDP-BMI) from Aldrich was purified by column chromatography, using silica gel as the column support and eluting with chloroform. The elutant was reduced in volume on a rotary evaporator and the bismaleimide was then precipitated using methanol as the non-solvent. 4,4′-diaminodiphenylmethane (DDM) from Aldrich was twice recrystallised from distilled water or a 80:20 water/methanol mixture, respectively.

The purified monomers were dried in a vacuum oven at 60–70°C for at least 24 h, before being weighed into a sample vial in the required amounts and the fine crystalline powders were mechanically mixed. The mixtures were then transferred into 5 mm external diameter Pyrex NMR tubes. All samples were degassed under high vacuum (<0.1 Pa) for 12 h and sealed either under high vacuum or after back filling to approximately 50 kPa with nitrogen.

A Mattson Instruments FTIR spectrometer fitted with a tungsten lamp, a quartz beam splitter and a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used and spectra were acquired in the NIR region from 8000 to 4000 cm^{-1} with a resolution of 8 cm^{-1} and triangular apodisation [11]. Usually 32 scans were co-added to give a good signal to noise ratio, but with particularly fast or slowly reacting samples 16 or 64 scans, respectively, were co-added to give the final spectrum. NIR spectra were acquired at regular intervals under computer control. For kinetic experiments, the sample tube was inserted into a pre-heated aluminium block mounted in the spectrometer, with the temperature controlled by a Eurotherm thermostat. The temperature of the block was constant to within ±0.2°C of the set temperature over several hours.

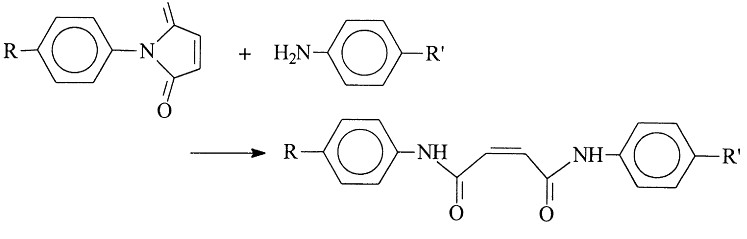

Fig. 2. Maleimide ring opening reaction in the presence of amine.

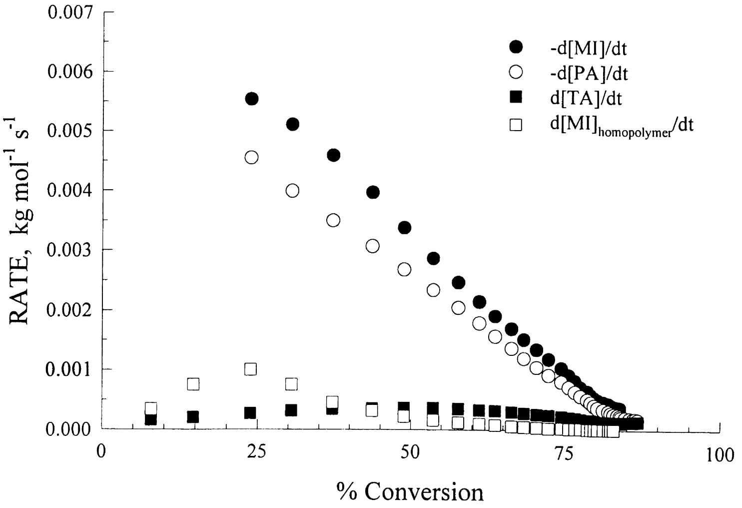

Fig. 3. Rate of reaction for the various constituent reactions in 1:1 MDP-BMI/DDM at 170°C.

3. Results and discussion

3.1. Polymerisation rates

One of the major advantages of the FT-NIR technique is that the concentration of each reactive functional group can be determined across the entire conversion range. The rate of consumption or formation of each functional group can be calculated by differentiation of the time dependence of the group concentration. In this case, from an analysis of the FT-IR data [11], the rate of consumption of the maleimide double bonds and of the primary amine, as well as the rate of formation of tertiary amine and the rate of maleimide homopolymerisation can be obtained. In Fig. 3, the rates for each of these individual reactions are plotted against the concentration (% conversion) of the maleimide double bonds for an equimolar mixture of MDP-BMI and DDM at 170°C. Similar data can be obtained at other reaction temperatures.

The maximum rates for the consumption of the maleimide double bond and of the primary amine occur at the beginning of the polymerisation of MDP-BMI with DDM. On the other hand, the rate of formation of the tertiary amine increases until the conversion reaches around 50%, then it decreases again. The increase in the reaction rate initially is to be expected due to the accumulation of secondary amine groups from the chain-extension reaction. The later decrease in reaction rate beyond 50% conversion is probably due to a combination of the vitrification effect and the depletion of maleimide double bonds.

The rate of tertiary amine formation in the MDP-BMI/DDM resin is much less than the rate of secondary amine formation, even when substantial amounts of secondary amine are present, clearly indicating that the secondary amine is much less reactive than the primary amine. This is highly significant, because many models for network formation assume equal reactivity of primary and secondary

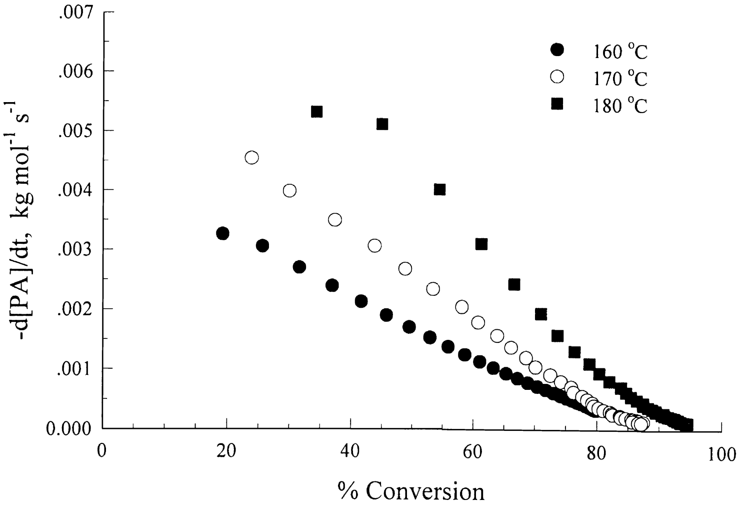

Fig. 4. Rate of primary amine consumption in 1:1 MDP-BMI/DDM at various temperatures plotted against the % conversion of maleimide.

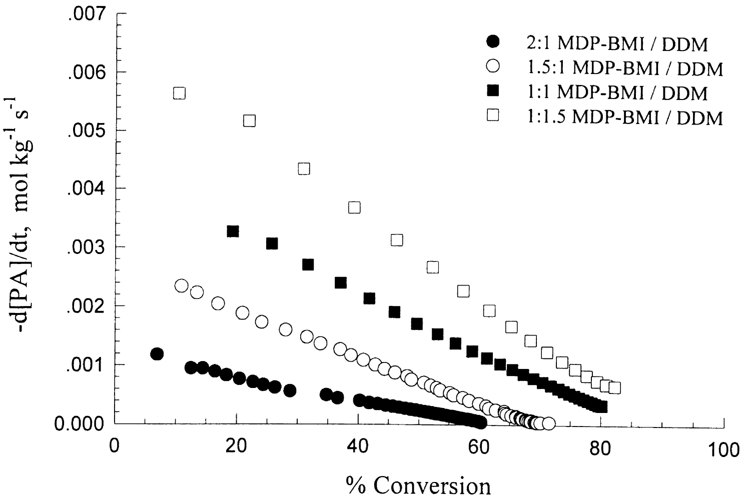

Fig. 5. Rates of primary amine consumption for various stoichiometries of MDP-BMI/DDM at 160°C.

amines, but this is clearly incorrect for the MDP-BMI/DDM system.

3.2. Reaction of maleimide with primary amine

Within the kinetically controlled region of the cure, a strong temperature dependence of the reaction rate is expected due to the temperature dependence of the rate constants. Fig. 4 shows the influence of an increase in the cure temperature on the total rate of primary amine consumption for equimolar mixtures of MDP-BMI and DDM. The rate data in Fig. 4 are plotted as a function of the concentration (% conversion) of maleimide double bonds, rather than time, to enable a direct comparison of the data from the different experiments.

Notably, the polymerisation rate falls virtually to zero well before the double bonds or primary amine groups have been totally consumed. The greatly decreased reaction rates at high conversion, despite there being reactive functional groups still present, shows how diffusion affects the rates at high conversion. At high conversion, the rate of primary amine consumption is similar for the different cure temperatures, as would be expected for a diffusion-controlled kinetic regime where the activation energy for diffusion is very large compared with that for chemical reaction.

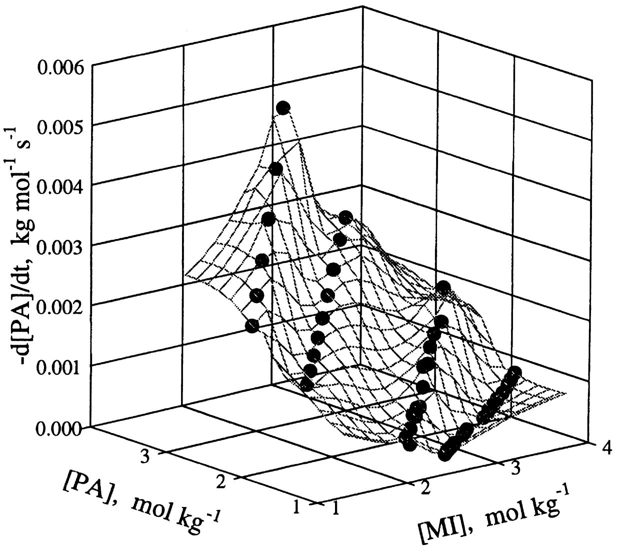

Fig. 6. Three-dimensional plot of rate of primary amine consumption for MDP-BMI/DDM at 160°C as a function of both maleimide and primary amine concentration.

The stoichiometry of the resin mixture has a major influence on the rate of primary amine consumption. This is confirmed with reference to Fig. 5. Increasing the relative amount of primary amine by changing the resin stoichiometry increases the rate of primary amine consumption.

One of the difficulties in determining the exact nature of the kinetic relationships in a thermoset resin is that the concentrations of the individual monomers cannot be varied independently. As the resin stoichiometry is changed, the initial concentrations of both the maleimide double bond and primary amine groups change simultaneously. The rate of primary amine consumption is expected to be a function of the concentration of both the primary amine and maleimide groups in the region preceding diffusion control. Therefore, to see the exact influence of functional group concentration on the polymerisation rate, it is necessary to plot the rate against both variables. Fig. 6 is such a plot for the MDP-BMI/DDM resins of various stoichiometry at 160°C. Only data below 50% maleimide conversion are plotted to exclude the effect of diffusion on the predictions of the rate law.

The hypersurface presented in Fig. 6 shows that the reaction rate has a higher dependence on the concentration of primary amine than on the concentration of double bonds, indicating that the reaction order with respect to the primary amine concentration is greater than that for the maleimide.

In order to determine the rate law expression and hence

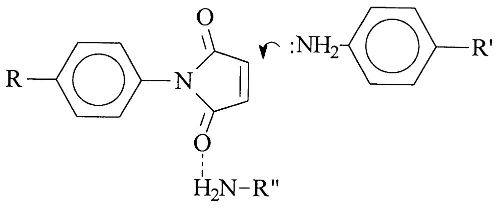

Fig. 7. Proposed complex and transition state involved in the reaction of maleimide with primary amine.

postulate a mechanism for the reaction, the initial rates were examined. The initial rate of primary amine consumption was estimated by extrapolation of plots such as those in Fig. 5 to the initial functional group concentrations. This procedure was adopted in order to avoid any uncertainty in the estimate of the initial rate that may arise if data were used from the period of the reaction during which thermal equilibrium was not yet established. It was then possible to plot the estimated initial rate of primary amine consumption as a function of the initial concentrations of the reactants.

Previous workers who have studied the reaction of maleimides with amines have reported the reaction follows second-order kinetics [2,4]; first order in both the primary amine and the maleimide. However, when the initial rate of loss of primary amine for different monomer stoichiometries was plotted against the product of the primary amine and maleimide concentrations, $[\mathrm{MI}]_0$ $[\mathrm{PA}]_0$, the data were not linear. This observation indicates that the reaction does not truly obey simple second-order kinetics.

One possible mechanism for the reaction of maleimide with primary amine that has not been addressed previously in the literature for BMI/DDM kinetics is the possibility of self-catalysis by the amine group. This mechanism involves a contribution from a second amine in the transition-state, thus giving rise to a rate expression that is second order with respect to the primary amine. It is possible that in the bulk polymerisation without the presence of hydrogen-donor solvents, the transition-state formed by nucleophilic attack on the electrophilic maleimide double bond can be stabilised by another amine acting as a proton donor. An analogous kinetic mechanism is thought to exist for epoxy-amine reactions in the absence of hydroxyl groups [13]. The most likely structure of the transition-state is one in which the amine, acting as the catalyst, is hydrogen bonded to a carbonyl oxygen, as shown in Fig. 7. The hydrogen bond to the carbonyl group will have the effect of reducing the electron density at the electrophilic carbon atom that is being attacked by the nucleophilic amine.

Thus, amine is capable of acting both as an electrophile in forming the complex with the maleimide and as a nucleophile in the addition to the double bond. This scheme is compatible with the importance of solvent polarity found by Crivello [2] for these reactions in solution, but instead of the transition-state being stabilised by the solvent, here the stability is promoted by hydrogen bonding.

If the mechanism involves the reaction of the primary amine–maleimide complex with free primary amine, as indicated in Fig. 7, then the rate of loss of primary amine would be given by the rate equation:

$$-\mathrm{d}[\mathrm{PA}]_t/\mathrm{d}t = k[\mathrm{PA}]_{\mathrm{f},t}[\mathrm{C}]_t \qquad (1)$$

where $[\mathrm{PA}]_{\mathrm{f},t}$ is the free primary amine concentration and $[\mathrm{C}]_t$ is the complex concentration at any time, t. The concentration of the complex can be expressed by the equation:

$$[\mathrm{C}]_t = K_1[\mathrm{PA}]_{\mathrm{f},t}[\mathrm{MI}]_{\mathrm{f},t} \qquad (2)$$

where K_1 is the equilibrium constant for complex formation, and $[\mathrm{MI}]_{\mathrm{f},t}$ is the free maleimide concentration at time t.

Because the primary amine may complex with the carbonyl groups of both the formed polymer and the unreacted maleimide, the concentration of the free primary amine can

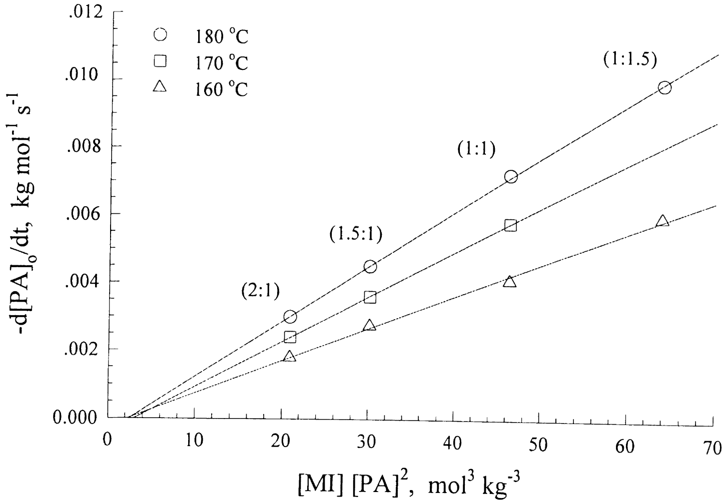

Fig. 8. Initial rate of primary amine consumption for various stoichiometries and temperatures, plotted against the assumed reaction order for MDP-BMI/DDM.

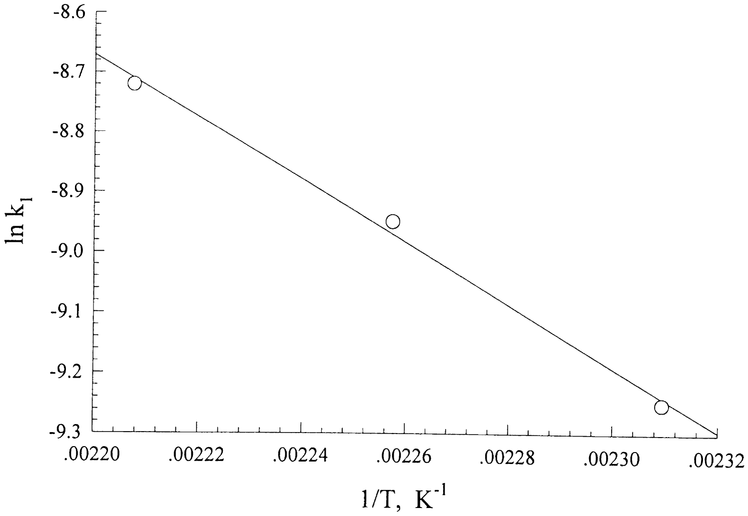

Fig. 9. Arrhenius plot of the rate constant for reaction of maleimide with primary amine in MDP-BMI/DDM.

be expressed by the equation:

$$[\mathrm{PA}]_{\mathrm{f},t} = [\mathrm{PA}]_t - [\mathrm{Complexed\ PA}]_t \tag{3}$$

$$= [\mathrm{PA}]_t - \mathrm{K}_1[\mathrm{PA}]_{\mathrm{f},t}[\mathrm{MI}]_0$$

$$= [\mathrm{PA}]_t/(1 + \mathrm{K}_1[\mathrm{MI}]_0)$$

where the equilibrium constant for complex formation is assumed to be the same for the carbonyl groups in the polymer and monomer and $[\mathrm{PA}]_t$ is the total concentration of primary amine remaining at time t.

Thus, Eq. (1) can be expressed as:

$$-\mathrm{d}[\mathrm{PA}]_t/\mathrm{d}t = kK_1[\mathrm{PA}]_t^2[\mathrm{MI}]_{\mathrm{f},t}/(1 + K_1[\mathrm{MI}]_0)^2 \tag{4}$$

If, to a first approximation, it is assumed that $[\mathrm{MI}]_{\mathrm{f},t}$ is a constant fraction of $[\mathrm{MI}]_t$,[2] then Eq. (4) can be expressed as:

$$-\mathrm{d}[\mathrm{PA}]_t/\mathrm{d}t = k_1[\mathrm{PA}]_t^2[\mathrm{MI}]_t \tag{5}$$

where the apparent rate coefficient k_1 will be dependent on the initial concentration of the maleimide. Thus the reaction would appear to be second order in primary amine and first order in maleimide.

The initial rate of primary amine consumption is plotted against the product $[\mathrm{PA}]_0^2\,[\mathrm{MI}]_0$ in Fig. 8. The data for each temperature were found to fall approximately on a straight line, thus supporting the mechanism outlined in Fig. 7 provided the apparent rate coefficient is not strongly dependent on the initial maleimide concentration over the concentration range shown. The apparent rate coefficients are given for each temperature in Table 1.

The activation energy, E_A, for this polymerisation reaction can be calculated from a plot of the temperature dependence of the rate coefficients (Fig. 9). This gives a value for E_A of 43 kJ mol^{-1}, which is in agreement with the activation energy previously calculated for this reaction [4].

Although the fit of the initial rate of the primary amine consumption to Eq. (5) was encouraging, the actual experimental data over the entire conversion range, plotted in Fig. 10, are not proportional to the product $[\mathrm{MI}]_t\,[\mathrm{PA}]_t^2$ as the reaction stoichiometry changes significantly during cure. The figure shows that as the reaction proceeds, the slopes of the experimental rate curves increase, except for the mixture with the highest initial primary amine content.

The inability of the rate law given by Eq. (5) to fit the data throughout the cure suggests that a composite mechanism is involved. As the slope of the plot in Fig. 10 increases as the product $[\mathrm{MI}]_t\,[\mathrm{PA}]_t^2$ decreases during the cure, it is likely that one of the products of the reaction plays a catalytic role. A possible explanation is that the secondary amine product of the reaction of the primary amine can also act as a catalyst for the reaction, again by complexation with carbonyl groups.

An analysis similar to that proposed for the complexation of primary amine with carbonyl groups leads to the rate law:

$$-\mathrm{d}[\mathrm{PA}]_t\mathrm{d}t = k_l[\mathrm{PA}]_t^2[\mathrm{MI}]_t + k_2[\mathrm{PA}]_t[\mathrm{SA}]_t[\mathrm{MI}]_t \tag{6}$$

where the apparent rate coefficient k_2, by analogy with Eq. (4), would also be a function of the initial maleimide

Table 1
Second-order rate parameter, k_1, for the reaction of maleimide with primary amine in MDP-BMI/DDM, calculated from initial rate data using Eq. (5)

Temperature	160°C	170°C	180°C
k_1 (kg mol^{-1} s^{-1})	9.6×10^{-5}	1.3×10^{-4}	1.63×10^{-4}

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[2] A more complete analysis shows that the factor relating the total and free maleimide concentrations is weakly dependent on the primary amine concentration, and increases slowly as the primary amine is consumed.

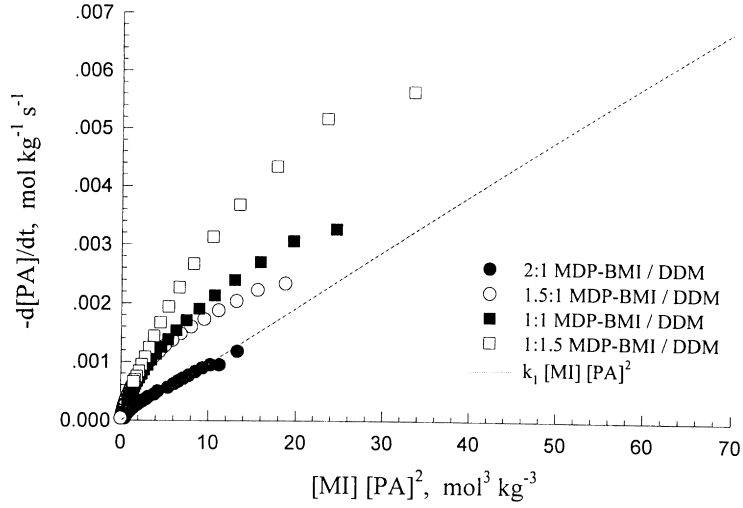

Fig. 10. Plot of instantaneous rate of primary amine consumption as a function of the product $[PA]_t^2$ $[MI]_t$. Data is from MDP-BMI/DDM resins at 160°C.

concentration, decreasing in value as the initial maleimide concentration increases.

Using a non-linear regression analysis, the kinetic data were fitted to Eq. (6). The calculated rates of primary amine consumption were first fitted using single values for the apparent rate coefficients k_1 and k_2. The results are compared with the experimental data for MDP-BMI/DDM resins of different stoichiometries at 160°C in Fig. 11. While the single-valued apparent rate coefficients described the experimental data for the stoichiometries 1:1 and 1.5:1 MDP-BMI/DDM reasonably well, the data were somewhat under-estimated for the 1:1.5 MDP-BMI/DDM mixture, and over-estimated for the 2:1 MDP-BMI/DDM mixture. This discrepancy arises because the apparent rate coefficients are not single valued but depend on the initial stoichiometry. According to Eq. (4), the rate coefficients should decrease as the initial maleimide concentration increases in the resin mixture.

If the apparent rate coefficients are evaluated separately for each stoichiometry, excellent fits are achieved using Eq. (6) as shown in Fig. 12, and the calculated values of the coefficients are given in Table 2. The change in the apparent rate coefficients k_1 and k_2 with the initial maleimide concentration is demonstrated in Fig. 13, which shows that the coefficients decrease as the initial maleimide concentration increases, as predicted from Eq. (4).

3.3. Reaction of maleimide with secondary amine

The secondary amine is far less reactive than the primary amine in the MDP-BMI/DDM system. As a consequence, the amount of tertiary amine formed is very small for some stoichiometries, which made the acquisition of accurate rate data difficult to obtain. However, the proposed reaction scheme for secondary amine with maleimide is identical to that for the reaction of primary amine with maleimide,

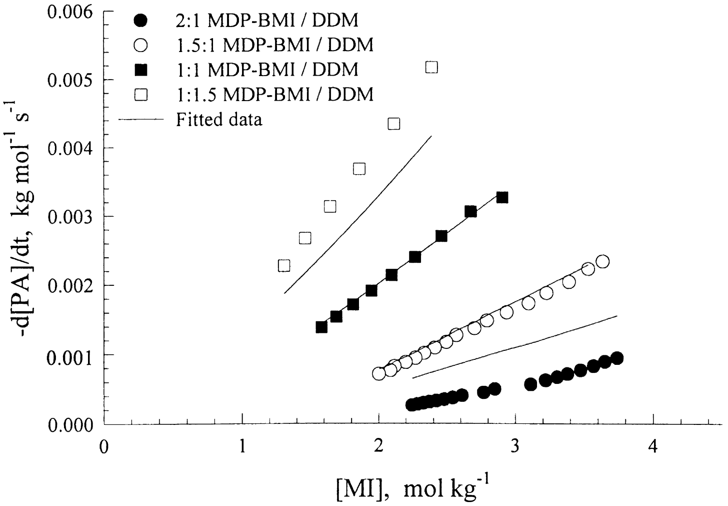

Fig. 11. Plot of experimental rate data with the calculated data fitted to Eq. (6) for MDP-BMI/DDM resins of various stoichiometry at 160°C.

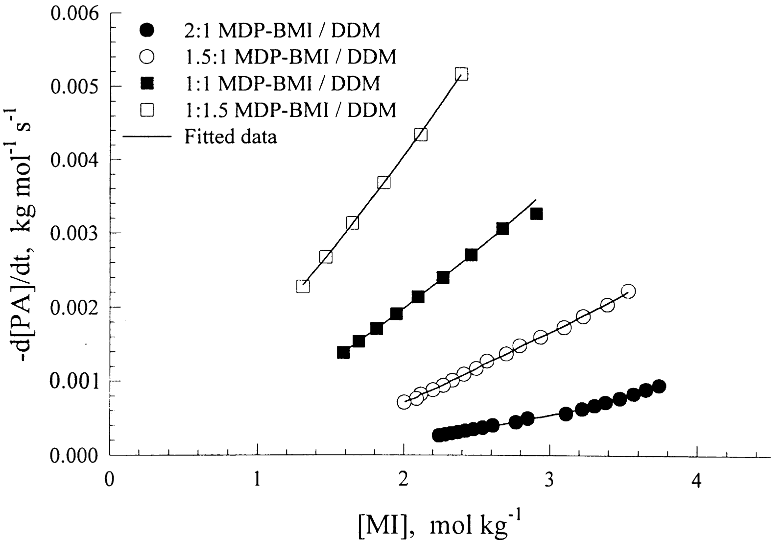

Fig. 12. Improved fit using Eq. (6) for MDP-BMI/DDM at 160°C, where rate parameters were calculated separately for each stoichiometry.

giving the rate Eq. (7)

$$d[TA]/dt = k_3[MI]_t[SA]_t[PA]_t + k_4[MI]_t[SA]_t^2 \qquad (7)$$

As for the case of the reaction of primary amine with maleimide, the apparent rate coefficients would be expected to be dependent on the initial stoichiometry of the resin.

From an analogous analysis to that used for the reaction of the primary amine with maleimide, the measured rate data can be used with Eq. (7) to generate the rate coefficients, k_3 and k_4. Fig. 14 is an example for an equimolar MDP-BMI/DDM mixture cured at 170°C. The rate coefficients were calculated by fitting the data up to 60% conversion. An excellent fit was achieved until beyond about 70% conversion at which point the experimental data fall below the calculated predictions, due to the effect of vitrification. The fitted apparent rate coefficients at 170°C were, $k_3 = 3.29 \times 10^{-5}$ kg^2 mol^{-2} s^{-1} and $k_4 = 4.84 \times 10^{-5}$ kg^2 mol^{-2} s^{-1} compared with $k_1 = 1.76 \times 10^{-4}$ kg^2 mol^{-2} s^{-1} and $k_2 = 1.59 \times 10^{-4}$ kg^2 mol^{-2} s^{-1}. This gives a ratio for the reactivity of secondary amine to that of the primary amine of 0.25 ± 0.05, so that the primary amine has four times the reactivity of secondary amine.

Table 2
Calculated rate coefficients, k_1 and k_2 for the reaction of maleimide with amine in MDP-BMI/DDM at 160°C

Rate constants	Stoichiometry			
	2:1	1.5:1	1:1	1:1.5
k_1 (kg^2 mol^{-2} s^{-1})	8.75×10^{-5}	9.40×10^{-5}	1.03×10^{-4}	1.18×10^{-4}
k_2 (kg^2 mol^{-2} s^{-1})	4.71×10^{-5}	1.04×10^{-4}	1.75×10^{-4}	2.21×10^{-4}

4. Conclusions

Kinetic data obtained by FT-NIR spectroscopy has been used to develop a mechanistic kinetic model for the cure kinetics of MDP-BMI/DDM thermosetting resin. A kinetic mechanism for the copolymerisation reactions of maleimide with amines in bulk has been postulated, where the reaction is between the nucleophilic amine and an activated complex of a maleimide with amine formed by hydrogen bonding. As a result, the reaction can be considered to show self-catalysis.

The catalytic effect on the polymerisation of both the primary amine and the secondary amine formed during the polymerisation may explain why second-order kinetics was reported in previous work. That is, the rate due to primary amine catalysis falls with a decrease in primary amine concentration, but this is compensated for by an increase in the rate due to secondary amine catalysis.

The experimentally derived apparent rate coefficients for the copolymerisation of maleimide with amine vary with the initial stoichiometry of the resin. This unusual result was attributed to the mechanism for the reaction, and the relative amount of free amine is determined by the initial concentration of the maleimide.

An excellent fit to the experimental data for the consumption of primary and secondary amine was obtained using the kinetic rate laws up to approximately 70% conversion. At higher conversions, a negative deviation from the predicted rates was found. This was attributed to vitrification leading to an element of diffusion-control in the reaction. The effect of diffusion-control can be accounted for by including in the kinetic equation a term related to the T_g of the network and an activation energy for segmental motion. This latter

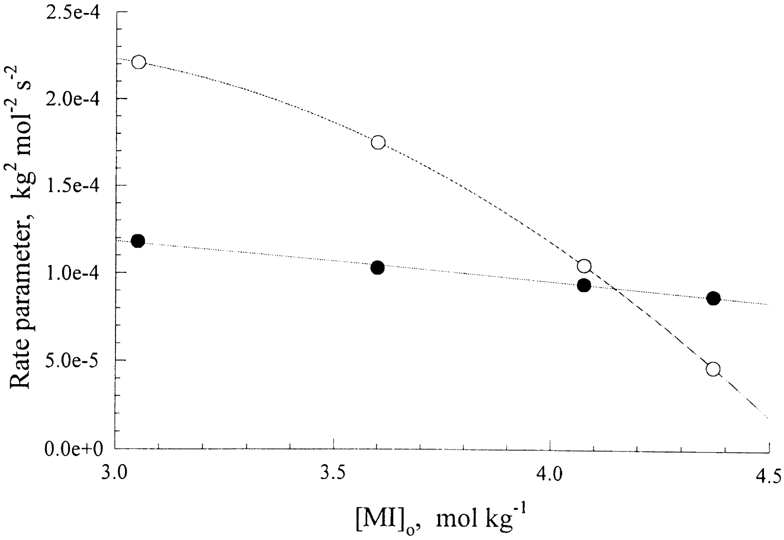

Fig. 13. The effect of initial composition on the fitted rate parameters, k_1 (●) and k_2 (○) for MDP-BMI/DDM at 160°C.

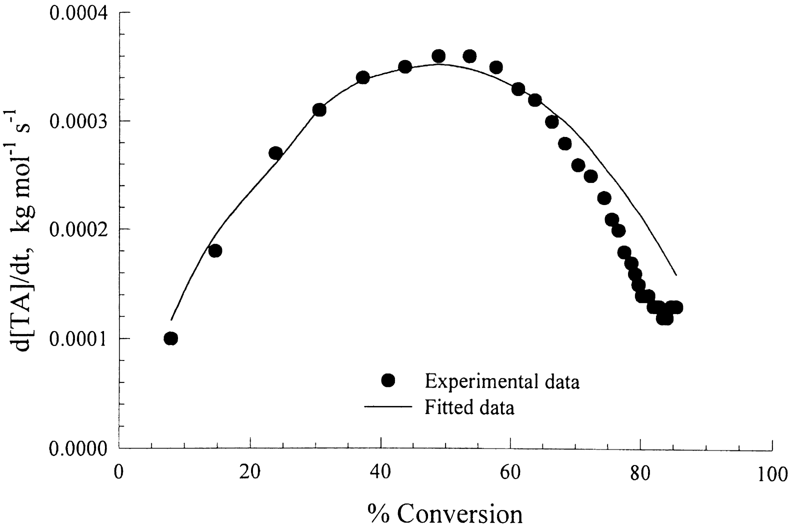

Fig. 14. Rate of formation of tertiary amine groups for a 1:1 MDP-BMI/DDM resin at 170°C and fitted rate using Eq. (7).

feature of the reactions will be discussed in detail in a later paper.

For the MDP-BMI/DDM mixtures cured over the temperature range studied, the homopolymerisation of maleimide only plays a minor role. It was observed however, that the rate of this reaction is very sensitive to the viscosity of the matrix, and it begins to decrease at an earlier stage of the reaction than does the Michael addition reaction.

Acknowledgements

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