

# Analysis of the Curing Behavior of Bismaleimide Resins

A. V. TUNGARE\* and G. C. MARTIN†

Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13244

## SYNOPSIS

The curing behavior of bismaleimide resins was investigated using formulations containing different stoichiometric ratios of 1,1'-(methylenedi-4,1-phenylene) bismaleimide (BMI) and 4,4'-methylenedianiline (MDA). The resin cure involved a low temperature primary amine addition to the maleimide double bonds and a high temperature homopolymerization of the maleimide double bonds. The kinetics of the amine addition and the homopolymerization reactions were determined using Fourier Transform Infrared Spectroscopy and Differential Scanning Calorimetry. The nucleophilic addition of the primary amines to the maleimide double bonds occurred by a second-order reaction, and was at least two orders of magnitude faster than the homopolymerization reaction, which occurred by a multistep mechanism involving thermal initiation of chain growth, followed by chain propagation. A kinetic model for the curing behavior was developed and used to predict the extents of the amine addition and the homopolymerization reactions in networks cured under isothermal or dynamic conditions.

## INTRODUCTION

Bismaleimide resins are used in the aerospace and electronics industries as matrix resins for high-performance composites. The cured resins exhibit low moisture absorption, excellent chemical stability, and thermal and mechanical properties superior to most epoxy resins.<sup>1,2,3</sup> Due to the aromatic nature and the high crosslink density of the cured network, the fully cured resins are brittle.<sup>4</sup> In order to increase the flexibility of the cured resin, bismaleimides are reacted with aromatic diamines, which reduce the crosslink density by increasing the distance between crosslinks.

Amine addition to the maleimide double bond occurs readily and at a lower temperature than the homopolymerization reaction of the maleimide double bonds.<sup>5</sup> As illustrated in Figure 1, the amine addition reaction causes extension of the network chains, whereas the homopolymerization reaction leads to chain extension and crosslinking in the network. As a result, the two reactions have different

effects on the thermal, mechanical, and rheological properties of the resin.

Since the curing of bismaleimide resin involves amine addition and BMI homopolymerization reactions, it is necessary to define two conversions: the amine addition and the BMI homopolymerization conversions. The amine addition conversion,  $\alpha_{\text{amine addition}}$ , is calculated from the fraction of the maleimide groups of the BMI that reacts with the primary amine groups of the MDA; the BMI homopolymerization conversion,  $\alpha_{\text{homopolym}}$ , is the fraction of the maleimide groups that homopolymerize. In order to relate the network properties to the curing chemistry and to select the optimum processing conditions for the resin, it is necessary to understand the effects of the resin composition, the curing conditions, and the curing chemistry on the amine addition and the homopolymerization conversions, and the effects of each curing reaction on the network properties.

The objectives of this research were to delineate the mechanism and kinetics of the amine addition and the homopolymerization reactions, and to develop a kinetic model for predicting amine addition and BMI homopolymerization conversions in bismaleimide resin networks cured under isothermal and dynamic conditions. The curing reactions were

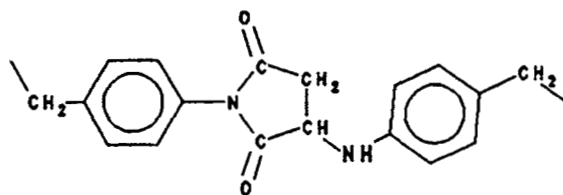
\* Present address: Allied-Signal Corporation, Research and Technology, Des Plaines, Illinois 60017.

† To whom correspondence should be addressed.

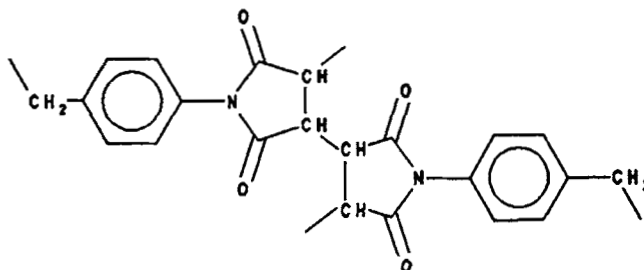
Journal of Applied Polymer Science, Vol. 46, 1125-1135 (1992)

© 1992 John Wiley & Sons, Inc.

CCC 0021-8995/92/071125-11



Chain Extension Due to Amine Addition



Crosslinking Due to Homopolymerization

**Figure 1** Chain extension and crosslinking in bismaleimide resins due to the amine addition and the homopolymerization reactions.

analyzed using formulations, containing different stoichiometric ratios of bismaleimide and diamine, and different curing conditions. Model compounds were used to elucidate the curing chemistry. The kinetic parameters of the reactions were determined from Fourier Transform Infrared (FTIR) Spectroscopy. The kinetic model forms the basis for developing relations between the curing chemistry and the network properties, and can be used for selecting the optimum processing conditions for the resin.<sup>6</sup>

## EXPERIMENTAL

### Materials

The 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI), with a purity of 95%, and the 4,4'-methylenedianiline (MDA), with a purity of 99.4%, that were used in this study were obtained from the Aldrich Chemical Company. The BMI resin was purified by repeated precipitation using methyl ethyl ketone. Gel permeation chromatography tests, performed on the precipitated BMI resin, yielded a single, sharp peak, indicating that the precipitated resin was free of impurities. Formulations containing different stoichiometric ratios of BMI to MDA were prepared by dissolving measured quantities of both components in methyl ethyl ketone and then stripping the solvent in a vacuum oven. *N*-phenyl ma-

leimide (NPM), with a 97% purity, was used as a model compound in this study and was obtained from the Aldrich Chemical Company.

### Procedures

Isothermal curing studies were performed on thin films of the resin using an IBM Instruments IR/32S FTIR spectrometer, equipped with a temperature controlled sample holder for *in situ* analyses of the curing reactions. Since the BMI resin melted between 155 and 160°C, the homopolymerization reaction kinetics were measured at 165, 175, 185, 206, 235, and 250°C. Two different experimental procedures were used to collect maleimide conversion data. In one procedure, NaCl cells were first heated to 165°C in the sample holder, and the BMI resin was applied to the surface to form a thin film. The initial spectrum was recorded at 165°C and the temperature was ramped to the isothermal test temperature (206, 235, and 250°C). Spectra were recorded at 73 sec intervals for one h. In another procedure, the BMI resin was coated onto the surface of a NaCl cell that was equilibrated at the isothermal test temperature (165, 175, and 185°C) and the spectra were recorded at 2 min intervals.

The amine addition reaction kinetics were determined from curing studies at 75, 100, and 125°C, in which BMI : MDA formulations with stoichiometric ratios of 1 : 2, 1 : 1, and 2 : 1 were used. Spectra

were recorded under a nitrogen purge at 2 min intervals and  $2\text{ cm}^{-1}$  resolution. The change in the concentration of the maleimide double bonds with time was determined from the area under the maleimide  $\text{C}=\text{H}$  stretching peak at  $3098\text{ cm}^{-1}$  using quantitative analysis software. The aromatic  $\text{C}-\text{C}$  stretching vibration at  $1514\text{ cm}^{-1}$  was used as the reference peak in the quantitative analysis.

Dynamic curing studies were performed on the 1 : 1 BMI : MDA resin in the FTIR spectrometer. Thin films of the resin were cast onto NaCl cells; the cells were placed in the sample holder; and the temperature was ramped to  $165^\circ\text{C}$  at a heating rate of  $12^\circ\text{C}/\text{min}$ . The resin temperature profile was measured by placing a thermocouple in close proximity to the sample. Spectra were recorded every 90 sec while the sample heated to the isothermal temperature.

DSC studies were performed using a Mettler DSC-30, equipped with a low temperature cell. The kinetics of the homopolymerization reaction were determined from isothermal studies at 165, 175, 185, and  $200^\circ\text{C}$ , in which the BMI resin was cured at the isothermal temperatures for 15, 30, 45, 60, and 120 min, were quenched to  $0^\circ\text{C}$ , and then were scanned at  $5^\circ\text{C}/\text{min}$  to  $350^\circ\text{C}$  to determine the residual heat of reaction. The DSC conversions were calculated from the residual heats of reactions using the total heat of reaction. The total heat of BMI homopolymerization,  $\Delta H_{2,\text{tot}}$ , was determined from the maximum heat released during the isothermal and dynamic curing of the BMI resin.

Size exclusion chromatography (SEC) tests were performed using a Waters Associates 150C ALC/GPC, with tetrahydrofuran (100%) as a solvent. The SEC tests were performed on 4 : 1 *N*-phenylmaleimide : MDA cured at 125, 175, and  $225^\circ\text{C}$  for 90 min.

## RESULTS AND DISCUSSION

### Amine Addition Reaction

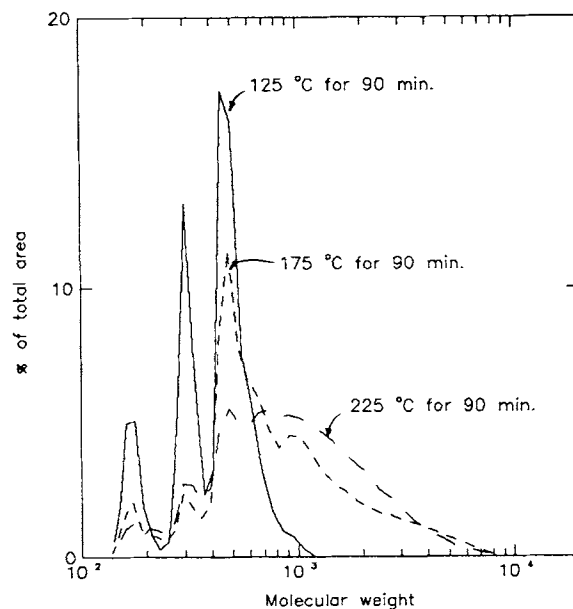
#### Reaction Mechanism

Mallet<sup>7</sup> and Kovacic and Hein<sup>8</sup> have reported that the maleimide double bonds of the bismaleimide resin are weakened by the electron withdrawing nature of the adjacent carbonyl groups and, hence, nucleophilic addition of amines to the maleimide double bonds occurs readily and at low temperatures. Crivello<sup>9</sup> conducted model compound studies using *N*-phenylmaleimide and aniline in a solvent medium and proposed that the amine addition occurs by a second order mechanism involving a charged inter-

mediate. The aniline reacts with *N*-phenylmaleimide to form *N,N'*-diphenylaspartimide. Though the reaction was conducted in a solvent medium and simple compounds were used, Crivello did not observe any reaction between the secondary amine hydrogens of *N,N'*-diphenylaspartimide and the maleimide double bonds of *N*-phenylmaleimide.

In the present study, SEC analyses of the curing behavior of *N*-phenylmaleimide with MDA were used to estimate the extent to which the secondary amine hydrogens of the MDA reacted with the maleimide double bonds. The chromatograms of the 4 : 1 NPM : MDA samples, cured at 125, 175, and  $225^\circ\text{C}$  for 90 min, are shown in Figure 2. The reactions that can occur during the curing of 4 : 1 NPM : MDA are the addition of primary amine hydrogens to maleimide double bonds, the addition of secondary amine hydrogens to maleimide double bonds, and the homopolymerization of maleimide double bonds.

For the sample cured at  $125^\circ\text{C}$ , major peaks occur at molecular weights of approximately 170, 300, and 500, and a minor peak is observed at approximately 950. The peak at 170 is assigned to the unreacted MDA and NPM; the peak at 300 occurs due to a compound formed by the reaction between one primary amine hydrogen of the MDA and the double bond of the NPM; and the peak at 500 is assigned to a compound with a molecular weight of 544, formed by the reaction between two primary amine hydrogens of the MDA and two NPM molecules. The peak at 950 occurs due to reaction of both the



**Figure 2** Chromatograms of 4 : 1 NPM : MDA, cured at 125, 175, and  $225^\circ\text{C}$  for 90 min.

primary and the secondary amine hydrogens of the MDA with four NPM molecules. The area under the peak at 950 comprises less than 2% of the total peak area of the chromatogram, but indicates that some reaction between the secondary amine hydrogens and the maleimide double bonds does occur at 125°C. The main reaction at 125°C, however, is between the primary amine hydrogens and the maleimide double bonds.

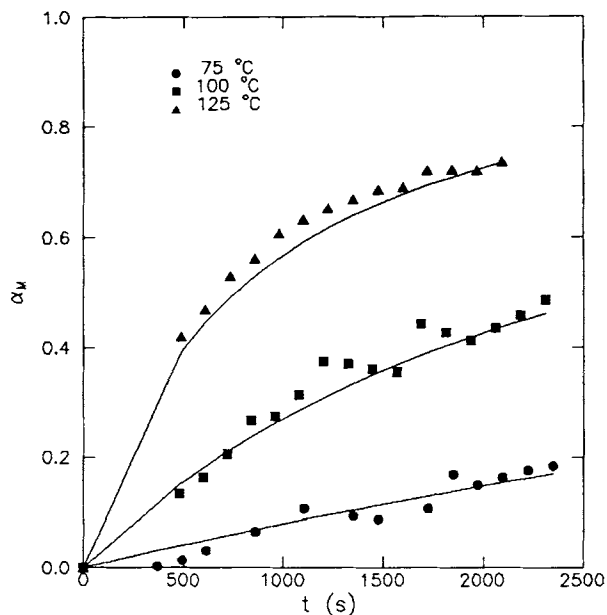
For the sample cured at 175°C, in addition to the peaks at molecular weights of 170, 300, and 500, a shoulder is observed above a molecular weight of 900. Peaks above 700 can occur due to reaction of secondary amine hydrogens of the MDA with NPM, or can occur due to homopolymerization of NPM. The peak above the molecular weight of 900 is broad and has a long tail that contains species with molecular weights up to 7000. Since species above a molecular weight of 900 can result only from homopolymerization of NPM, the long tail provides evidence that NPM homopolymerization occurs at 175°C.

The chromatogram of 4 : 1 NPM : MDA cured at 225°C is qualitatively similar to that of the sample cured at 175°C. The broad peak above molecular weight of 900, however, is more prominent in the sample cured at 225°C, indicating that there is a considerable amount of NPM homopolymerization at 225°C.

The SEC analyses of the curing behavior of model compounds demonstrate that the secondary amine hydrogens react with the maleimide double bonds at high temperatures. However, it was not possible to quantitatively determine the extent of the secondary amine hydrogen reaction that occurred in the model compounds at 175 and 225°C. Since the results indicate that the reaction of the secondary amine hydrogen is negligible as compared with the reaction of the primary amine hydrogen at 125°C, it is assumed that the amine addition reaction during the melt polymerization of 1 : 1, 2 : 1, and 1 : 2 BMI : MDA resins occurs mainly by the reaction of the primary amine hydrogens with the maleimide double bonds.

### Reaction Kinetics

The MDA can be schematically represented by A-R'-A, where A is the amine group and R' is the backbone diphenyl methane molecule. Maleimide conversion data at 75, 100, and 125°C for the 1 : 1, the 1 : 2, and the 2 : 1 BMI : MDA resins were used to develop a kinetic model for the amine addition reaction. The conversion data, shown in Figures 3, 4, and 5, were modeled using a second-order reaction



**Figure 3** Maleimide conversions determined from FTIR studies for the cure of 1 : 1 BMI : MDA at 75, 100, and 125°C. The solid lines are the conversion profiles predicted using eq. (3).

mechanism in which one maleimide group reacts with one amine group. The depletion of the maleimide groups is given by:

$$\frac{d[M]}{dt} = -K_1[M][A] \quad (1)$$

where  $[A]$  is the concentration of the amine groups,  $[M]$  is the concentration of the maleimide groups,  $t$  is the reaction time, and  $K_1$  is the second-order reaction rate constant. For initial concentrations of maleimide groups,  $[M_0]$ , and amine groups,  $[A_0]$ , the maleimide conversion,  $\alpha_M$ , is

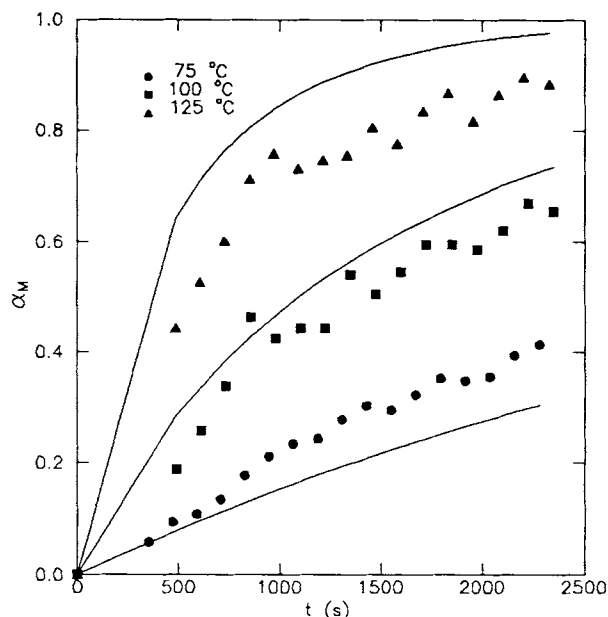
$$\alpha_M = \frac{[M_0] - [M]}{[M_0]} \quad (2)$$

and the amine conversion,  $\alpha_A$ , is

$$\alpha_A = \frac{[A_0] - [A]}{[A_0]} \quad (3)$$

Equation (1) can be written in terms of the maleimide conversion as:

$$\frac{d\alpha_M}{dt} = K_1^0 \exp\left(-\frac{\Delta E_{K_1}}{RT}\right) \times [1 - \alpha_M] \left[1 - \alpha_M \frac{[M_0]}{[A_0]}\right] [A_0] \quad (4)$$



**Figure 4** Maleimide conversions determined from FTIR studies for the cure of 1 : 2 BMI : MDA at 75, 100, and 125°C. The solid lines are the conversion profiles predicted using eq. (3).

where  $K_1^0$  is the pre-exponential factor,  $\Delta E_{K_1}$  is the activation energy for the amine addition reaction, and  $R$  is the gas constant.

The parameters,  $K_1^0$  and  $\Delta E_{K_1}$ , were evaluated using the maleimide conversion data and the optimum values are listed in Table I. The conversion profiles predicted using the kinetic model are compared with the experimental data in Figures 3, 4, and 5. There is agreement between the predicted profiles and the experimental data, even though the values of  $K_1^0$  and  $\Delta E_{K_1}$  used are averages over three resin compositions and temperatures ranging from 75 to 125°C.

Since one maleimide group reacts with one amine group, the extent of the amine addition reaction, using the initial concentration of the maleimide groups as a basis, can be calculated using eqs. (5) or (6):

$$\alpha_{\text{amine addition}} = \frac{[A_0] - [A]}{[A_0]} \quad (5)$$

$$\alpha_{\text{amine addition}} = \alpha_A \frac{[A_0]}{[M_0]} \quad (6)$$

## Homopolymerization Reaction

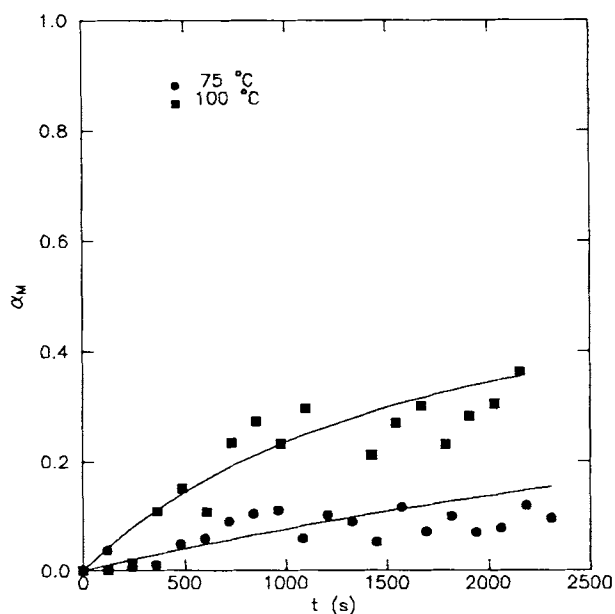
### Reaction Mechanism

The double bonds of the bismaleimide resin are weakened by the electron withdrawing nature of the

adjacent carbonyl groups and readily react in the molten state by free radical polymerization.<sup>7,10,11</sup> Kwiatkowski et al.<sup>12</sup> observed a marked increase in the polymerization rate of bismaleimide resins in the presence of peroxides and a 20- to 50-fold increase in the presence of reactive olefins, and concluded that the polymerization reaction involves a free radical, rather than an anionic addition mechanism. The most direct evidence of free radical curing reactions was obtained by Brown and Sandreczki,<sup>13</sup> based on electron spin resonance spectroscopy studies on thermally crosslinked bismaleimide resins.

Figure 6 shows the maleimide conversion data obtained during the isothermal cure of BMI at 165, 175, 185, 206, 235, and 250°C. The filled and unfilled symbols are used to differentiate between the data obtained using the two different FTIR techniques. The conversion data are marked by an initial rapid increase in the maleimide conversion, which is followed by a steady increase in conversion over time. DiGiulio et al.<sup>14</sup> and Tung<sup>15</sup> studied the curing behavior of bismaleimide resins using FTIR spectroscopy and observed similar isothermal conversion profiles for the homopolymerization reaction.

Based on the conversion data in Figure 6, the homopolymerization reaction is postulated to occur by a multistep mechanism involving thermal initiation of chain growth, followed by chain propagation reactions. Thermal initiation is a reversible reaction,



**Figure 5** Maleimide conversions determined from FTIR studies for the cure of 2 : 1 BMI : MDA at 75 and 100°C. The solid lines are the conversion profiles predicted using eq. (3).

**Table I** Optimum Kinetic Parameters of the Amine Addition and the Homopolymerization Reactions

$K_1^0$	$2.25 \times 10^5$ (conc.-s) <sup>-1</sup>	$\Delta E_{K_1}$	62.3 (kJ/mol)
$K_{2i}^0$	$1.64 \times 10^3$ (s <sup>-1</sup> )	$\Delta E_{K_{2i}}$	49.5 (kJ/mol)
$K_{2t}^0$	$4.20 \times 10^2$ (s <sup>-1</sup> )	$\Delta E_{2t}$	43.6 (kJ/mol)
$K_{2p}^0$	$6.49 \times 10^4$ (conc.-s) <sup>-1</sup>	$\Delta E_{K_{2p}}$	74.2 (kJ/mol)

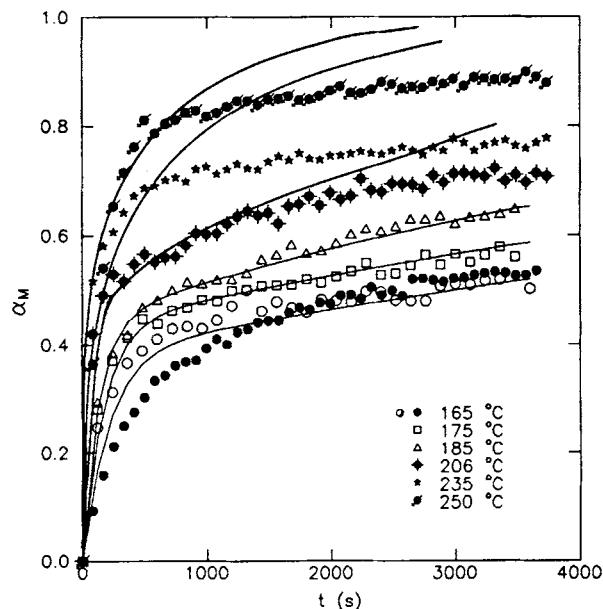
in which the maleimide double bonds dissociate upon heating to generate maleimide di-radicals and a thermal equilibrium concentration of the di-radicals is rapidly established. The initiation reaction occurs readily at high temperatures, as is evident from the initial rapid increase in the maleimide conversion. Maleimide di-radicals, generated in the initiation step, can react with the maleimide double bonds to form long chain ( $n$ -mer) di-radicals, and thus propagate the network. Network propagation can also occur by the reaction between  $n$ -mer di-radicals and the maleimide di-radicals, and between  $n$ -mer di-radicals and the maleimide double bonds. The propagation reactions consume maleimide double bonds at a slower rate than the initiation reaction and cause a steady increase in the maleimide conversion.

Propagation of the network continues until the growing radicals are immobilized in the gelled network.<sup>16</sup> Hummel et al.<sup>17</sup> conducted studies on a homologous series of aliphatic bismaleimide resins, and observed that the rate of polymerization was determined by both the reactivity of the maleimide groups and the mobility of the reactive sites in the resin.

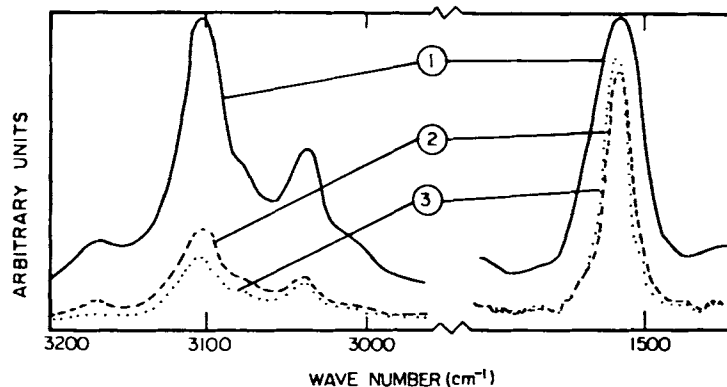
The thermal initiation process is evident from the changes in the maleimide =C—H stretching peak and the reference peak with temperature during the homopolymerization of BMI resin, as shown in Figure 7. Spectrum 1 shows the maleimide and the reference peaks at 175°C at the start of the curing reaction; spectrum 2 shows the two peaks at 175°C and a reaction time of 60 min. The area under the maleimide peak in spectrum 2 is smaller than the area in spectrum 1, due to the consumption of the maleimide double bonds in the homopolymerization reaction. Spectrum 3 shows the maleimide and the reference peaks after the reacted sample has been cooled to room temperature. The maleimide peak area in spectrum 3 is greater than that in spectrum 2. If the increase in the maleimide peak area were to occur only due to cooling, the ratio of the maleimide peak area to the reference peak area in spectrum 2 would be the same as the corresponding ratio in spectrum 3. Based on a quantitative comparison of the two spectra, in which the ratio of the maleimide peak area to the reference peak area in spec-

trum 2 is normalized to 1, the corresponding ratio for spectrum 3 is 1.46. The increase in the maleimide peak area, above that expected from cooling, may be due to the recombination of unreacted maleimide di-radicals to form maleimide double bonds.

In order to demonstrate that the behavior of the maleimide peak on cooling is different from other peaks in the high frequency region of the spectrum, a comparison was made with the methylene C—H stretching peak at 2916 cm<sup>-1</sup>. For a ratio of the methylene peak area to the reference peak area in spectrum 2 that was normalized to 1, the corresponding ratio in spectrum 3 was 1.08; that is, the methylene peak exhibited an 8% increase in the peak area upon cooling. The maleimide peak area increased by 46% upon cooling: an increase that was greater than that expected solely due to cooling.



**Figure 6** Maleimide conversions determined from FTIR studies for the cure of BMI at 165, 175, 185, 206, 235, and 250°C. The filled and unfilled symbols indicate data acquired using two different experimental procedures. The solid lines are the predictions from the kinetic model for homopolymerization.



**Figure 7** Variation of the maleimide  $=C-H$  stretching peak at  $3098\text{ cm}^{-1}$ , and the reference peak at  $1514\text{ cm}^{-1}$ , during BMI resin cure. Spectrum 1 shows the peaks at  $175^\circ\text{C}$  and time  $t = 0$ ; spectrum 2 shows the peaks at  $175^\circ\text{C}$  and  $t = 60\text{ min}$ ; spectrum 3 shows the peaks when the sample is cooled to room temperature.

The thermal initiation process during the homopolymerization of bismaleimide resins is different than that of styrene. In the case of thermally initiated polymerization of styrene, the formation of monomer di-radical, or a radical and a hydrogen atom, is not possible because energy in excess of  $200\text{ kJ}$  is necessary to break the bond.<sup>18</sup> The thermal initiation reaction in styrene, therefore, is postulated to occur by an energetically favorable termolecular initiation mechanism, in which three monomer molecules react and form a pair of monoradicals.<sup>18</sup> Unlike the double bonds in styrene, the double bonds in the maleimide group are weakened by the electron withdrawing nature of the adjacent carbonyl groups. Hence, it is postulated that the dissociation of the maleimide double bonds into di-radicals requires much less energy than a similar dissociation of double bonds in styrene.

### Reaction Kinetics

The BMI resin can be schematically represented by  $M-R-M$ , where  $M$  is the maleimide functional group. The chemical species present in the reaction mixture are the maleimide groups;  $\dot{M}$ , the maleimide di-radicals,  $\ddot{M}_1$ , and the  $n$ -mer di-radicals,  $\ddot{M}_n$ , where  $n \geq 2$ .

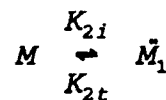
A kinetic model for BMI homopolymerization is shown in Figure 8 and consists of a reversible, first order, initiation reaction, and five second-order propagation reactions. In Figure 8,  $K_{2i}$ ,  $K_{2t}$ , and  $K_{2p}$  are the rate constants of the initiation, the termination, and the propagation reactions.

In order to reduce the mathematical complexity of a kinetic model, the rates of the propagation reactions are assumed to be equal and independent of the chain length<sup>19</sup> and the sum of the concentrations

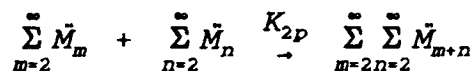
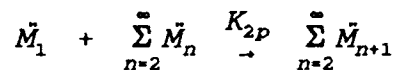
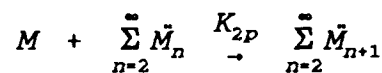
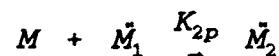
of all the  $n$ -mer di-radicals in the reaction mass is defined by  $\ddot{M}$ , where

$$\begin{aligned} [\ddot{M}] &= \sum_{n=2} [\ddot{M}_n] \\ &= [\ddot{M}_2] + [\ddot{M}_3] + \dots + [\ddot{M}_n] + \dots \quad (7) \end{aligned}$$

### Initiation



### Propagation



**Figure 8** Model for the homopolymerization of bismaleimide resins.

The mole balance equations for the chemical species present in the reaction mixture are:

$$\frac{d[M]}{dt} = K_{2i}[\dot{M}_1] - K_{2t}[M] - K_{2p}[M][\dot{M}_1] - K_{2p}[M][\dot{M}] \quad (8)$$

$$\frac{d[\dot{M}_1]}{dt} = K_{2i}[M] - K_{2t}[\dot{M}_1] - K_{2p}[M]\dot{M}_1 - K_{2p}[\dot{M}_1]^2 - K_{2p}[\dot{M}_1][\dot{M}] \quad (9)$$

$$\frac{d[\dot{M}]}{dt} = K_{2p}[M][\dot{M}_1] + \frac{K_{2p}}{2}[\dot{M}]^2 - \frac{K_{2p}}{2}[\dot{M}][\dot{M}_1] - \frac{K_{2p}}{2}[\dot{M}]^2 \quad (10)$$

where

$$K_{2i} = K_{2i}^0 \exp\left(-\frac{\Delta E_{K_{2i}}}{RT}\right) \quad (11)$$

$$K_{2t} = K_{2t}^0 \exp\left(-\frac{\Delta E_{K_{2t}}}{RT}\right) \quad (12)$$

and

$$K_{2p} = K_{2p}^0 \exp\left(-\frac{\Delta E_{K_{2p}}}{RT}\right) \quad (13)$$

Here,  $K_{2i}^0$ ,  $K_{2t}^0$ , and  $K_{2p}^0$  are the pre-exponential factors, and  $\Delta E_{K_{2i}}$ ,  $\Delta E_{K_{2t}}$ , and  $\Delta E_{K_{2p}}$  are the activation energies of the initiation, the termination, and the propagation reactions.

The pre-exponential factors and the activation energies were estimated from the experimentally measured maleimide conversion profiles, shown in Figure 6, using a conjugate direction search algorithm<sup>20</sup> and a package for the integration of systems of ordinary differential equations.<sup>21</sup> The optimum values of the kinetic parameters are listed in Table I. As shown in Figure 6, the maleimide conversion profiles predicted using the kinetic model are in agreement with the experimental data at 165, 175, and 185°C, and with the data at 206°C up to 65% maleimide conversion. The maleimide conversions at 235 and 250°C, predicted using the kinetics model, are higher than the experimentally measured conversions.

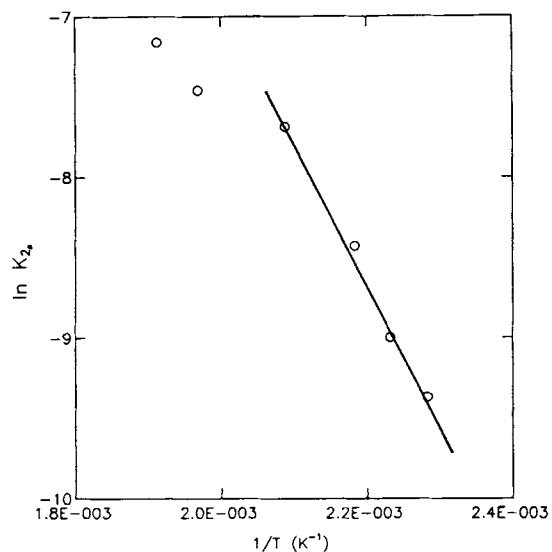


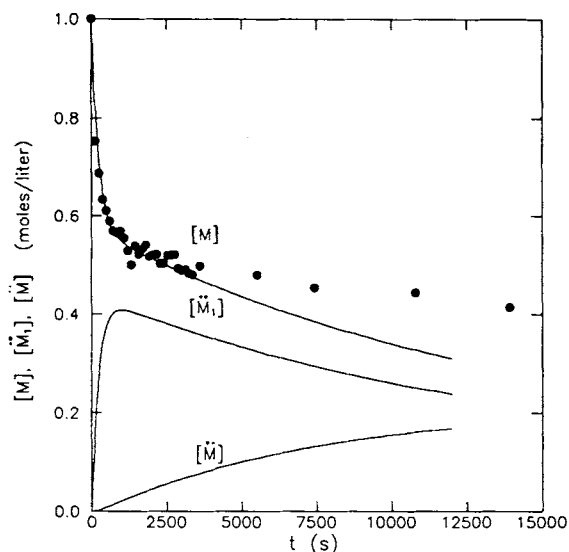
Figure 9 Arrhenius plot of the propagation rate constant for BMI homopolymerization.

An Arrhenius plot of the propagation rate constants is shown in Figure 9. The propagation rate constants for the isothermal curing at 165, 175, 185, and 206°C are on a straight line with a correlation coefficient of 0.997. The Arrhenius relation at 235 and 250°C is different from that at 165, 175, 185, and 206°C and, hence, only the data at 165, 175, 185, and 206°C were used to calculate the activation energy and the pre-exponential factor of the propagation reaction. The kinetic model for BMI homopolymerization, therefore, is valid only between 165 and 206°C.

The maleimide concentration data, determined from FTIR studies during the isothermal cure of BMI resin at 165°C, are compared with the concentration profiles calculated from the kinetic model in Figure 10. The profiles of  $[\dot{M}_1]$  and  $[\dot{M}]$  are also shown in the figure. In Figure 10, there is agreement between the measured and the calculated maleimide conversions for cure times under 2 h, beyond which the measured concentrations are higher than those calculated from the kinetic model. The result suggests that the rate of the propagation reaction decreases at long cure times.

The concentration profiles of  $[M]$ ,  $[\dot{M}_1]$ , and  $[\dot{M}]$  can be used to calculate the maleimide and the BMI homopolymerization conversions for the resin. The depletion of the maleimide double bonds during homopolymerization,  $\alpha_M$ , can be calculated using eq. (2). Some of the depleted maleimide double bonds remain as di-radicals while others react and are incorporated into the crosslinked network. The BMI homopolymerization conversion,  $\alpha_{\text{homopolym}}$ , is the





**Figure 10** Concentration profiles of  $M$ ,  $[M_1]$ , and  $[M_2]$ , calculated using the kinetic model for homopolymerization during the cure of BMI at  $165^\circ\text{C}$ . The discrete data are the concentrations of  $M$  determined from FTIR studies.

fraction of the depleted maleimide double bonds that are incorporated into the network, and is given by:

$$\alpha_{\text{homopolym}} = \frac{[M_0] - [M] - [M_1]}{[M_0]} - \alpha_{\text{amine addition}} \quad (14)$$

In the case of bismaleimide resin formulations that do not contain MDA,  $\alpha_{\text{amine addition}}$  is zero.

The maleimide conversions at 165, 175, and  $185^\circ\text{C}$  are compared with the corresponding extents of BMI homopolymerization in Figure 11. Although the maleimide conversions increase rapidly, polymerization of the network occurs slowly, as is evident from the gradual increase in the extent of BMI homopolymerization. Resin properties, such as the glass transition temperature, the viscosity, the chemical stability, and the sol fraction, are dependent on the amount of maleimide reacted and, hence, are dependent on the extent of BMI homopolymerization rather than the maleimide conversion.

### Model for Bismaleimide Resin Cure

The homopolymerization reaction was empirically modeled by a thermally initiated, multistep, diradical polymerization and the amine addition reaction was

modeled by a nucleophilic second order addition of the amine to the maleimide double bond. Equation (1) and eqs. (6) to (8) can be combined into a kinetic model for bismaleimide resin cure, the mole balance relations for which are given by eqs. (15) to (18):

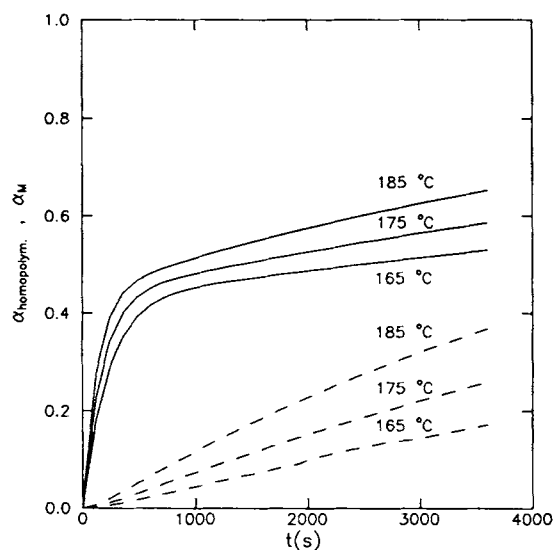
$$\frac{d[A]}{dt} = -K_1[M][A] \quad (15)$$

$$\frac{d[\dot{M}_1]}{dt} = K_{2i}[M] - K_{2t}[\dot{M}_1] - K_{2p}[\dot{M}_1]^2 - K_{2p}[\dot{M}_1][\ddot{M}] \quad (16)$$

$$\frac{d[\ddot{M}]}{dt} = K_{2p}[M][\dot{M}_1] + \frac{K_{2p}}{2}[\dot{M}_1]^2 - \frac{K_{2p}}{2}[\ddot{M}][\dot{M}_1] - \frac{K_{2p}}{2}[\ddot{M}]^2 \quad (17)$$

$$\frac{d[\ddot{M}]}{dt} = K_{2p}[M][\dot{M}_1] + \frac{K_{2p}}{2}[\dot{M}_1]^2 - \frac{K_{2p}}{2}[\ddot{M}][\dot{M}_1] - \frac{K_{2p}}{2}[\ddot{M}]^2 \quad (18)$$

Since the rate constants,  $K_1$ ,  $K_{2i}$ ,  $K_{2t}$ , and  $K_{2p}$  are known, eqs. (15) to (18) can be solved numerically



**Figure 11** BMI homopolymerization (---) and maleimide (—) conversion profiles during the cure of BMI at 165, 175, and  $185^\circ\text{C}$ .

for different stoichiometric ratios of BMI : MDA and different curing conditions and the extents of the amine addition and the homopolymerization reactions in the network can be determined. In combining the homopolymerization and the amine addition reactions to formulate a kinetic model for bismaleimide resin cure, the rate constants of the homopolymerization reactions are assumed to remain unchanged, even when the reaction occurs in the presence of MDA.

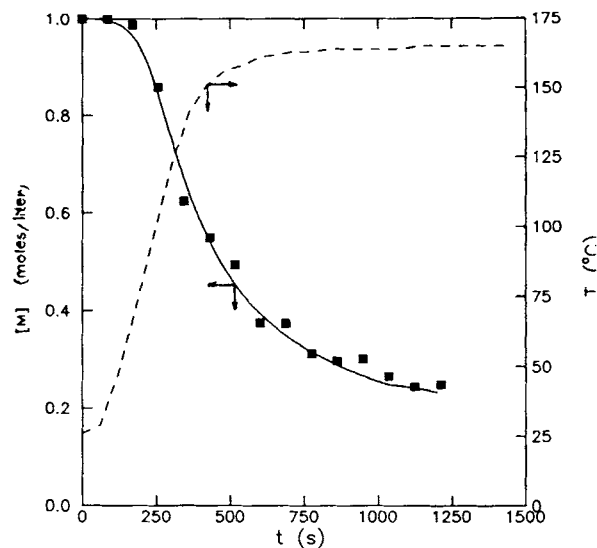
In the multistep homopolymerization of bismaleimide resins, the chain propagation reaction is an order of magnitude slower than the initiation and the termination reactions and is the rate controlling step. The amine addition reaction is a one-step reaction and, as illustrated by the data in Table II, occurs more rapidly than the chain propagation reaction during BMI homopolymerization. At low temperatures, the amine addition reaction is favored over the propagation reaction; however, the propagation reaction becomes competitive at higher temperatures. A similar conclusion was drawn by Tung,<sup>15</sup> based on the initial slopes of the intensity profiles of FTIR spectra of bismaleimide resins.

The kinetic model for bismaleimide resin cure was developed using conversion data obtained from isothermal FTIR spectroscopy. In order to confirm the validity of the model, the extent of the amine addition and the homopolymerization reactions predicted from the kinetic model were compared with conversion data obtained experimentally using FTIR spectroscopy and Differential Scanning Calorimetry under dynamic and isothermal conditions.

The maleimide concentration data, measured during the dynamic curing of 1 : 1 BMI : MDA resin in the FTIR spectrometer, are compared with predictions from the kinetic model for bismaleimide resin cure in Figure 12. The kinetic model was solved numerically to calculate the maleimide concentration profile for the temperature history experienced by the resin. The calculated maleimide concentration profile, which is shown by the solid line in Figure

**Table II** Ratio of the Rate Constants of the Amine Addition and the Chain Propagation Reactions

Temperature (°C)	$\frac{K_1}{K_2}$
150	100
175	83
200	70
225	60



**Figure 12** Comparison between the maleimide concentrations from FTIR studies (■) and the kinetic model predictions (—) for the 1 : 1 BMI : MDA. The dashed line is the temperature profile in the FTIR cell.

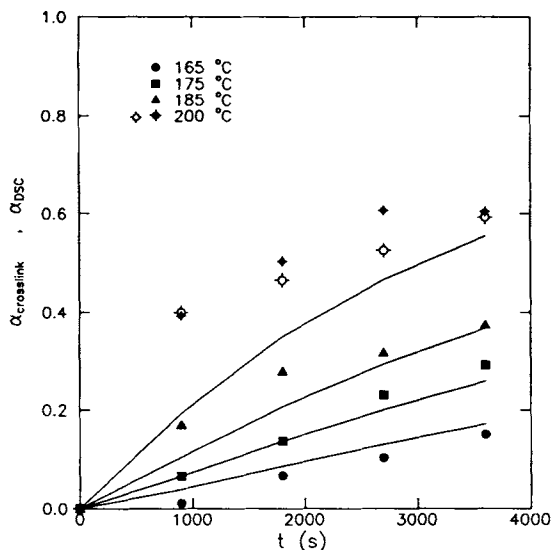
12, is in agreement with the experimentally determined maleimide concentrations.

The BMI conversion profiles, predicted from the kinetic model for homopolymerization, are compared with the conversions measured from DSC studies in Figure 13. The DSC conversion,  $\alpha_{\text{DSC}}$ , was calculated from the residual heat of reaction using;

$$\alpha_{\text{DSC}} = \frac{\Delta H_{2,\text{max}} - \Delta H_{2,\text{res}}}{\Delta H_{2,\text{max}}} \quad (19)$$

In eq. (19),  $\Delta H_{2,\text{max}}$  is 78.8 kJ/mol of BMI and is the maximum heat of the homopolymerization reaction measured in the DSC. Since BMI homopolymerization occurs by a multistep reaction mechanism, each reaction having a unique heat of reaction, the numerator in eq. (19) is the cumulative value of the heats released by all the reactions that occur during homopolymerization. In Figure 13, except for the DSC conversion data at 165°C, there is little agreement between the kinetic model predictions and the experimental data. The DSC conversions at 175, 185, and 200°C are higher than the conversions predicted by the kinetic model. Apparently, the maximum heat of the homopolymerization reaction, measured in the DSC, is not the true total heat of BMI homopolymerization and some BMI remains unreacted.

The FTIR studies, reported above, indicate that the kinetic model for bismaleimide resin cure can be used to predict the amine addition and the BMI homopolymerization conversions for isothermal and



**Figure 13** DSC conversion profiles during the homopolymerization of BMI at 165, 175, 185, and 200°C. The solid lines are the homopolymerization conversion profiles predicted using the kinetic model.

nonisothermal curing conditions. Since the amine addition reaction occurs more rapidly than the homopolymerization reaction, the amount of amine addition and BMI homopolymerization in the network is governed primarily by the resin composition and, to a lesser extent, by the curing conditions. Diffusion effects, which have been neglected in the kinetic model, may affect the rate of the curing reactions at relatively long cure times.

## CONCLUSIONS

The curing of bismaleimide resin involves a low temperature amine addition reaction and a high temperature homopolymerization reaction. Amine addition to the maleimide double bond occurs by a second-order reaction mechanism and results in extension of the network chains. Homopolymerization of BMI resin can be modeled by a thermally initiated, multistep, radical mechanism, and eventually leads to crosslinking in the network.

A kinetic model for the curing behavior of bismaleimide resin was developed and the model predictions were tested using experimental data. The model can be used to select the resin formulation and curing conditions necessary to achieve the desired degree of amine addition and BMI homopolymerization in the network. Since the amine addition and the homopolymerization reactions affect the glass transition temperature and the viscosity

of the resin, the kinetic model can be used as a basis for developing predictive models of the network properties.

This research was supported by a grant from IBM Corporation. The FTIR spectra at 206, 235, and 250°C were collected by A. Osei-Owusu at Syracuse University, and the size exclusion chromatography data were provided by G. Kohut and Dr. J. T. Gotro of IBM Corporation.

## REFERENCES

1. C. L. Leung, T. T. Liao, and P. J. Dynes, *Proc. 28th Nat. SAMPE Symp.*, 818 (1983).
2. K. N. Ninan, K. Krishnan, and J. Mathew, *J. Appl. Polym. Sci.*, **32**, 6033 (1986).
3. J. J. King, M. Chaudhari, and S. Zahir, *Proc. 29th Nat. SAMPE Symp.*, 392 (1984).
4. I. K. Varma and S. Sharma, *Indian J. Tech.*, **25**, 136 (1987).
5. I. K. Varma, Sangita, and D. S. Varma, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1419 (1984).
6. A. V. Tungare, Ph.D. Dissertation, Syracuse University, 1990.
7. M. A. J. Mallet, *Mod. Plast.*, **50**(6), 78 (1973).
8. P. Kovacic and R. W. Hein, *J. Amer. Chem. Soc.*, **81**, 1181 (1959).
9. J. V. Crivello, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 1185 (1973).
10. H. D. Stenzenberger, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **22**, 77 (1973).
11. H. D. Stenzenberger, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **31**, 91 (1977).
12. G. T. Kwiatkowski, L. M. Robeson, G. L. Brode, and A. W. Bedwin, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 961 (1975).
13. I. M. Brown and T. C. Sandreczki, *Proc. ACS Div. Polym. Mat. Sci. Eng.*, **59**, 612 (1988).
14. C. DiGiulio, M. Gautier, and B. Jasse, *J. Appl. Polym. Sci.*, **29**, 1771 (1984).
15. C. M. Tung, *Polym. Prepr. ACS Div. Polym. Chem.*, **28**(1), 7 (1987).
16. A. C. Lind and C. G. Fry, *Proc. ACS Div. Polym. Mat. Sci. Eng.*, **59**, 466 (1988).
17. D. O. Hummel, K. U. Heinen, H. Stenzenberger, and H. Siesler, *J. Appl. Polym. Sci.*, **18**, 2015 (1974).
18. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 131.
19. A. Kumar and S. K. Gupta, *Fundamentals of Polymer Science and Engineering*, Tata McGraw-Hill, New Delhi, 1978, p. 56.
20. M. J. D. Powell, *Comp. J.*, **7**, 155 (1964).
21. A. C. Hindmarsh and G. D. Byrne, *EPISODE: An Effective Package for the Integration of Systems of Ordinary Differential Equations*, Lawrence Livermore Laboratory Report, DC1D-30112, Rev. 1 (1977).

Received December 31, 1991

Accepted January 9, 1992