

# Addition Polyimides. I. Kinetics of Cure Reaction and Thermal Decomposition of Bismaleimides

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## Synopsis

The thermal polymerization of four structurally different bismaleimide resins, prepared by reacting maleic anhydride with four aromatic diamines, viz., 4,4'-diaminodiphenyl methane, 4,4'-diamino diphenyl ether, 4,4'-diamino diphenyl sulfone, and 3,3'-diamino diphenyl sulfone, was followed by differential scanning calorimetry (DSC). The enthalpy change and the kinetic constants for the polymerization reactions were evaluated from the DSC curves. Thermal stability of the cured polymers was studied by thermogravimetry (TG). The kinetic parameters, viz., activation energy  $E$  and preexponential factor  $A$ , for the thermal decomposition of the cured bismaleimides were calculated from the TG curves using three nonmechanistic integral equations. The kinetic constants ( $E$  and  $A$ ) follow a trend similar to the thermal stability of the polymers.

## INTRODUCTION

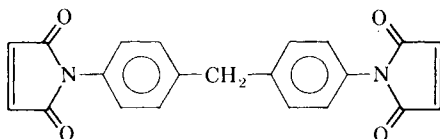
High temperature polymers find extensive applications as matrix for rigid and lightweight fiber-reinforced structural composites, metal to metal adhesives, electrical insulations, etc. Aromatic polyimides are the prime candidates of this category and they show excellent thermal and oxidative stability and high zero strength temperatures.<sup>1</sup> Addition polyimides have certain advantages over condensation polyimides, which are generally difficult and expensive to process and also give rise to voids due to elimination of water molecules. The polyimides which cure by addition polymerization via their reactive terminal groups give void-free structures, at only a modest sacrifice in thermal stability. The thermal stability and flame retardancy of bismaleimides, prepared with different diamines, have been extensively studied by Varma et al.<sup>2-5</sup> In addition to their high thermal stability, bismaleimides possess low moisture absorption properties. This is because the imide functionality has lower capacity for hydrogen bonding than  $-\text{OH}$  or  $-\text{NH}_2$  containing polymers.<sup>6</sup> The major disadvantage of bismaleimides is their brittle character; they are high modulus materials with very low elongation at break.

The present work is mainly concerned with the synthesis and characterization of highly crosslinked, heat-resistant addition polyimides and their monomers, based on maleic anhydride and four different aromatic diamines. The cure characteristics, thermal stability and thermal decomposition kinetics of

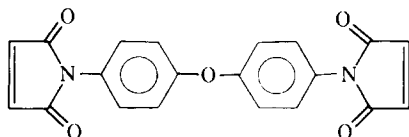
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these polyimides were evaluated by DSC and TG. The maleimides studied are:

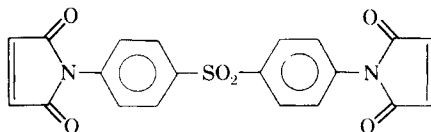
I. 4,4'-Bismaleimido diphenyl methane:



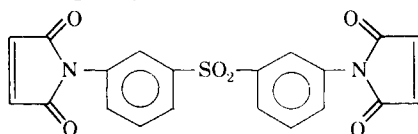
II. 4,4'-Bismaleimido diphenyl ether:



III. 4,4'-Bismaleimido diphenyl sulfone:



IV. 3,3'-Bismaleimido diphenyl sulfone:



## EXPERIMENTAL

### Starting Materials

Maleic anhydride was purified by distillation with acetic anhydride and the fraction distilling between 190 and 200°C was collected. It was further purified by recrystallization from chloroform. The product was then dried in vacuum for about 3 h and its melting point was found to be 54–56°C. The four diamines used were: 4,4'-diamino diphenyl methane (mp = 91–93°C) from BDH, 4,4'-diamino diphenyl ether (mp = 188–190°C) and 4,4'-diamino diphenyl sulfone (mp = 175–177°C) from Fluka, and 3,3'-diamino diphenyl sulfone (mp = 176–178°C) from Hindustan Organic Chemicals Ltd.

### Preparation of Bismaleimide Monomers

Bismaleimide monomers were prepared by reacting maleic anhydride with stoichiometric amounts of the diamines in acetone as per the reported procedures<sup>7,8</sup> involving the following two steps.

#### *Preparation of Bismaleimic Acid Intermediate*

The respective diamines were dissolved in purified acetone in a round-bottomed flask equipped with a stirrer and a condenser. Maleic anhydride was added with constant stirring in two portions. The resulting solution was refluxed at a temperature of 50–57°C for about 3 h. The amic acids were

isolated, washed with acetone, and dried. The acid values of the products were determined by chemical analysis.

#### *Imidization of the Amic Acids*

Imidization of the amic acids was done by refluxing 1 mol of the amic acid in acetone medium (temp 50–57°C) with 3 mol of acetic anhydride, added dropwise, till all the amic acid has gone into solution. Anhydrous sodium acetate was used as the catalyst. The solution was then added to cold water. The precipitate was collected, washed with sodium bicarbonate till all free acids were removed, and finally washed with distilled water. The sample was then purified by recrystallization from methanol, and dried at 60–70°C under vacuum.

#### **Instrumental**

The IR spectra were recorded using Perkin-Elmer Model 283 Infrared Spectrophotometer. <sup>1</sup>H-NMR spectra were recorded in pyridine-d<sub>5</sub> with a Jeol MH-100 NMR Spectrometer, using tetramethyl silane as the internal standard. Carbon-hydrogen estimations were done with a Hermann-Moritz Model 10 semimicro semiautomatic elemental analyzer.

Thermal characterization of the polymers was carried out using a DuPont 990 Modular Thermal Analyzer system, in conjunction with 951 Thermogravimetric Analyzer and Cell Base Module II-905 DSC. All the TG and DSC experiments were carried out in dry nitrogen atmosphere, purged at a rate of 50 cm<sup>3</sup> min<sup>-1</sup>. A constant heating rate of 10°C min<sup>-1</sup> and sample mass of 10 ± 0.1 mg were employed for the entire study. Computational work was done with a CDC computer using a FORTRAN IV program.

#### **RESULTS AND DISCUSSION**

Bismaleimic acids, prepared from the respective diamines, were characterized by their IR spectra. The characteristic bands are due to —COOH at 1730 cm<sup>-1</sup> and the N—H stretching at 3310 cm<sup>-1</sup>. Other prominent absorptions are those due to unsaturation at 1630 cm<sup>-1</sup> and phenyl group at 1600 and 1490 cm<sup>-1</sup>. In the case of sulfone-based acids the peaks due to the SO<sub>2</sub> group were at 1330 and 1155 cm<sup>-1</sup>.

The acid value of the maleimic acid intermediates was determined by titration with sodium hydroxide using DMSO as solvent and cresol red as indicator. The results are given in Table I, from which it is found that the purity of the bismaleimic acids are above 98% in all the cases.

Melting points of the four bismaleimides are:

$$\begin{array}{ll} \text{I} = 122\text{--}125^\circ\text{C}, & \text{II} = 157\text{--}160^\circ\text{C} \\ \text{III} = 246\text{--}250^\circ\text{C}, & \text{IV} = 203\text{--}205^\circ\text{C} \end{array}$$

Spectral characterization was done by IR and NMR methods.<sup>9</sup> The IR spectra of the maleimides have characteristic broad carbonyl bands with maxima near 1720 cm<sup>-1</sup>. The peak due to unsaturation is at around 1620 cm<sup>-1</sup>. The other prominent absorptions are due to phenyl group at 1600 and

TABLE I  
Acid Value of Bismaleimic Acids

Sample	Acid value	
	Experimental	Theoretical
I	279.1	284.8
II	277.7	283.3
III	250.3	252.7
IV	247.0	252.7

TABLE II  
Elemental Analysis Results of Bismaleimide Monomers<sup>a</sup> (%)

Sample	C	H	N	S
I	69.20 (70.39)	4.00 (3.91)	7.81 (7.82)	—
II	64.50 (66.67)	3.60 (3.33)	7.47 (7.78)	—
III	57.80 (58.82)	3.10 (2.94)	6.38 (6.86)	7.78 (7.84)
IV	59.20 (58.82)	3.30 (2.94)	6.65 (6.86)	7.62 (7.84)

<sup>a</sup>Theoretical values are given in parentheses.

1490  $\text{cm}^{-1}$ , —C—N— at 1390  $\text{cm}^{-1}$ , and  $\text{SO}_2$  at 1330 and 1155  $\text{cm}^{-1}$ . This assignment is in accordance with the work of Jones et al.<sup>10</sup> In the proton NMR spectra of bismaleimides, multiplets due to aromatic protons and singlet due to olefinic protons were observed.

The results of the elemental analysis of the bismaleimide monomers are given in Table II, along with the theoretical values, which show good agreement. (Carbon and hydrogen were estimated with the CH analyzer, N by the Kjeldahl method, and S by sodium carbonate fusion.)

The IR spectra of the thermally cured (250°C for 8 h) polymer samples were also recorded. The spectra of the monomers and polymers are alike, except for the broadening of the important absorption bands and disappearance of the peak due to unsaturation.

### Heat and Kinetics of Polymerization

The heat and kinetics of the thermal polymerization of the four bismaleimides were evaluated from their DSC curves which are shown in Figure 1. The peak exothermic temperature  $T_{(\text{exo})}$ , temperature of onset of cure reaction,  $T_1$ , and temperature of the completion of reaction,  $T_2$ , were determined from the DSC curves and their values are given in Table III. It is found that  $T_1$  varies from 190 to 250°C for I–IV imides; but the  $T_2$ , the completion of cure reaction, is almost the same, except for sample IV. From Figure 1, it can be seen that all the imides melt before curing begins. In the case of sample III the curing is very fast and starts immediately after melting of the sample.

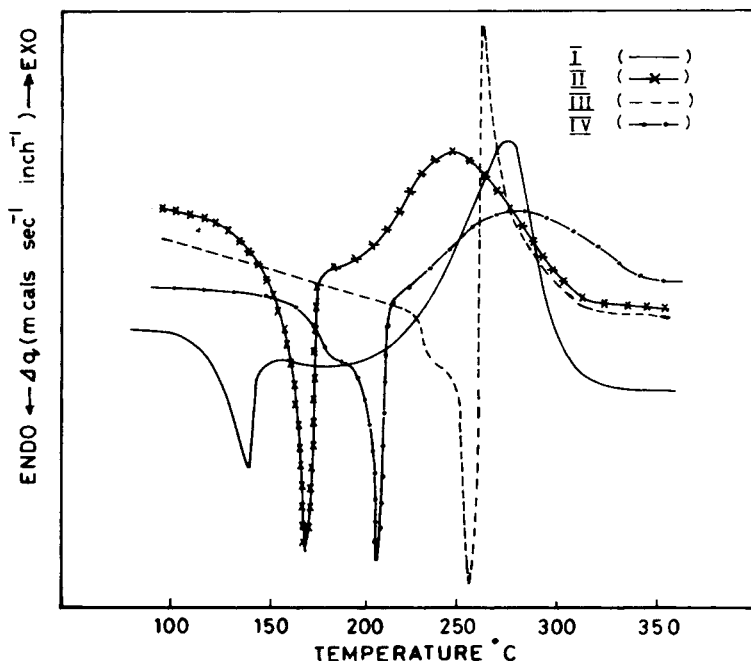


Fig. 1. DSC cure curves of  $N,N'$ -bismaleimides: (—) I; (-\*-) II; (---) III; (---) IV.

TABLE III  
Exothermic Reaction Temperatures and  $\Delta H$  of Polymerization from DSC Curves

Sample	$T_1$ ( $^{\circ}\text{C}$ )	$T_{(\text{exo})}$ ( $^{\circ}\text{C}$ )	$T_2$ ( $^{\circ}\text{C}$ )	$\Delta H$ ( $\text{cal g}^{-1}$ )
I	195	275	330	24.90
II	185	245	325	18.40
II	260	263	330	8.04
IV	220	285	350	16.90

### Heat of Polymerization

The area under the DSC curve is a measure of heat of polymerization,  $\Delta H$ . The instrument was calibrated using pure indium of  $\Delta H = 6.8 \text{ cal g}^{-1}$  and  $\text{mp} = 156.4^{\circ}\text{C}$ . The  $\Delta H$  values of the sample were determined using the equation

$$\Delta H_s = \Delta H_i \cdot \frac{W_i \cdot A_s}{W_s \cdot A_i} \quad (1)$$

where  $\Delta H_s$  = heat of polymerization of the sample,  $\Delta H_i$  = heat of fusion of indium,  $W_i$  = weight of indium,  $W_s$  = weight of the sample,  $A_s$  = area under cure curve of the sample, and  $A_i$  = area of indium fusion. The calculated values of  $\Delta H$  of polymerization are also given in Table III. The  $\Delta H$  values are ranging from 8 to 25  $\text{cal g}^{-1}$  for the four samples; para sulfone imide shows the lowest value of  $\Delta H$ .

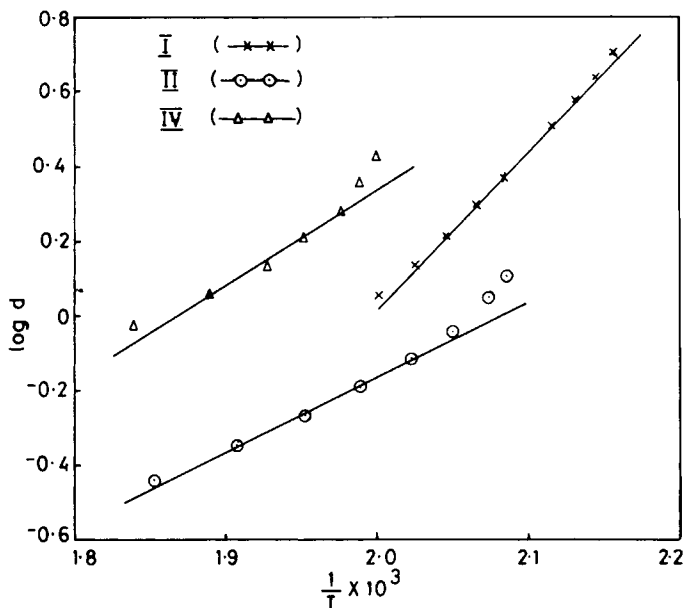


Fig. 2.  $\log d$  vs.  $1/T$  plots of  $N,N'$ -bismaleimides from DSC data: (x) I; (o) II; ( $\Delta$ ) IV.

### Kinetics of Polymerization

The kinetic parameters for the cure reaction of the various polyimides were calculated from DSC curves using the method proposed by Rogers et al.<sup>11,12</sup> (Since the curing of para sulfone imide is very fast, the kinetic constants cannot be determined by this method.) The distance between the base line and the exothermic curve at different temperature ( $K$ ) were measured. The distance is proportional to the rate of heat evolution at the particular temperature, and this rate is in turn proportional to the rate constant. A number of data points were taken (distance and corresponding temperatures) between the onset and the maximum of the cure curve. The plots of logarithm of the distance vs. reciprocal absolute temperature ( $1/T$ ) were made, and Figure 2 shows the plots for the three bisimides. From these plots the best linear portion of the curve was chosen. The distances  $d_1$  and  $d_2$  are the two extremes at the linear portion of the curves and the corresponding temperatures are  $T_1$  and  $T_2$ . By substituting the values of  $d_1$ ,  $d_2$ ,  $T_1$ , and  $T_2$  in the equation

$$-E = \frac{4.58 \log(d_1/d_2)}{1/T_1 - 1/T_2} \quad (2)$$

the energy of activation,  $E$ , was calculated. The preexponential factor  $A$  was calculated by substituting the value of  $E$  in the equation

$$A = \frac{\phi E e^{E/RT_{(\max)}}}{RT_{(\max)}^2} \quad (3)$$

TABLE IV  
Kinetic Parameters for the Polymerization of Bismaleimides from DSC Analysis

Sample	$E$ (kcal mol <sup>-1</sup> )	$A$ (s <sup>-1</sup> )
I	18.40	$1.14 \times 10^5$
II	28.61	$1.02 \times 10^{10}$
III	—	—
IV	24.90	$6.01 \times 10^7$

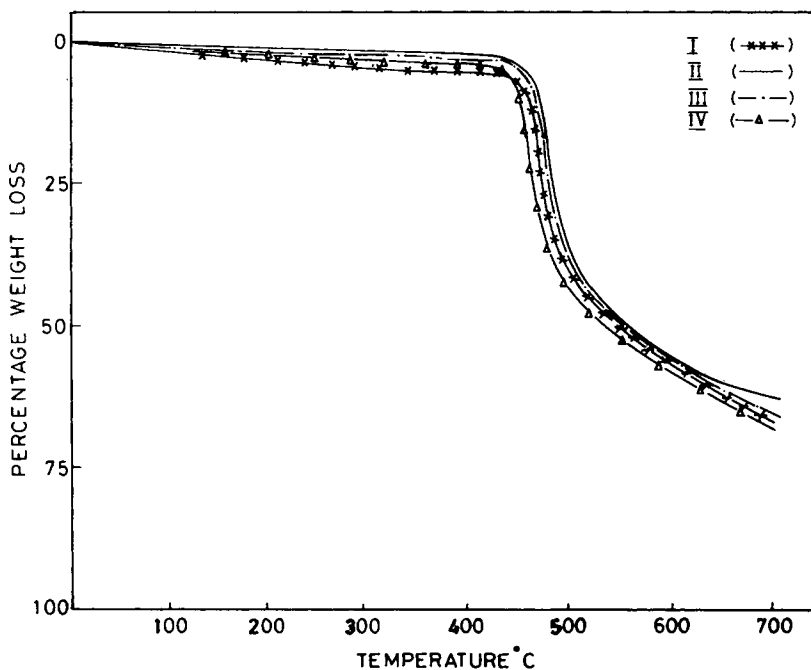


Fig. 3. TG curves of  $N,N'$ -bismaleimides in  $N_2$  atmosphere: (—×—) I; (—) II; (---) III; (—△—) IV.

where  $\phi$  is the linear heating rate,  $R$  is the gas constant, and  $T_{(\max)}$  is the maximum of the DSC cure curve. The calculated values of  $E$  and  $A$  are given in Table IV, and they are in the range  $E = 18\text{--}28$  kcal mol<sup>-1</sup> and  $A = 10^5\text{--}10^{10}$  s<sup>-1</sup>.

### Thermal Stability and Thermal Decomposition Kinetics

The thermal stability of the cured bismaleimides was evaluated from TG studies. Figure 3 shows the TG curves of the four bismaleimides. It is found that the initial portion of decomposition is quite rapid. Above 500°C the rate of weight loss gradually decreases. This indicates that, in the initial stage of polymer decomposition, the extent of crosslinking is less than the extent of bond rupture. However, at the later stage of decomposition, this trend is reversed, and hence decomposition rate is low.<sup>8</sup> The temperature of inception of reaction,  $T_i$ , the temperature of maximum decomposition,  $T_g$ , and the

TABLE V  
 TG Results of Bismaleimides

Sample	$T_i$ (°C)	$T_s$ (°C)	$T_f$ (°C)	Char yield (%) at 600°C
I	445	483	530	55
II	450	487	530	56
III	450	475	525	56
IV	440	475	515	54

temperature of completion of decomposition reaction,  $T_f$ , were determined from the TG curves and are given in Table V. The percentage char yield at 600°C for the four samples is also given in this table. From Table V, it is found that the thermal stability and the char yield of the four polyimides are not much different. Among the four, ether- and para-sulfone-based imides have marginally higher stability, methane-based has medium stability, and meta-sulfone-based has marginally low thermal stability.

Comparison of data for para and meta sulfone imides shows that para substitution increases the thermal stability. The restricted mobility of the chains due to better packing in para substitution increases the thermal stability. In polymers with para phenylene groups, C-N scission would lead to radical stabilization by resonance.<sup>13</sup> With meta substitution, such stabilization is not effective.

### Thermal Decomposition Kinetics

Kinetic parameters, viz. activation energy  $E$ , preexponential factor  $A$ , and order parameter  $n$ , for the thermal decomposition of the four cured bismaleimides were evaluated from the TG data. The fractional decomposition  $\alpha$  for the respective temperature was calculated from the TG curves. The order parameter  $n$  for the decomposition reaction was first determined by an iteration method described earlier.<sup>14,15</sup> Using a computer, the best fit value of  $n$  was determined for the decomposition of the four bismaleimides, and it was found to be 2 in all the cases. Using this value of  $n$ , the kinetic parameters were calculated using the three nonmechanistic integral equations:

*Coats-Redfern equation*<sup>16</sup>:

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1-n)T^2} \right] = \ln \left[ \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (4)$$

*MacCallum-Tanner equation*<sup>17</sup>:

$$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1-n)} \right] = \log \frac{AE}{\phi R} - 0.483E^{0.435} - \frac{(0.449 + 0.217E) \times 10^3}{T} \quad (5)$$

*Horowitz-Metzger equation*<sup>18</sup>:

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1-n)} \right] = \ln \frac{ART_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\Theta}{RT_s^2} \quad (6)$$



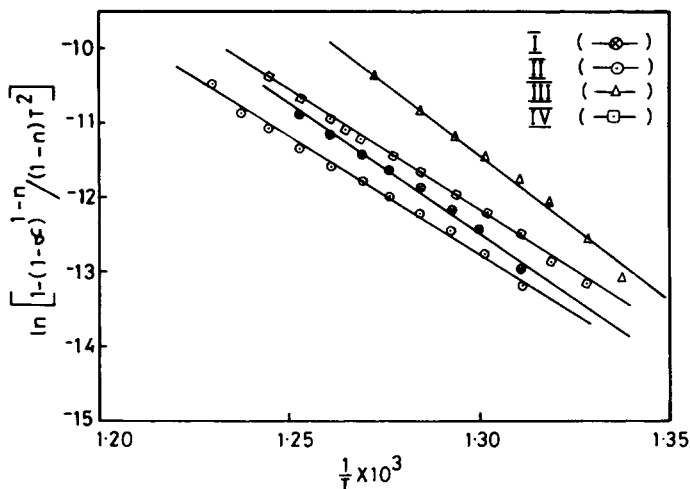


Fig. 4. Coats-Redfern plots for decomposition of  $N,N'$ -bismaleimides: (⊙) I; (○) II; (Δ) III; (□) IV.

The left-hand side of the above equations was plotted against reciprocal absolute temperature ( $1/T$ ) for eqs. (4) and (5) and against  $\Theta = (T - T_s)$  for eq. (6). From the slope and intercept (for  $\alpha$  in the range of 0.75–0.05),  $E$  and  $A$  were calculated. Typical Coats-Redfern plots for the four bismaleimides are shown in Figure 4. The  $E$  and  $A$  values obtained from the three equations are given in Table VI, from which it can be seen that the values of  $E$  and  $A$  from the three equations are nearly the same. It is also found that the activation energy for the decomposition reaction is in the range of 66–90 kcal mol<sup>-1</sup>. In general, the greater the thermal stability of a compound, the larger is the activation energy for decomposition. Thus between the para and meta sulfone imides, the para sulfone imide has given the higher value of activation energy. The methane- and ether-based imides have given intermediate values of  $E$ . A similar trend is observed in the case of the preexponential factor also. For para sulfone (III) the preexponential factor  $A$  is about 6 orders of magnitude higher (i.e.,  $\log A$  is about 33% higher) than the other imides. However, this is partially compensated by a corresponding higher value of  $E$  (approx. 30% higher). Thus the wide range in the values of  $A$  can be explained on the basis of the kinetic compensation effect,<sup>19</sup> relating  $E$  and  $\log A$ .

TABLE VI  
Kinetic Parameters for the Thermal Decomposition of Bismaleimides Using Three Equations

Sample	Coats-Redfern <sup>16</sup>		MacCallum-Tanner <sup>17</sup>		Horowitz-Metzger <sup>18</sup>	
	$E^a$	$A^b$	$E^a$	$A^b$	$E^a$	$A^b$
I	74.20	$7.345 \times 10^{18}$	74.85	$3.685 \times 10^{19}$	73.00	$4.514 \times 10^{18}$
II	71.30	$2.711 \times 10^{18}$	72.92	$1.219 \times 10^{19}$	70.05	$1.139 \times 10^{18}$
III	90.87	$6.050 \times 10^{24}$	92.56	$3.550 \times 10^{25}$	90.06	$3.419 \times 10^{24}$
IV	66.50	$2.150 \times 10^{17}$	68.03	$8.774 \times 10^{17}$	65.48	$1.065 \times 10^{17}$

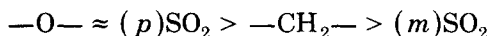
<sup>a</sup> $E$  in kcal mol<sup>-1</sup>.

<sup>b</sup> $A$  in s<sup>-1</sup>.

### CONCLUSIONS

The important conclusions from thermoanalytical studies of the four bismaleimides can be summarized as follows:

i. The initial decomposition temperature of the four structurally different polyimides are in the range of 440–450°C, and it follows the order



ii. The heat of polymerization for polyimides calculated from DSC curves ranges from 8 to 25 cal g<sup>-1</sup>, while the kinetic constants for the polymerization reaction are in the range

$$E = 18-28 \text{ kcal mol}^{-1} \quad \text{and} \quad A = 10^5-10^{10} \text{ s}^{-1}$$

iii. Activation energy for decomposition of the polyimides is in the range of 66–90 kcal mol<sup>-1</sup> and the values of *A* are in the range of 10<sup>17</sup>–10<sup>24</sup> s<sup>-1</sup>.

iv. The para sulfone imide has higher thermal stability than the meta sulfone. This is reflected in their values of *E* and *A* also. The ether and methane imides (II and I) have intermediate values of *E* and *A*.

We thank Mr. M. R. Kurup and Dr. K. V. C. Rao for their keen interest and encouragements.

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Received March 11, 1986

Accepted March 17, 1986