

# Kinetic Studies on Bismaleimide Polymerization Using Inverse Gas Chromatography

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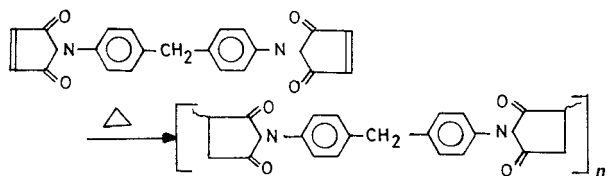
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**ABSTRACT:** Kinetics of polymerization of 4,4'-bismaleimidodiphenyl methane (BMI) were studied in the temperature range of 158–222°C by inverse gas chromatography (IGC) technique. BMI was synthesized and purified and then coated on DMCS treated chromosorb for preparation of GC column. Retention behavior of dimethyl formamide was studied at different temperatures and at different time intervals to follow the phase changes and kinetics of polymerization, respectively. The kinetic data obtained by IGC were compared with those obtained by differential scanning calorimetry. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1613–1619, 1997

**Key words:** polymerization kinetics; bismaleimide; inverse gas chromatography; dimethyl formamide; differential scanning calorimetry

## INTRODUCTION

4,4'-Bismaleimidodiphenyl methane, commonly known as bismaleimide (BMI), polymerizes on heating by the condensation reaction as shown below:



It is the material of choice for rigid and light weight fiber reinforced structural composites due to its excellent thermal and oxidation stability and due to the fact that no voids are formed because of the evolution of the condensation products. The thermal stability and flame re-

tardancy of BMI prepared with different amines were studied extensively by Verma et al.<sup>1–4</sup> Many techniques have been used to study its polymerization behavior and kinetics such as Calvet microcalorimetry,<sup>5</sup> differential scanning calorimetry (DSC),<sup>6,7</sup> and FTIR.<sup>8</sup> However, in all these techniques polymerization of BMI was never studied in the form of a thin film, which is indeed the form in which resin exists in all fiber reinforced structural composites. In view of this we thought it worthwhile to study the polymerization of BMI by the inverse gas chromatography (IGC) technique in which the material exists in the form of a thin film on an inert solid support.

IGC was used by Marie Florence et al.<sup>5</sup> to study the kinetics of the epoxy amine reaction, but most of the kinetic parameters were obtained by viscosity measurements and Calvet microcalorimetry. In the present study we used lab synthesized and purified BMI of better than 99% purity<sup>9</sup> for making the GC columns and followed the kinetics of polymerization by studying the retention behavior of dimethyl formamide (DMF) at different temperatures. The results obtained were compared with kinetic data obtained from the DSC

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method, adopting the procedure proposed by Rogers et al.<sup>10,11</sup>

## EXPERIMENTAL

### Material

BMI was synthesized by the single pot process and purified to 99% purity. The experimental details of the BMI synthesis and purification procedure have been reported elsewhere.<sup>9</sup> DMF of 99.95% purity (Fluka) was used as the probe material. Other chemicals used for making the column were AR grade. IOLAR nitrogen from Indian Oxygen Ltd. (New Delhi, India) was used as a carrier gas.

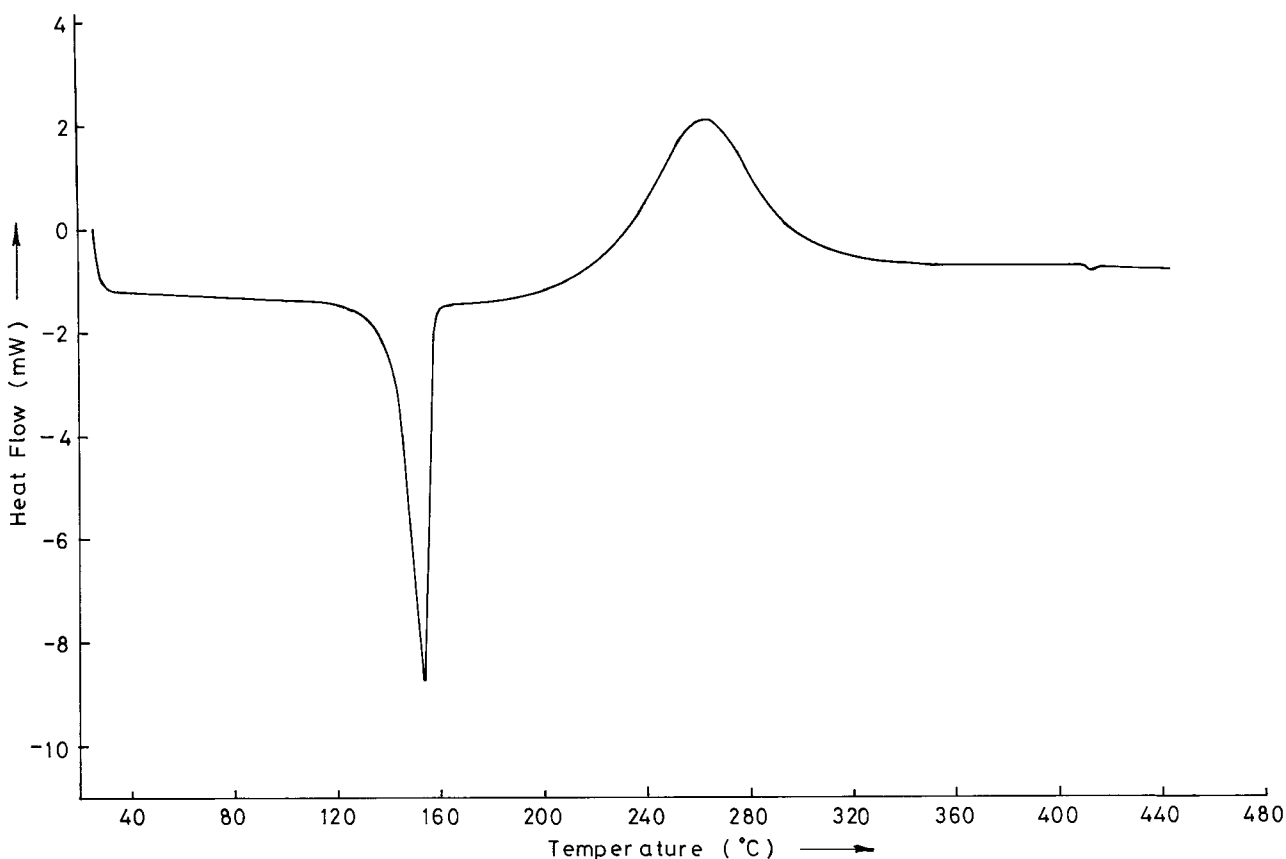
### Procedure

#### *Column Preparation and Retention Time Measurements*

An Aimil Nucon 5700 dual column GC unit (Nuccon Engineers, New Delhi, India) with a thermal

conductivity detector was used for retention time measurements. The temperature of the GC oven was measured with an accuracy of 0.5°C using a mercury thermometer. The flow rate of the carrier gas was measured by a soap bubble flowmeter with an accuracy of 0.1 mL/min at room temperature and atmospheric pressure. A Hewlett–Packard (HP 3394A) integrator was used for retention time measurements and had an accuracy of 0.01 min. The retention of the probe varies with the advancement of the polymerization reaction. The retention time refers to the apex of the peak. The integrator locates the apex by finding a segment from which three further segments show a downward slope. The segment locates the region of the apex. The HP 3394A uses the segments immediately before and immediately following the maximum in a quadratic fit to find the true apex.

Freshly crystallized BMI dissolved in acetone was coated on dimethylchlorosilane (DMCS) treated chromosorb using the incipient wetting technique. BMI was coated on the chromosorb in different loadings such as 10 and 25% (w/w). A



**Figure 1** DSC cure curve of pure BMI.

**Table I Phase Change Region of BMI Polymerization Recorded by IGC and DSC**

	IGC (°C)	DSC (°C)
Melt transition	158	154
Polymerization		
Onset	222	223
Completion	279	300

constant 2.500-g weight of column material was filled in a  $\frac{1}{8}$ -in. stainless steel column of 6-ft length. The prepared columns were conditioned at 60°C in a nitrogen atmosphere for 8 h. After screening various probe materials, DMF was found to be the best, because it interacts with the polymer and gives a measurable retention time. A constant volume of 0.2  $\mu$ L of DMF was injected throughout the study.

#### DSC Measurements

Thermal polymerization of BMI was studied on a Dupont 1090 thermal analyzer system. All the DSC experiments were carried out in an IOLAR grade nitrogen atmosphere flowing at the rate of 50 mL/min. A constant sample weight of  $5.155 \pm 0.01$  mg and a constant heating rate of 10°C/min were employed for the entire study. Melt transition, onset of polymerization, and peak exotherms were obtained from the thermogram shown in Figure 1.

## RESULTS AND DISCUSSION

#### DSC of BMI

The DSC thermogram for curing of BMI is shown in Figure 1. Table I shows the temperature corresponding to the melt transition as evident from the endothermic peak and that for the polymerization reaction as given by exothermic peak. The ascending portion of the exothermic peak was used to compute the kinetic parameters using the procedure suggested by Rogers et al.<sup>10,11</sup> As suggested in this method, the log of the height of the peak was plotted against the corresponding  $1/T$  (Figure 2) and extremes of the linear portion of the plot were used for computation of the energy of activation  $E$  and frequency factor  $A$  by the following equation:

$$E/R = \frac{\ln d_1/d_2}{1/T_1 - 1/T_2} \quad (1)$$

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

where  $d_1$  and  $d_2$  are heights of the DSC exothermic peak at temperatures  $T_1$  and  $T_2$ ,  $Q$  is the reaction rate, and  $T_{\max}$  is the temperature corresponding to the maximum of the DSC curing peak. The  $E$  and  $A$  values obtained are recorded in Table II.

#### IGC

In the IGC studies the retention volume of the DMF probe was measured at different temperatures. DMF was selected as a probe because it is a good BMI solvent and it gave a measurable retention time in the temperature range studied. In normal GC the retention time varies linearly with temperature whether the stationary phase is solid or liquid. If the stationary phase undergoes phase changes as is the case in the present studies, distinct breaks in  $\ln V_R$  versus  $1/T$  plots are obtained. Figure 3 shows the  $\ln V_R$  versus  $1/T$  plot for DMF. Four zones can be distinguished.

#### Zone I

At a temperature lower than  $T_1$  (158°C), the stationary phase is solid. Retention is mainly due to adsorption of solute compounds on solid polymers. In this region retention volume decreases with temperature. The linear portion of the plot marked as I is a case of solid GC.

#### Zone II

In this zone retention volume decreases at a relatively slower rate compared to zone I. In this part melt transition takes place along with polymerization. Due to the mobility of the chains, solute tends to diffuse into the polymer matrix. The surface mechanism is now followed by sorption in the molten mass. Hence, an upward deviation in the  $\ln V_R$  versus  $1/T$  plot is observed. Due to the slow rate of polymerization in this range, which would deplete the number of sites for interaction, the upward deviation, although slowed down, is still quite distinct.

#### Zone III

In this zone polymerization of BMI proceeds at a much faster rate and therefore sites available for interaction with the solute molecules decrease quickly with the temperature; hence, a downward deflection in the  $\ln V_R$  versus  $1/T$  plot is observed.

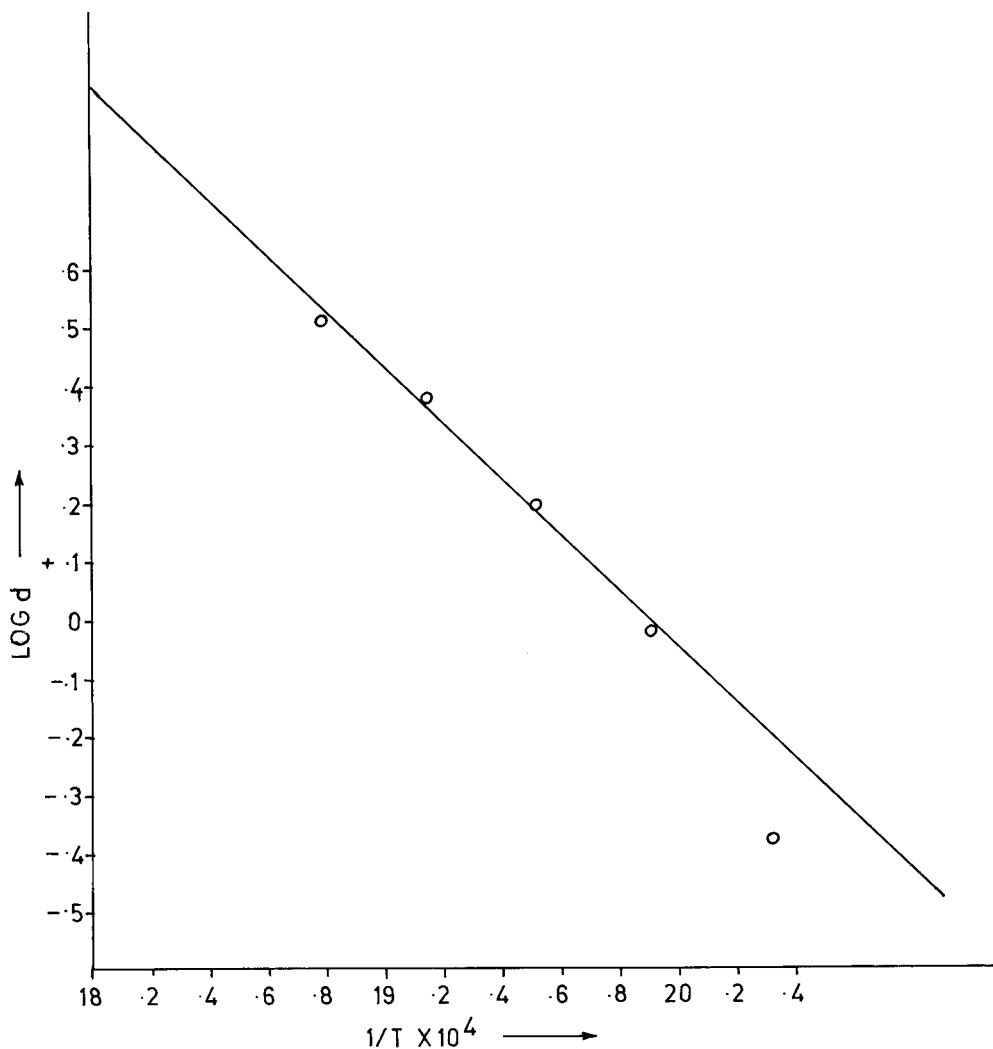


Figure 2 Log  $d$  versus  $1/T$  from DSC data.

The next break in the plot indicates the completion of the polymerization reaction.

#### Zone IV

After completion of polymerization, a situation similar to zone I exists in which retention is solely due to adsorption of the solute.

#### Kinetics of Polymerization by IGC

Kinetic parameters of BMI polymerization were also worked out using IGC. The temperature range for the kinetic studies by the IGC technique chosen was 158–222°C. In fact the DSC thermogram gives only heat absorbed or evolved in a given temperature range. The DSC thermogram

Table II Comparison of Kinetic Data from IGC and DSC

Parameter	DSC	IGC
Order of reaction	First	First
Preexponential factor	$5 \times 10^5 \text{ min}^{-1}$	$5.027 \times 10^5 \text{ min}^{-1}$
Activation energy	$22 \text{ kcal g}^{-1} \text{ mol}^{-1}$	$13.3 \text{ kcal g}^{-1} \text{ mol}^{-1}$

of Figure 1 shows that in the temperature range from 158 to 222°C, no peak is observed; heat absorption due to melting of BMI is probably counterbalanced by heat evolved due to the start of the polymerization process. In the DSC plot a peak will only be observed when the heat of polymerization exceeds the heat of melting. The rate of polymerization in the region of the exothermic peak was very fast and was found to not be suitable for kinetic studies. The temperature range of 158–222°C was selected for the IGC kinetic studies for this reason. Retention volumes were measured after different intervals of time while keeping the temperature constant. A typical plot of  $V_R$  versus time at 167°C is shown in Figure 4. As polymerization proceeds the retention volume decreases with temperature.

The values of activation energy  $E$  and the pre-

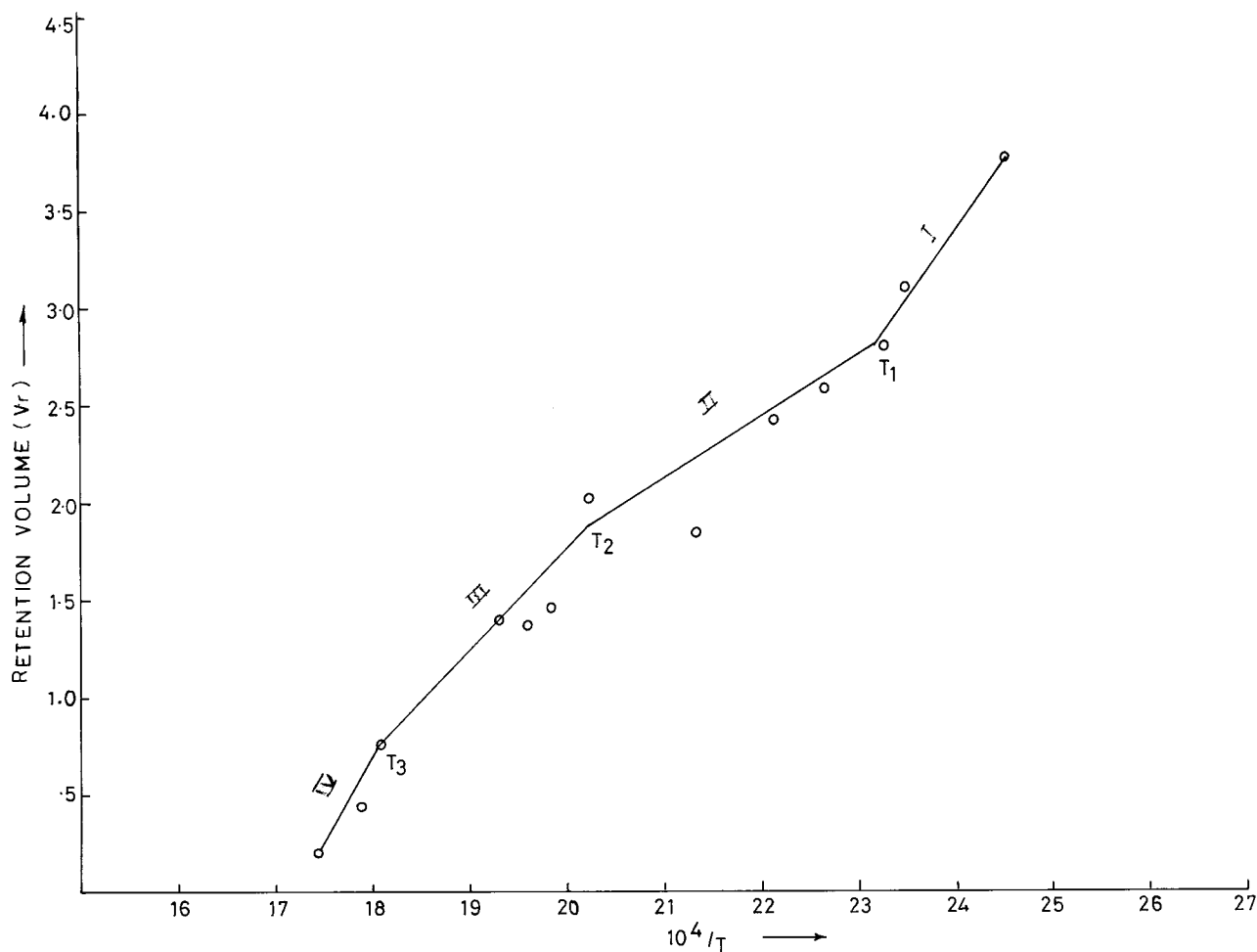
exponential factor from IGC were calculated using the differential method of analysis. A change in retention volume  $V_R$  is assumed to be a function of advancement of the reaction. The reaction of BMI is considered to be first order, giving a complete rate equation,

$$r_A = Ae^{-E/RT} \cdot C_A$$

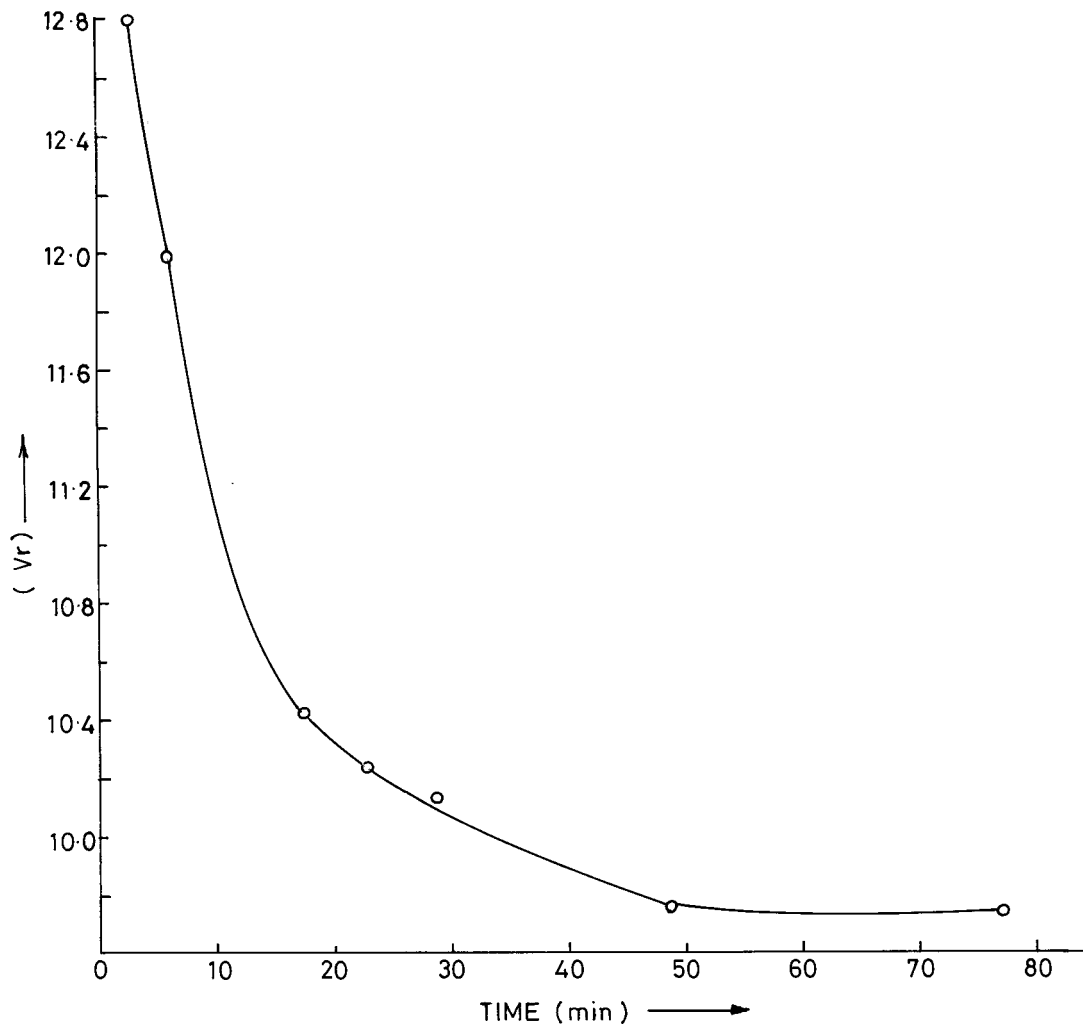
$$r_A = 5.027 \times 10^5 e^{-1.32 \times 10^4/RT} \cdot C_A$$

Kinetic data from IGC and DSC are compared in Table II.

It is interesting to note from Table II that although preexponential factors obtained from the DSC exothermic peak by the procedure adopted by Rogers et al.<sup>10,11</sup> compares very well with the IGC values, the activation energy ob-



**Figure 3** Variation in retention volume as a function of temperature for BMI polymerization by IGC; DMF probe molecule.



**Figure 4** Retention volume ( $V_R$ ) as a function of time for BMI polymerization by IGC; DMF probe,  $T = 167^\circ\text{C}$ .

tained by the IGC method is lower than that obtained from the DSC curve. This may be due to the fact that a variable temperature DSC plot does not lead to accurate kinetic parameters.<sup>12</sup> Moreover, the physical state of resin in the column is quite different compared to that in the DSC run. It may be that the temperature equilibrium is reached much faster in thin films than in a solid mass of resin.

## CONCLUSIONS

It may be inferred from the above studies that if a proper probe is chosen for IGC studies, phase changes are reflected very well by variations in retention time. A kinetic parameter can be calculated with a greater degree of confidence from iso-

thermal IGC studies, and by varying the loading on the column it is possible to simulate the resin to a fiber ratio in the actual composition used in composites.

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