

# Relationships in a Bismaleimide Resin System. Part I: Cure Mechanisms

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A series of bismaleimide resin systems has been examined in order to identify the molecular features responsible for the mechanical response of these materials. A range of network structures was produced both by formulation of resins with different ratios of N,N'-bismaleimido-4,4'-diphenylmethane (BMI) and methylene dianiline (MDA), and by the use of different thermal processing cycles. Spectrographic and chromatographic techniques were used to study the reactions that occurred during the cure. Two principal reactions were confirmed: a Michael addition reaction which provides linear chain growth, and an addition reaction which produces crosslinking through the double bonds of the maleimide group. In general, curing at a lower temperature or increasing the MDA content served to favor chain extension over crosslinking, which might be expected to increase molecular mobility in the resin.

## INTRODUCTION

Bismaleimides (BMIs) are addition polyimides which can be cured without the evolution of volatiles, and this has made them attractive candidates for a wide variety of high temperature applications. However, BMIs are often very brittle: the "Kerimid" systems introduced by Rhone-Poulenc in the early 1970s had fracture energies ( $G_{IC}$ ) of approximately  $50 \text{ J/m}^2$ - $90 \text{ J/m}^2$  (1). By contrast, epoxy resins typically have  $G_{IC}$  values in the range of  $100 \text{ J/m}^2$ - $500 \text{ J/m}^2$  (2). Among other problems, this brittleness leads to an increased susceptibility to impact damage in composite laminates (3).

Recently, Leung, *et al.* (4-7), stated that the fracture toughness of Kerimid-type BMI resins could be altered significantly by variations in the cure cycle used to produce the network. In their work they produced resins with different molar ratios of N,N'-bismaleimido-4,4'-diphenylmethane (BMI) to methylene dianiline (MDA). They also studied the effect of two different processing cycles for the formulations. One cycle was a fast cure at a high temperature and the other was a slow cure which had a low temperature, long time hold step followed by the high temperature cure step.

Their results indicated that the slow cure cycle increased the resin fracture energy by approximately 40%. Significantly, it was also found that the tensile behavior and thermal stability of the resins were unaffected by the cure route. The explanation proposed by the authors for the improvement in fracture energy was that the low temperature/long time cure cycle enhanced the amount of chain extension that occurred prior to crosslinking of the resin into a network. This suggests that it might be possible to manipulate the fracture toughness without affecting the mechanical or thermal behavior of the materials.

Stenzenberger (1) has recently provided an overview of BMI resin chemistry and properties. In general, there are two principal reactions observed during cure of BMI/MDA resin systems (8). The first is a Michael addition reaction which is a nucleophilic attack of the amine on the maleimide double bond. This is a chain-extending step reaction. The second is a crosslinking addition reaction that has been described as both anionic and free radical (9-13) in nature. In addition, ring opening by nucleophilic attack on the imide ring by the amine is a possible side reaction. This possibility is suggested by Kumar, *et al.* (14), who described the synthesis

of amine terminated bisaspartimides which cured via a ring opening amidation reaction mechanism. Other authors have commented on the ring opening reaction mechanism as well (15, 16). Gherasim and Zugravescu (15) in particular found that ring opening reactions with N,N'-BMI occurred only when aliphatic amines were used. The reaction between the BMI and aromatic amines produced succinimides.

The relative importance of chain extension versus crosslinking reactions can be expected to control molecular rigidity, and thus the many thermal and mechanical properties related to molecular motions. Chang, *et al.* (17-20), used this concept in a study of diglycidylether of butanediol (DGEb)-diamino diphenyl sulfone (DDS) epoxy systems. These authors found that resin density, modulus, glass transition temperature, and yield stress all increased as the degree of cure increased. The increase in resin density was seen as a direct measure of the reduction in free volume  $V_f$  as crosslinking occurred during cure. The reduction in  $V_f$  was found in turn to correlate with a decrease in fracture toughness, as expected. They also noted that annealing tended to reduce toughness, as that leads to accelerated physical ageing with its associated loss of excess free volume.

## CHEMICAL REACTIONS IN BMI/MDA RESIN SYSTEMS

### Materials and Sample Preparation

N,N'-bismaleimido-4,4'-diphenylmethane (BMI) and methylene dianiline (MDA) were obtained commercially for this study; their chemical formulas are shown in Fig. 1. Neat resin plaques were produced with BMI:MDA ratios of 2.5:1, 1.5:1, 1.25:1, and 1:1. Each of these formulations were prepared using two different cure cycles: one with a 48 h low temperature hold at 145°C followed by a cure at 220°C for 6 h, and the other having only the cure at 220°C for 6 h. The low temperature step was performed in an air circulating oven and the higher temperature step was performed in a nitrogen environment.

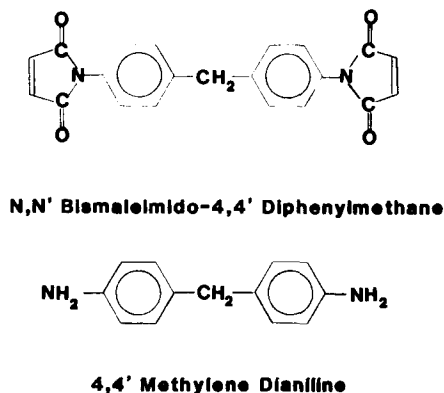


Fig. 1. Monomers used in the study.

### FTIR Analysis

Infrared spectra were obtained from specimens which had been held for various times at the curing temperature. Using a Perkin Elmer Model 1800 FTIR instrument, data were obtained from 20 cycle scans over the range of 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . Initially, specimens were prepared by melt mixing the resin, allowing the mixture to cool, grinding and pressing the powder into a KBr pellet. However, better results were obtained by casting thin films of the melt mixed resin between KBr salt plates.

Following the work of DiGuilio, *et al.* (21), reaction progress was followed by monitoring the time dependency of peak heights for infrared absorption bands thought to be involved in the reaction; these included the bands at 3469  $\text{cm}^{-1}$  ( $\text{NH}_2$ ), 3099  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ), 1137  $\text{cm}^{-1}$  ( $\text{C}-\text{N}-\text{C}$ ), 2490  $\text{cm}^{-1}$  ( $\text{CH}_2$ ), and 825  $\text{cm}^{-1}$  (benzene ring in the maleimide unit). The benzene bend peak at 3040  $\text{cm}^{-1}$  was used as an internal standard.

A typical spectrum of the region of interest is shown in Fig. 2. This spectrum is for a sample of resin mix of 1.5:1 mole ratio of BMI to MDA that had been exposed at 145°C for 30 min. The most obvious feature of the scan is that the portion containing the peaks of interest (3000  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ ) is extremely crowded. DiGuilio resolved this region with 12 component peaks. The region also contains bands corresponding to the reaction products (e.g. the  $\text{NH}$  band at 3373  $\text{cm}^{-1}$ ). This limits the amount of quantitative information that can be obtained from infrared spectroscopy.

However, the spectra do provide at least qualitative information on the reactions which occur during the low temperature hold step at 145°C. Figures 3 to 5 show the change in absorption peak height at

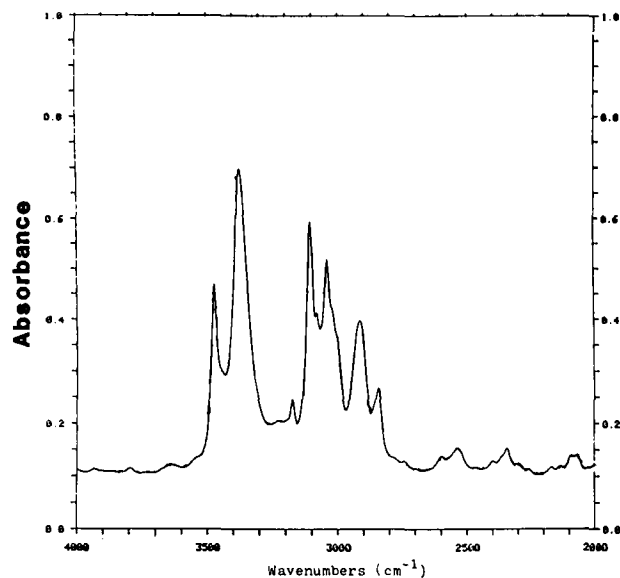


Fig. 2. FTIR Spectrum for a 1.5 BMI:1 MDA molar mixture.

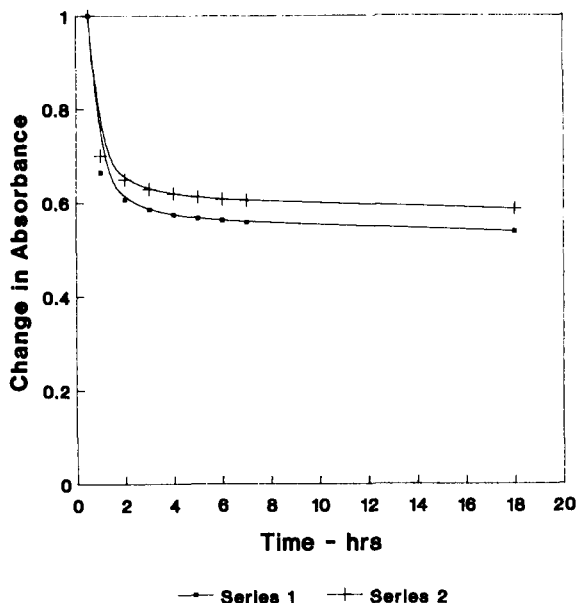


Fig. 3. Change in absorbance for a 1:1 mixture resin sample held at 145°C. The  $\square$  symbol represents the primary amine peak absorbance and + indicates the vinyl group absorbance.

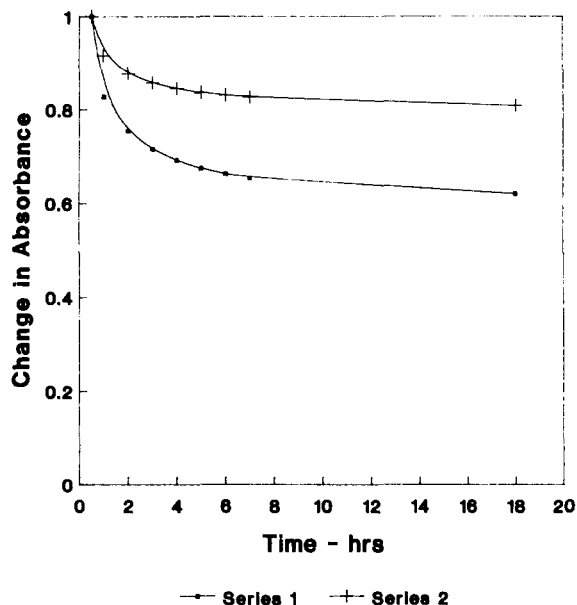


Fig. 5. Change in absorbance for a 2.5:1 mixture resin sample held at 145°C. Symbols have same meaning as in Fig. 3.

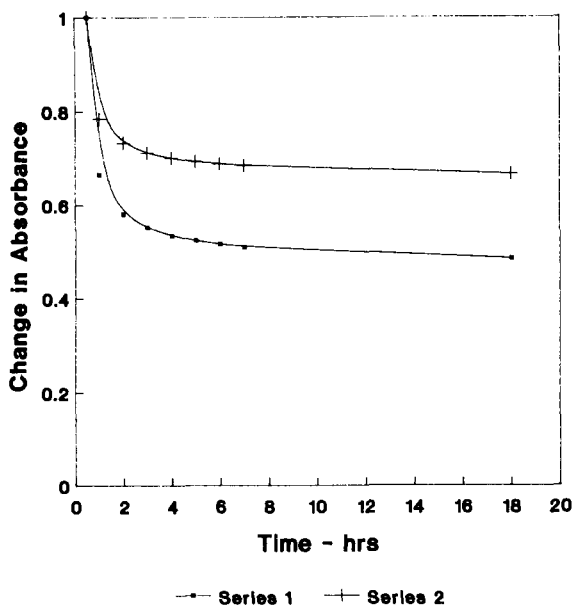


Fig. 4. Change in absorbance for a 1.5:1 mixture resin sample held at 145°C. Symbols have same meaning as in Fig. 3.

3469  $\text{cm}^{-1}$  and 3099  $\text{cm}^{-1}$ , as functions of cure time at 145°C for samples 1:1, 1.5:1, and 2.5:1 BMI to MDA mixtures, respectively. These data have been calibrated with the internal standard and normalized to the first data point.

These figures show that the amounts of amine and vinyl groups decrease as the reaction proceeds. As the percentage of BMI in the resin is increased, the relative amount of unreacted vinyl groups is increased. In addition, as the reaction proceeds,

peaks in bands assigned to succinimide groups were seen to grow. There was no appreciable growth of peaks attributable to amide groups observed. These results indicate that the principal reaction that occurs at this temperature is the Michael addition chain extension reaction.

The infrared spectra indicate that the rate of reaction decreases as cure proceeds, and stopped completely after approximately six hours. This is thought to be due not to the depletion of reactive sites, but rather vitrification of the resin, as has been discussed by Gillham, *et al.* (22, 23).

The reactions occurring during the final cure step at 220°C were also followed. By using the Beer-Lambert law, it was possible to estimate the concentration of vinyl groups present at any given time. Figures 6 through 8 show the results for samples of 1:1, 1.5:1, and 2.5:1 mixtures cured by each of the two cure cycles studied. These data indicate that the effect of the low temperature hold step on the final extent of reaction is very small. Also, as expected, the residual vinyl group content is increased as the initial vinyl group concentration is increased. The growth of the peak at 2940  $\text{cm}^{-1}$  (CH) indicated that the crosslinking reaction was occurring during the process.

Examination of the spectra obtained during the high temperature cure step indicated that a small peak in the region of 1640  $\text{cm}^{-1}$  formed as the reaction proceeded. Analysis of the peak height was difficult because it appeared as a very small shoulder on the strong carbonyl peak. DiGuilio attributed this peak to an oxidation reaction and the formation of carbonyl groups. They found that the amine group absorbance peak decreased as a function of time at

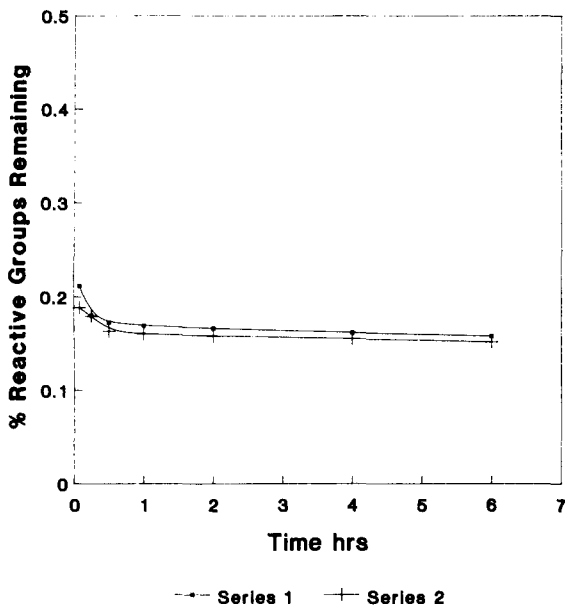


Fig. 6. Percent vinyl groups remaining for the 1:1 resin system as a function of time at 220°C. The + symbol represents the two step 145°C/220°C cure cycle and □ denotes the one step cure at 220°C.

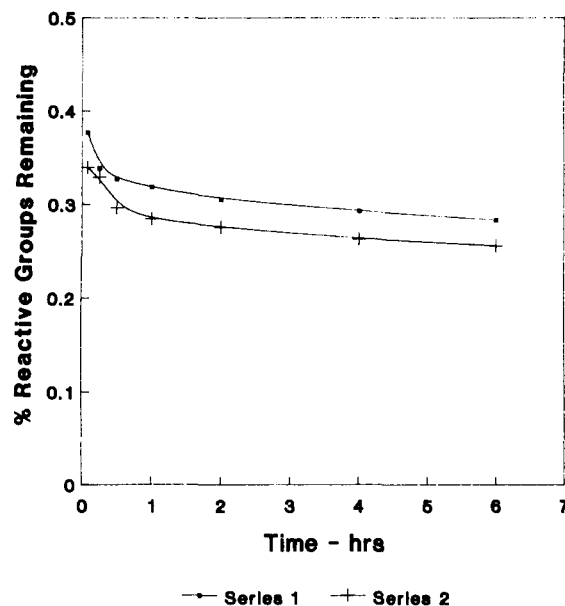


Fig. 8. Percent vinyl groups remaining for the 2.5:1 resin system as a function of time at 220°C. Symbols have same meaning as in Fig. 6.

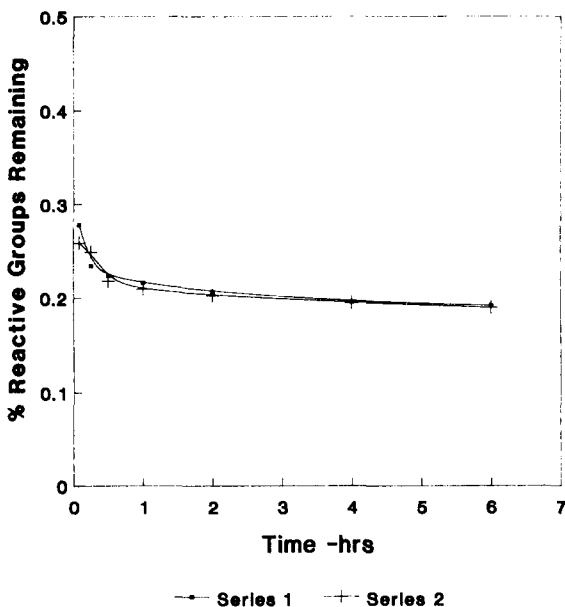


Fig. 7. Percent vinyl groups remaining for the 1.5:1 resin system as a function of time at 220°C. Symbols have same meaning as in Fig. 6.

223°C due to an interaction with a harmonic band of the carbonyl group which occurred in the same region ( $3515\text{ cm}^{-1}$ ). The location, however, could also indicate that the carbonyl occurred as a result of the ring opening amidation reaction since the C=O of an amide should occur in the  $1630\text{ cm}^{-1}$  to  $1710\text{ cm}^{-1}$  region. Conclusive interpretation based on the data obtained was not possible. However, the fact that no trend in peak height at  $1640\text{ cm}^{-1}$  was

found as the amine content of the reactant mixture was changed indicates that oxidation is a more plausible explanation of the observed results. Also, examination of the amine peak absorbance of the resins produced in this study did not indicate any decrease in peak height as a function of time at 220°C. Figure 9 shows the amine peak absorbance for the 2.5:1 mix resin. Since these resins were processed in a nitrogen environment, oxidation reactions would occur more slowly. The difference in behavior between the work performed here and that reported by DiGuilio supports the idea that the peak observed is due to an oxidation reaction.

In summary, the infrared analyses provide qualitative insight into the reactions which occur during various phases of the processing schedule. The chain extension reaction is dominant at the low temperature hold, but chain extension and crosslinking reactions occur simultaneously during the high temperature cure step.

### NMR Analysis

The FTIR data on the high temperature cure step indicated the possibility that amidation by ring opening had occurred to some extent. In an effort to determine whether this reaction would occur, solution NMR experiments were performed on samples which had an excess of amine (2:1 molar mix MDA to BMI). A Varian CFT Model 20 NMR was used in this study. Proton NMR spectra were examined in the 8 ppm to 10 ppm region (TMS Standard) where the amide proton would be expected to appear. The solution of resin in deuterated DMSO was heated for 8 h at 160°C and NMR spectra were run after 1, 2, 4, and 8 h. The spectra showed no evidence of an

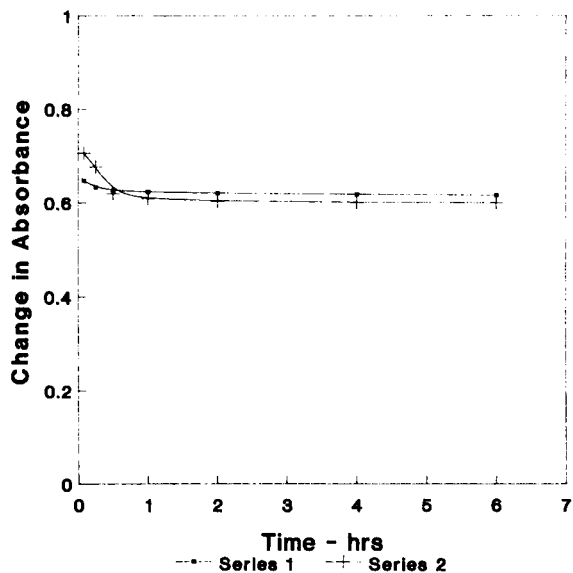


Fig. 9. Change in absorbance due to amine for the 2.5:1 resin system at 220°C. Symbols have same meaning as in Fig. 6.

amide proton at the expected range. This does not prove conclusively that the amidation reaction does not occur, but it again indicates that the major crosslinking reaction is via an addition mechanism through the vinyl groups in the BMI.

#### Size Exclusion Chromatography (SEC)

SEC analysis were performed in order to obtain additional information on the nature of the low temperature processing step. A Hewlett Packard Model 1084A HPLC was used with 100Å and 40Å Phenogel columns in series, and with tetrahydrofuran (THF) solvent. Resin mixtures of 1:1, 1.5:1, and 2.5:1 BMI:MDA stoichiometry which had been cured for various times at 145°C were examined to follow the development of higher molecular weight species. Specimens were first dissolved in dimethyl formamide (DMF), and subsequently diluted to a 2:1 volumetric mix of THF to DMF. The concentration of sample was approximately 0.95%. The system was operated at a flow rate of 1 ml/min, and an ultraviolet detector operating at 254Å was used to examine the species which eluted from the columns. The system was calibrated to obtain molecular weights from elution times by means of diglycidyl ether of bisphenol-A epoxy resin standards which were run under the same conditions.

Figures 10 through 12 show the relative change in concentration of a particular molecular weight species (2100 g/mol) as a function of cure time at 145°C. The growth is shown relative to the concentration after the 30 min melt mix step. The absolute concentration of all higher molecular weight species was dependent of the formulation chemistry. Three aspects of the low-temperature cure chemistry are apparent from these figures. First, as was also observed by Leung, *et al.*, the resins stay soluble after

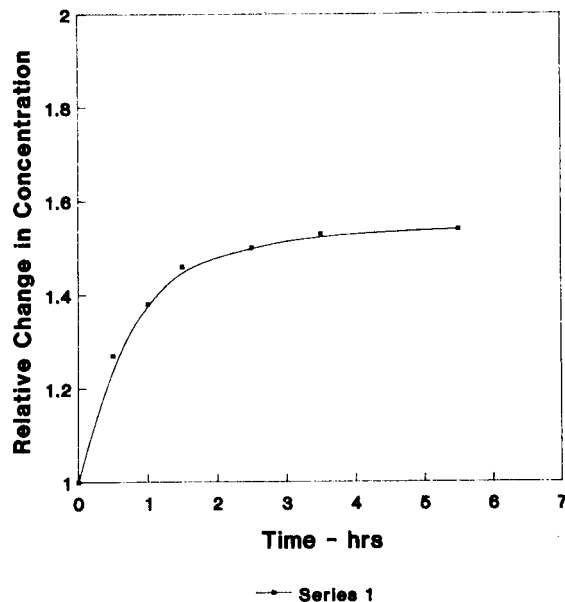


Fig. 10. SEC data for the 1:1 resin system showing the change in concentration of a higher molecular weight species (2100 g/mol) as a function of time at 145°C.

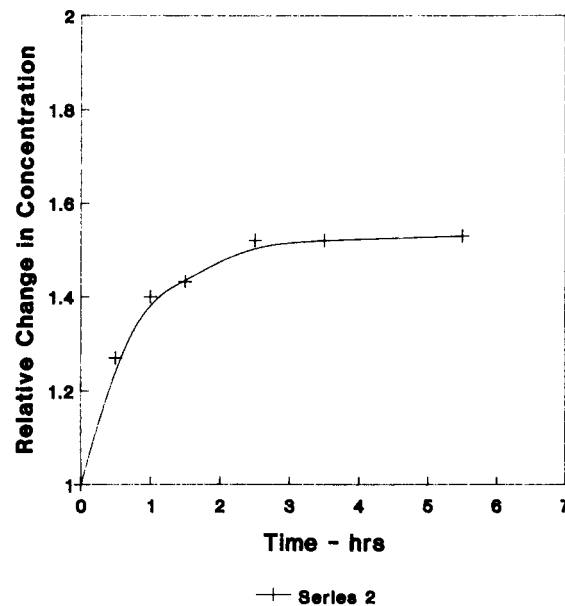


Fig. 11. SEC data for the 1.5:1 resin system showing the change in concentration of a higher molecular weight species (2100 g/mol) as a function of time at 145°C.

6 h at 145°C, indicating that extensive crosslinking has not occurred. Second, it can be seen that there is more high molecular weight species formed in the stoichiometric mixture than in the BMI-rich mixtures. Finally, the reaction stops after a finite time, due presumably to the increasing viscosity or even vitrification of the resin. This same effect was noted in the FTIR study. In summary, curing at 145°C is dominated by a chain-extending reaction in which short chain linear segments are formed.

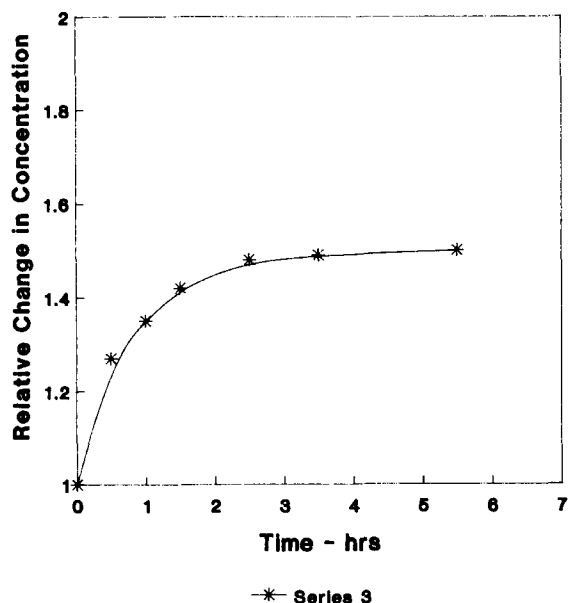


Fig. 12. SEC data for the 2.5:1 resin system showing the change in concentration of a higher molecular weight species (2100 g/mol) as a function of time at 145°C.

### CONCLUSIONS

Spectrographic and chromatographic techniques were used to confirm the reactions which occurred during cure of BMI/diamine resin systems. The principal reaction at the intermediate processing temperature (145°C) is a Michael addition reaction which acts to produce linear chain growth. At higher temperature (220°C), both the Michael addition reaction and a crosslinking addition reaction occur simultaneously. In general, curing at a lower temperature or increasing the amine content of the resin acts to favor the chain extension mechanism. Thus the series of resins produced provides a means to study the effect of a systematic change of network structure on BMI polymer properties.

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