

# Fourier Transform Infrared Spectroscopic Characterization of Aromatic Bismaleimide Resin Cure States

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## Synopsis

Interesting polyimide materials, possessing good mechanical and thermal properties, are obtained by homopolymerization or reaction of 4,4'-bis(maleimidodiphenylmethane) with a diamine. Fourier transform infrared spectroscopy has been used to characterize the crosslinking of such materials using maleimide and amine absorption bands. Amine group reaction on double bonds is readily achieved and appears to be insensitive to the temperature of curing. On the other hand, the decrease of maleimide double bonds is strongly dependent on the reaction temperature. The residual amount of double bonds present in the cured material is a function of the temperature: a linear relationship holds between residual double bond concentration vs. curing temperature. The general behavior during crosslinking of this kind of polyimide was related to glass transition temperature changes.

## INTRODUCTION

In the class of high temperature resistant polymers, polyimides are the most common commercial materials, and their preparation and properties have been recently reviewed.<sup>1</sup> The creation of the imide group usually implies a phase of off-gas creating voids and severe weaknesses in finished products. In order to circumvent the off-gas generation, polymerizable monomers containing the imide group have been developed. Among them, Kerimid 601 (Rhône-Poulenc C°) based on 4,4'-bis(maleimidodiphenylmethane) represents an interesting material. This monomer can be cured either by diamine addition reaction on the double bond and/or polymerization and copolymerization. Final materials, which are highly crosslinked, present good mechanical and thermal properties. Because of the dependence of mechanical properties on the cure state, there is a need to obtain measurable parameters that uniquely describe the specific cure state of crosslinked polymers. Chemical characterization remains limited to the early stages of the reaction, i.e., to very low conversion rates. Spectroscopic methods, in particular Fourier transform infrared spectroscopy (FT-IR), appear as interesting tools to get an insight into chemical changes occurring during the curing process.

The present work deals with the FT-IR characterization of Kerimid 601 cured at different temperatures.

## BACKGROUND

Kerimid 601 results from the condensation of 2.5 mol of 4,4'-bis(maleimidodiphenylmethane) (I) with one mole of 4,4'-diaminodiphenylmethane (II). A

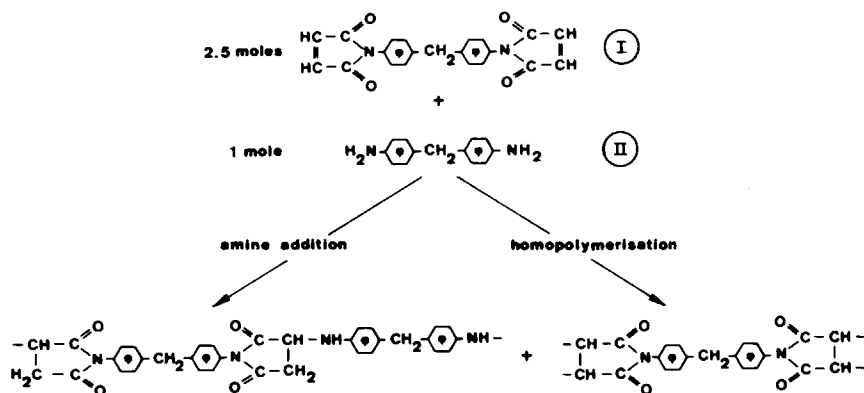


Fig. 1. Scheme of the curing reaction.

pre-cured commercial polymer is obtained by melting the previous blend; it is a yellow powder softening around 80°C which begins to polymerize around 160°C.

Curing reaction follows two different pathways. As shown in Figure 1, maleimide double bonds can react either by homopolymerization or by addition of the diamine. As a matter of fact, both reactions occur simultaneously during polymerization.

## EXPERIMENTAL

Model compounds and prepolymer were kindly provided to us by Rhône-Poulenc C°.

Infrared spectra were obtained on a Nicolet 7199 Fourier transform infrared spectrometer. 32 co-added interferograms were scanned at 2 cm<sup>-1</sup> resolution. According to Griffiths,<sup>2</sup> absorbance values not greater than 0.7 have been used for quantitative measurements. The normal Nicolet curve analysis program was used for curve resolving.

For molar extinction coefficient ratio determination, thin films were obtained by melting the sample between two KBr plates. KBr was then removed by dissolution in water. In this way, a spectrum of amorphous samples could be obtained. This was important because in the spectrum of crystalline samples, many absorption bands were split into a doublet whereas, in amorphous samples, they were a singlet. For kinetic studies, thin films suitable for infrared measurements were obtained by melting the prepolymer below the polymerization temperature between two KBr plates. 10–15 min were necessary to reach the reaction temperature which was monitored at ±1°C. Infrared spectra of solid samples for band assignment were obtained using KBr pellets (1% concentration).

## RESULTS

### Vibrational Analysis

Infrared spectra of different model molecules were run beside I and II compounds in order to warrant band assignments. 4,4'-bis(succinimidophenyl-

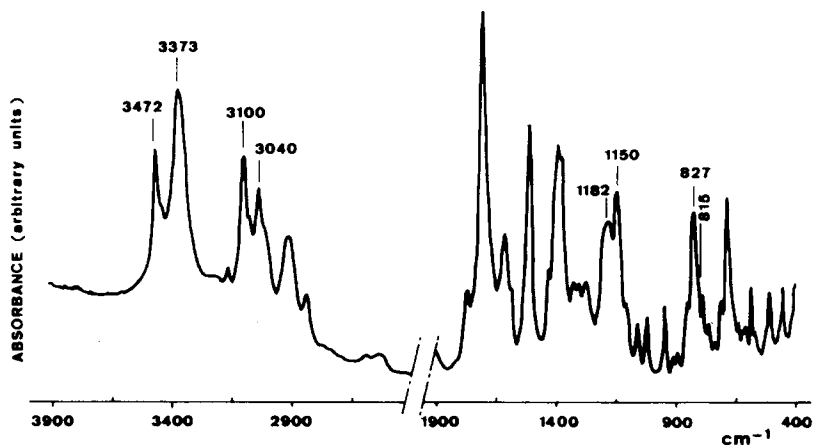
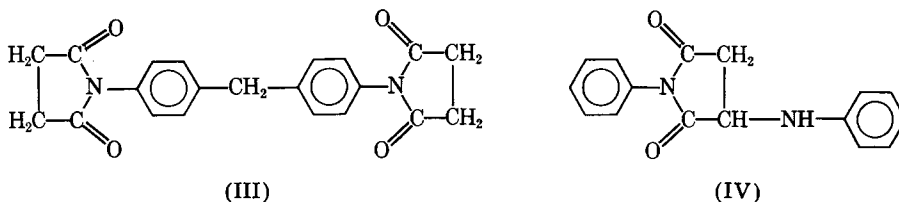


Fig. 2. Infrared spectrum of polyimide prepolymer.

methane) (III) and *N*-anilinophenylsuccinimide (IV) were used for this purpose



The compound (III) foreshadows homopolymerization while the molecule (IV) is representative of amine addition on maleic double bond.

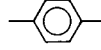
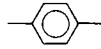
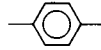
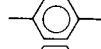
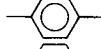
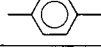
Although we do not intend to give a complete vibrational assignment of these molecules, we are interested in the characterization of the main absorption bands of the polymer, the spectrum of which is shown in Figure 2.

Benzene ring vibrational modes were assigned according to Varsanyi<sup>3</sup> while imide group vibrations were assigned from previous results on polyimide polymers.<sup>4,5</sup> The results are given in Table I.

### Polymerization Study

As shown in Figure 3, a difference spectrum characteristic of the crosslinking mechanism can be generated by subtracting the absorbance spectrum of the polymer cured 120 min at 189°C from the initial absorbance spectrum at 189°C. Absorption bands which do not change during the reaction, such as the benzene ring mode at 3040  $\text{cm}^{-1}$ , are eliminated. Absorption decreases are observed at 3469  $\text{cm}^{-1}$  [ $\nu(\text{NH}_2)$ ], 3099  $\text{cm}^{-1}$  [ $\nu(=\text{C}-\text{H})$ , maleimide], 1137  $\text{cm}^{-1}$  [ $\nu(\text{C}-\text{N}-\text{C})$  of the maleimide group] and 825  $\text{cm}^{-1}$  [ $\nu_{17b}$  of the benzene ring in the maleimide unit]. Intensity increases induced by the formation of succinimide groups and near by structures are observed at 3326  $\text{cm}^{-1}$  [ $\nu(\text{NH})$ ], 2942  $\text{cm}^{-1}$  [ $\nu(\text{CH}_2)$ ], 1180  $\text{cm}^{-1}$  [ $\nu(\text{C}-\text{N}-\text{C})$  of the succinimide group] and 781  $\text{cm}^{-1}$  [ $\nu_{17b}$  of the benzene ring in the succinimide unit]. As absorption bands badly overlap in the 2000–4000  $\text{cm}^{-1}$  range, we will only consider the 2800–3600  $\text{cm}^{-1}$  region. Subtraction

TABLE I  
Tentative Assignment of Main Absorption Bands of Kerimid 601 and Some Model Compounds<sup>a</sup>

Compound					
I	II	III	IV	Prepolymer	Tentative assignment
3465 w		3464 w		3472 m	harm. $\nu\text{C}=\text{O} + \text{NH}_2$ harm. $\nu\text{C}=\text{O}$
	3446 s 3415 s				} $\text{NH}_2$ antisym.
			3389 m 3330 w	3373 m	
	3338 s 3210 m				NH <sub>2</sub> sym. harm. NH <sub>2</sub>
3109 m 3098 m 3038 w				3100 w	} $\nu=\text{C}-\text{H}$ maleimide
	3033 m	3051 w 2987 w 2937 w	3051 vw	3040 w	}  20b
2920 vw		2920 w	2926 vw	2923 w	
	2899 m 2885 m				
2850 vw	2826 m	2853 vw	2852 vw	2856 vw	
1770 w 1705 vs		1773 m 1700 vs	1779 w 1707 vs	1774 w 1717 vs	$\nu\text{C}=\text{O}$ in phase $\nu\text{C}=\text{O}$ out-of-phase $\beta_s\text{NH}_2$
	1632 s				
1603 w			1603 s	1618 m	}  8a
1514 vs	1518 vs	1512 s	1514 m,sh 1499 s	1516 s	
1395 vs 1377 vs		1400 s 1387 vs	1397 s	1396 s	} $\nu\text{C}-\text{N}-\text{C}$
	1289 s 1275 s				} $\nu\text{C}-\text{N}$
		1188 vs	1190 s	1182 m	$\nu\text{C}-\text{N}-\text{C}$ succinimide
	1178 m		1172 s		}  9a
1149 vs				1150 s	
1020 m		1020 w	1025 w	1020 w	}  18a
950 m		952 vw	946 w	950 w	
841 vs	843 m	838 w			
832 s				827 s	}  maleimide
		819 m		815 m,sh	
691 vs		680 m	696 s	693 s	}  4

<sup>a</sup> vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

spectra allow to detect qualitative changes in the amount of the different functional groups. As shown in Figure 4, the decrease of maleimide groups first develops quickly, then does not change any more. Figure 5 shows that the amine addition reaction reaches a similar final level whatever the reaction temperature is. At 223°C, an oxidation reaction can be detected by the appearance of a

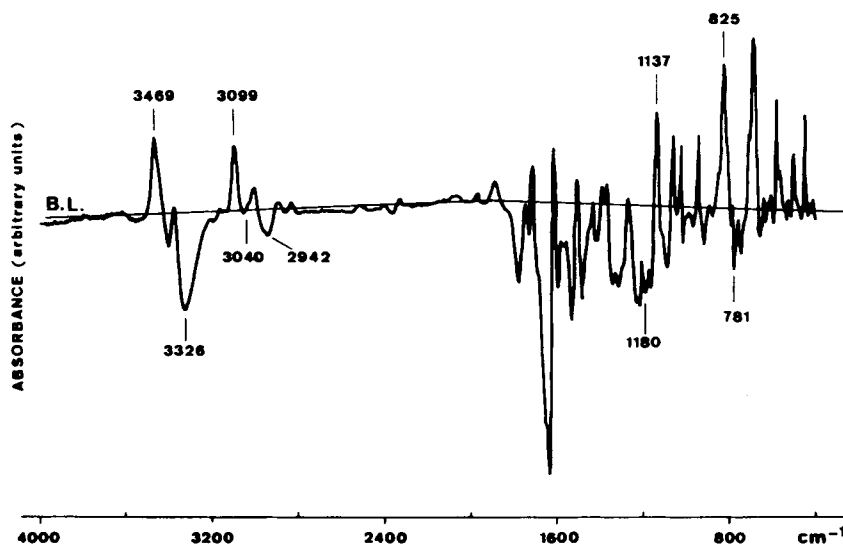


Fig. 3. Polyimide difference spectrum from 189°C polymerization data: polyimide (13 min) – polyimide (120 min). B.L.: base line.

$\nu(\text{C}=\text{O})$  harmonic negative peak at  $3515\text{ cm}^{-1}$  increasing with the reaction time. This peak overlaps the  $\text{NH}_2$  peak inducing an artificial increase of the number of  $\text{NH}_2$  groups. These results show that the amine addition reaction is fast and almost complete, while the double bond polymerization strongly depends on the temperature of reaction. Subtraction technique allows us to get qualitative information on the polymerization process. In order to obtain quantitative results the  $2800\text{--}3400\text{ cm}^{-1}$  region was analyzed by curve resolving. On account of the carbonyl harmonic band overlapping the  $\text{NH}_2$  band, one can only measure the ratio  $\epsilon_2/\epsilon_1$  of the molar extinction coefficients of the  $3035\text{ cm}^{-1}$  ( $\epsilon_1$ ) and  $3100\text{ cm}^{-1}$

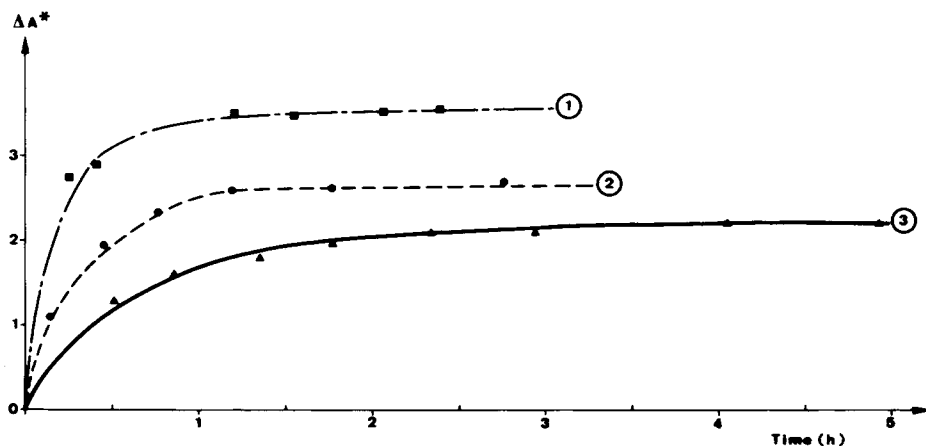


Fig. 4. Decrease of the  $3099\text{ cm}^{-1}$  maleimide absorption band as a function of time and temperature of reaction: (1)  $223^\circ\text{C}$ ; (2)  $189^\circ\text{C}$ ; (3)  $164^\circ\text{C}$ .  $\Delta A^*$  = normalized absorbance difference (arbitrary units).

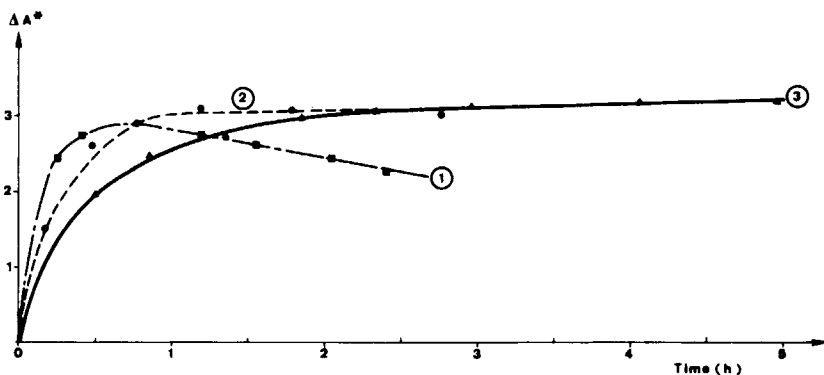


Fig. 5. Decrease of the  $3469\text{ cm}^{-1}$   $\text{NH}_2$  absorption band as a function of time and temperature of reaction: (1)  $223^\circ\text{C}$ ; (2)  $189^\circ\text{C}$ ; (3)  $164^\circ\text{C}$ .  $\Delta A^*$  = normalized absorbance difference (arbitrary units).

( $\epsilon_2$ ) absorption bands, the  $3035\text{ cm}^{-1}$  band [ $\nu(\text{C}-\text{H})$  mode of the benzene ring] being used as internal thickness band. From the Beer-Lambert law

$$\epsilon_2/\epsilon_1 = A_2C_1/A_1C_2 \quad (1)$$

where  $A_1$  and  $A_2$  are the absorbances of the  $3100\text{ cm}^{-1}$  and  $3035\text{ cm}^{-1}$  bands, respectively,  $C_1$  the double bond concentration, and  $C_2$  the phenyl group con-

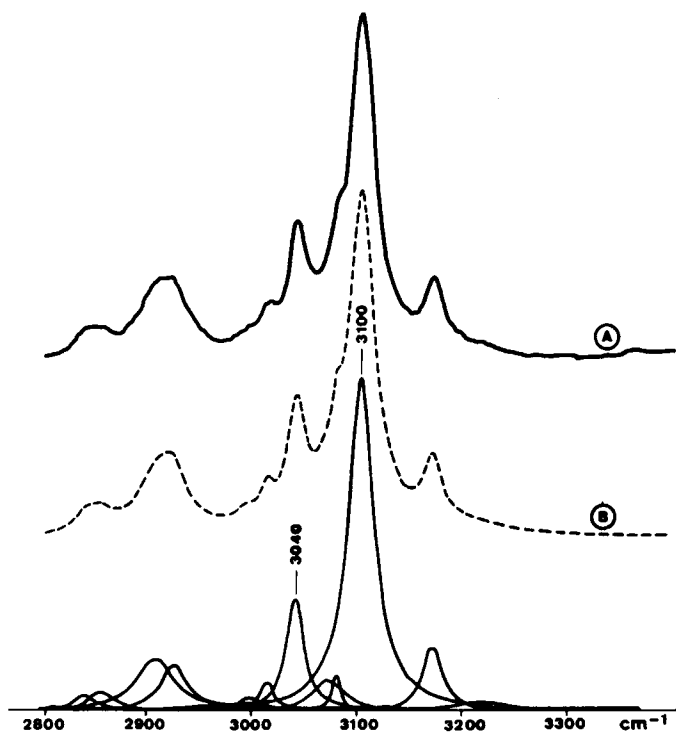


Fig. 6. Spectrum analysis of compound I in the  $2800\text{--}3400\text{ cm}^{-1}$  range: (A) original spectrum; (B) best fit with elementary bands.

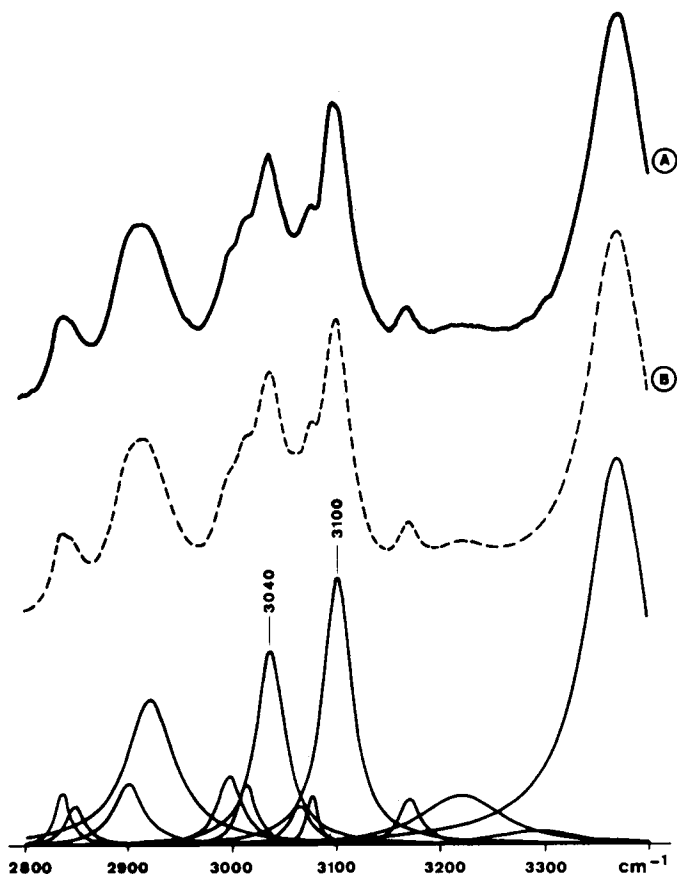


Fig. 7. Spectrum analysis of polyimide prepolymer in the 2800–3400  $\text{cm}^{-1}$  range: (A) original spectrum; (B) best fit with elementary bands.

centration. The ratio  $\epsilon_2/\epsilon_1$  was measured using the molecule (I) and different low condensed polymers.

As far as compound (I) is concerned, two double bonds and two aromatic rings are present.  $C_1 = C_2$  and  $\epsilon_2/\epsilon_1 = A_2/A_1$ . As shown in Figure 6, the 2800–3400  $\text{cm}^{-1}$  region was analyzed using 12 Lorentzian peaks. We thus obtained a value  $\epsilon_2/\epsilon_1 = 0.34 \pm 0.02$ .

When considering low condensed polymers, seven benzene rings for five double bonds are present in the initial mixture, i.e.,  $C_1^0 = (5/7) C_2$  with  $C_1^0$  and  $C_2$  the initial double bond and benzene ring concentrations, respectively. For any polymerized sample,  $p = C_1/C_1^0$  represents the residual double bond percentage.

From the relation (1) one get

$$\epsilon_2/\epsilon_1 = A_2 p C_1^0 / A_1 C_2$$

$$\epsilon_2/\epsilon_1 = 5p A_2 / 7 A_1$$

We used soluble samples containing from 87.1% to 81.9% double bonds determined in solution by chemical titration. Curve analysis of the 2800–3400  $\text{cm}^{-1}$  range requires two additional Lorentzian peaks to take amine absorption bands

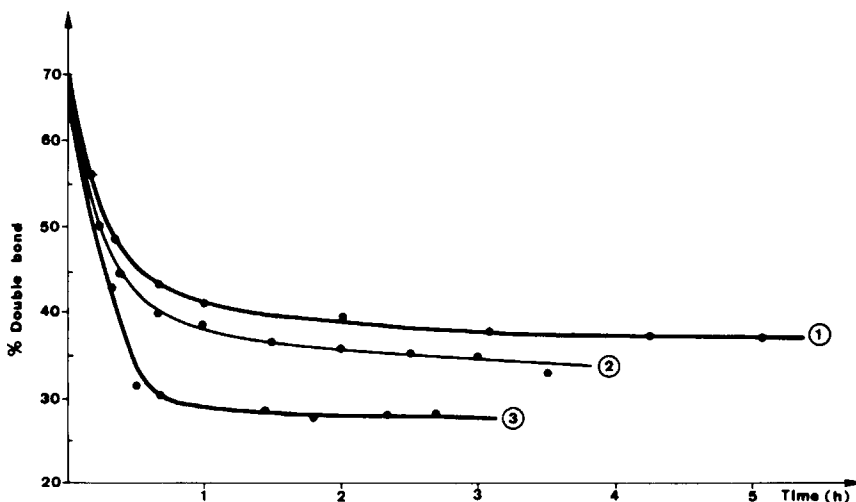


Fig. 8. Change of the amount of double bonds in the polyimide as a function of time and temperature of polymerization: (1) 164°C; (2) 189°C; (3) 223°C.

into account, as shown in Figure 7. Measurements over four different samples gave a mean value  $\epsilon_2/\epsilon_1 = 0.36 \pm 0.02$ . We used a value  $\epsilon_2/\epsilon_1 = 0.35$  for subsequent analysis. The change of maleic double bonds for different temperatures of reaction is given in Figure 8.

For a given reaction temperature, the double bond percentage decreases rapidly then reaches a constant level. This level is a function of the reaction temperature. Furthermore, a linear relationship holds in the measured range between residual double bond percentage and reaction temperature. On the other hand, after reaction at a given temperature, an increase of the temperature induces a new polymerization step. The final double bond amount is only dependent on the final reaction temperature, whatever the number of steps used to reach it. As an example, 25% of double bonds remains in the polymer at a final 237°C reaction temperature. Such a behavior, previously observed in aliphatic bismaleimides,<sup>6</sup> is clearly related to the mobility of the reactive sites in the tridimensional network created. The  $T_g$ 's of polyimides cured at different temperatures are given in Table II. As a matter of fact, reaction stops when the glass transition of the created network, linked to the degree of crosslinking, reaches a value close by to the reaction temperature. A further increase of temperature above the actual  $T_g$  results in a new increase of mobility of the reactive groups

TABLE II  
Glass Transition Temperatures of Polyimides Cured at Different Temperatures

Curing temp (°C)	$T_g$ (°C)
164	165
170	173
180	181
189	200
200	190



in the system, and the reaction starts again till the mobility at the new temperature becomes low enough to stop it. In other words, one can say that the final polymerization state of this kind of bismaleimides is directly monitored by the reaction temperature, i.e., by the glass transition temperature of the polymer network obtained.

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