

Eutectic mixture of two bismaleimide monomers: thermal and mechanistic study in the molten state

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Differential scanning calorimetry analysis of two bismaleimide monomers (N,N-diphenylmethane-4,4'-bismaleimide and *m*-phenylenebismaleimide) mixed in different proportions has enabled a phase diagram to be constructed. There is a relationship between the melting and solubility of each constituent of the binary system via the different liquid and solid phases. The concept of a eutectic mixture having special thermal properties has thus been demonstrated. The eutectic melting temperatures are very interesting because they are much lower than that of the compound with the lowest melting point, making easier the use of these monomers in the molten state. In addition, the reduction of the temperatures of crosslinking onset becomes maximal in these systems at the eutectic point, at which point there is a unique and perfectly homogeneous melting. In this unique liquid phase, the two monomers can combine to form the network after a copolymerization reaction. Once the network forms, *m*-phenylenebismaleimide radicals that are more highly stabilized by resonance are more reactive in the initial stages of the copolymerization reaction.

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INTRODUCTION

Among thermohardening polymers with high thermo-stability, bismaleimides (BMI) have long been used to manufacture printed circuit supports. A major problem associated with this type of resin is its relatively difficult utilization, whose attendant high cost restricts its use to certain hi-tech fields. Considerable efforts are thus being devoted to improving the ease of use of bismaleimides¹. In most cases, the double bond of these maleimide compounds, activated by the presence of α -carbonyls, is excessively electron depleted. Its reactivity towards nucleophilic and anionic reactants is thus increased in comparison to that of a simple ethylene bond. As a result of this, a large number of homopolymerization, copolymerization or addition reactions^{2–5} can occur on the maleimide function albeit with several restrictions, in particular their very high melting (T_m) and polymerization onset temperatures (T_o). These high melting points have oriented research to the study of mixtures of maleimide systems with lower melting points for better molten state process management. The use of binary mixtures, which may be a method for arriving at this improvement, has been investigated in this work.

There are several published examples of mixtures with reduced melting temperatures^{6,7}, most of them lower than 150°C. Most often, they are binary mixtures composed of two bismaleimide monomers containing an aromatic structure in well defined stoichiometric ratios;

one of the components is N,N-diphenylmethane-4,4'-bismaleimide (BM) (*Figure 1*) often used in industrial systems³. Varma and Tiwari⁶ have clearly shown a concentration effect of the mixtures, responsible for the general lowering of melting (T_m) and polymerization onset temperatures (T_o) in comparison to the individual thermal characteristics of each pure monomer. More recently, Nagai *et al.*⁷ published results of the thermal study of a mixture of BM and another BMI monomer. In this study, it was shown that melting occurred at lower temperatures when the proportion of the monomer with the lower melting temperature was increased. The maximal decrease observed corresponded to the melting of a particular mixture, a eutectic mixture, in which the minimal temperature (noted T_e , eutectic temperature) could be determined by both thermal measurements and theoretical calculations.

Prior work in our laboratory⁸ on several bismaleimide compounds show a non-negligible variation of the zones of reactivity of maleimide functions depending on the structure of the central group, that induces relatively high melting and polymerization temperatures as a function of the chemical skeleton in question. In order to expand the field of application of these systems at the same time as facilitating their use, we initially ought to lower T_m and T_o by the use of mixtures with suitable monomer concentrations, based on published data. Changes in the thermal behaviour of two basic systems composed of bismaleimide monomer mixtures at different concentrations were investigated by d.s.c. (*Figure 1*). Subsequently, we carried out a mechanistic study of a

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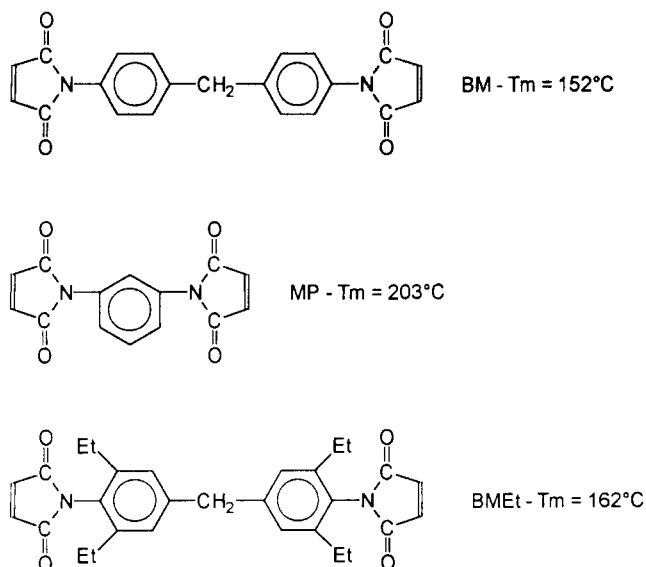


Figure 1 Chemical structure of bismaleimide monomers BM, MP and BMEt studied alone and in a BM/MP and BM/BMEt mixtures

particular mixture (eutectic mixture) having all the desired thermal characteristics. Its aim was to determine if the observed change of reactivity was directly related to a modification of the reaction mechanism or simply to a mixture effect with compatibility of the compounds. The results obtained have been compared to published data^{6,7}.

EXPERIMENTAL

Description of the monomers

The chemical structure of the monomers contains one variable central group with one or two aromatic rings between the two maleimide substituents, with or without a central pivot methylene group $-\text{CH}_2-$ (Figure 1). This choice was governed by the fact that the mixtures have very different thermal characters (melting and zone of reactivity) resulting from the difference in the chemical skeleton. Two of these compounds are available commercially: N,N-diphenylmethane-4,4'-bismaleimide (BM) and *m*-phenylenebismaleimide (MP) (OUV Chemie Linz) and were used without further purification. The third monomer, tetrasubstituted by ethyl groups *ortho* to each maleimide function (BMEt), was synthesized in the laboratory⁸.

Preparation and examination of BM/MP and BM/BMEt mixtures

Mixtures containing varying concentrations of two monomers, BM/MP and BM/BMEt, were prepared in solvent after dissolution in chloroform at room temperature and under magnetic stirring. All the resulting solutions were perfectly homogeneous. After evaporating the solvent and drying for several hours in an oven, the resulting powders were finely ground to obtain the finest mixtures possible. The drying step is very important for this in order to eliminate solute-solvent complexes that may sometimes appear as artifacts in thermal analyses.

The powders thus obtained were examined by i.r. absorption spectroscopy in the zone of $4000-400\text{ cm}^{-1}$. In comparison to the FTi.r. spectra of the two pure

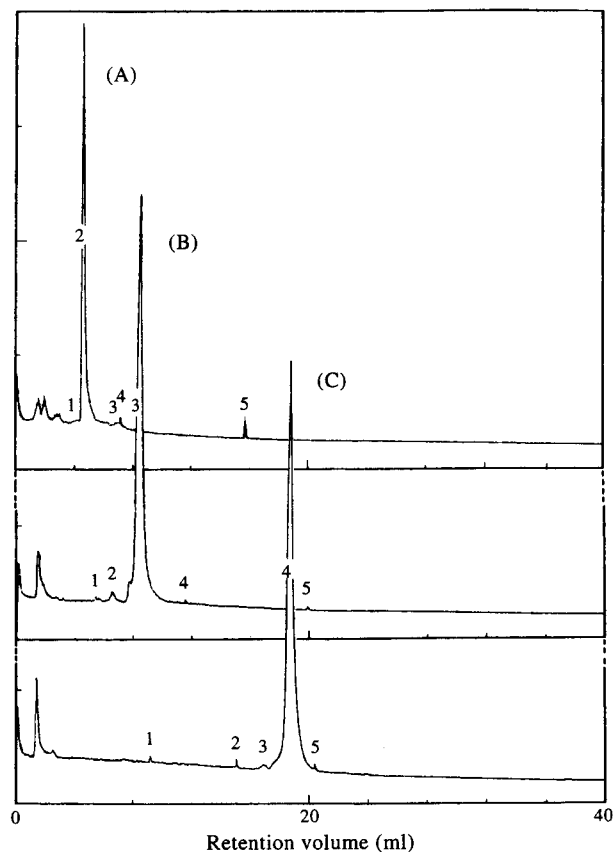


Figure 2 Chromatograms of compounds: (A) MP; (B) BM; (C) BMEt

compounds, we observed no change in the position or intensity of bands characteristic of the maleimide functions of each monomer in the mixtures was observed, showing that the systems did not change during the preparation of the mixtures.

Experimental techniques

Fourier transform infrared absorption spectroscopy (FTi.r.). Spectra were recorded with a BRUKER IFS 45 spectrometer in the following conditions: spectral bandwidth $4000-400\text{ cm}^{-1}$, 32 accumulations, resolution 2 cm^{-1} , signal processing by triangular apodization. All solid samples were recorded as a potassium bromide pellet.

High performance liquid chromatography (h.p.l.c.). A VARIAN 5000 high performance liquid chromatograph coupled to an ICS light scattering detector was used. The column was apolar ODS- C_{18} (C_{18} bonded silica). The eluent was a water-acetonitrile mixture programmed so that the percentage of acetonitrile varied from 50 to 90% in 40 min, at a flow-rate of 1 ml min^{-1} .

Nuclear magnetic resonance (n.m.r.). High resolution liquid state ($\text{DMSO-}d_6$) ^1H and ^{13}C n.m.r. spectra were recorded with a BRUKER AM 400 spectrometer in the following conditions: pulse angle 90° [$7\text{ }\mu\text{s}$ (^1H) and $4.2\text{ }\mu\text{s}$ (^{13}C)], digital resolution 0.122 Hz/point (^1H) and 0.375 Hz/point (^{13}C) corresponding to a spectral width of 4000 Hz (^1H) and $20\,000\text{ Hz}$ (^{13}C) for a memory space of 64 K (^1H) and 128 K (^{13}C).

Solid state ^{13}C CP/MAS (cross polarization with magic angle spinning) n.m.r. spectra were recorded with a BRUKER ARX 300 spectrometer in quadrupole

Table 1 Proton and carbon chemical shifts of the maleimide double bond by liquid state ^1H and ^{13}C n.m.r. with infrared frequencies characteristic of the maleimide function for pure BM, MP and BMEt

Monomer	BM	MP	BMEt
Chemical shifts (ppm) of maleimide protons	7.2 ₄	7.3 ₀	7.2 ₇
Chemical shifts (ppm) of maleimide carbons and of carbonyl carbons	170.4 ₈ (C=O) 134.1 ₄ (C=C)	170.3 ₁ (C=O) 135.3 ₂ (C=C)	171.7 ₄ (C=O) 135.9 ₀ (C=C)
Infrared frequencies (cm ⁻¹) characteristic of the maleimide function	~3100 ($\nu=\text{CH}$) 1149 ($\nu\text{C}-\text{N}-\text{C}$) 832 ($\delta\text{C}=\text{C}$) 690 [$\delta\text{C}=\text{C}-\text{H}(\text{cis})$]	~3100 ($\nu=\text{CH}$) 1147 ($\nu\text{C}-\text{N}-\text{C}$) 827 ($\delta\text{C}=\text{C}$) 693 [$\delta\text{C}=\text{C}-\text{H}(\text{cis})$]	~3095 ($\nu=\text{CH}$) 1153 ($\nu\text{C}-\text{N}-\text{C}$) 832 ($\delta\text{C}=\text{C}$) 693 [$\delta\text{C}=\text{C}-\text{H}(\text{cis})$]

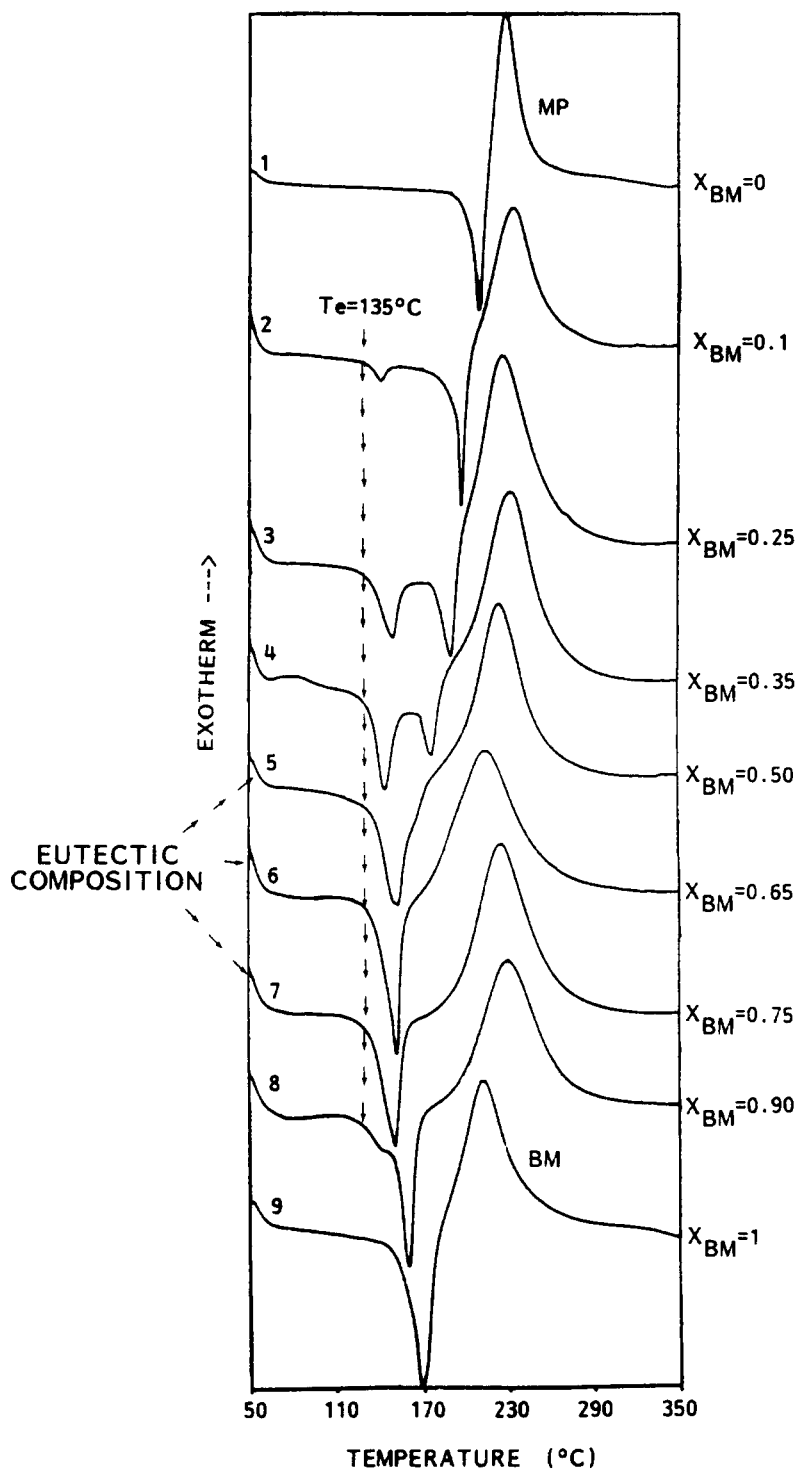
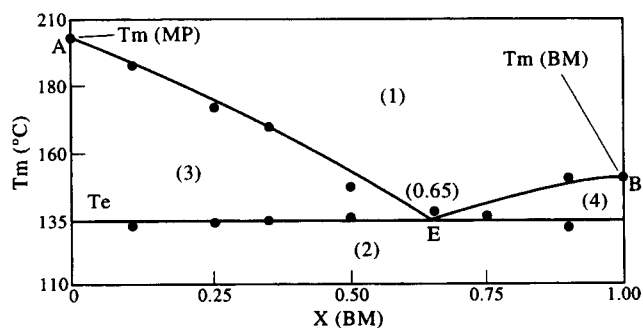
N.m.r. solvent: DMSO-*d*₆**Figure 3** D.s.c. diagrams of BM and MP monomers alone and in mixture as a function of the molar fraction of BM

Table 2 D.s.c. thermal characteristics of BM and MP mixtures as a function of the molar fraction of BM (X_{BM})

Molar fraction (X_{BM})	Thermal characteristic			
	T_{f_1} (°C)	T_{f_2} (°C)	T_o (°C)	T_{exo} (°C)
0	203	/	203–215	230
0.1	133	193	210	233
0.25	134	178	206	228
0.35	135	170	205	230
0.50	136	148	198	225
0.65	138	/	176	215
0.75	136	/	206	227
0.90	133	150	207	232
1	152	/	178	214

Heating rate 5°C min^{-1} **Figure 4** Phase diagram: melting equilibrium with formation of a eutectic: (1) domain 1; (2) domain 2; (3) domain 3; (4) domain 4

detection. Samples reduced to a fine powder were placed in a boron nitride sample holder. A contact time of $100\ \mu\text{s}$ and a 5 s interval between sequences as well as 6500 Hz spinning were used. A mean of 5000 contacts was necessary in order to obtain an interpretable spectrum with suitable signal/noise ratio. Chemical shifts were calculated with reference to the line of polyoxymethylene (Delrin) at 80 ppm (internal standard).

Differential scanning calorimetry (d.s.c.). D.s.c. diagrams of BM, MP and BMEt monomers, alone or in BM/MP and BM/BMEt mixtures, were recorded with a SETARAM DSC 111G differential calorimeter in conditions of programmed temperature gradient at 5°C min^{-1} .

ANALYSIS OF THE RESULTS

Physicochemical characterizations of BM, MP and BMEt monomers

Polymerization of bismaleimide monomers by thermal priming is difficult to study because of the need for rigorous purification, since traces of impurities can play a primer and/or catalytic role^{9–11}. This possibility of parasite priming was reduced by conducting an h.p.l.c. purity check on each compound: chromatographic purity was found to be greater than 98% in all cases (Figure 2).

The expected chemical structures of products were confirmed by ^1H and ^{13}C in solution and by solid state FTi.r. spectroscopy. We identified and attributed all chemical shifts in products, in particular those of the protons and carbons of reactive maleimide functions, as

well as the i.r. vibrations characteristic of the maleimide ring (Table 1) on the basis of published data¹³.

N.m.r. showed that differences in the structure of the central skeleton between the two maleimide rings affected proton and carbon chemical shifts of the maleimide double bond and thus the electron density of the maleimide function. As a result of this, the molten state homopolymerization reaction via radical opening of the maleimide double bond⁹ (noted C=C in Table 1) undoubtedly occurred at markedly different polymerization temperatures (T_o and T_{exo}) depending on the molecular architecture of the compounds.

Following the physicochemical characterizations and purity check of the products, a dynamic d.s.c. study of the monomers alone and in mixtures was conducted in the $50\text{--}350^\circ\text{C}$ temperature range with a 5°C min^{-1} gradient.

Thermal studies

The d.s.c. diagrams of each BM/MP mixture recorded after a first dynamic scan in the same conditions of temperature gradient (5°C min^{-1}) are shown in Figure 3. Table 2 lists the melting (T_m) and polymerization onset (T_o) temperatures, as well as those of the exotherm maximum (T_{exo}). Processing thermal data as a function of the stoichiometric ratio of the mixture is shown in Figures 4 and 5 which will be successively commented.

Programmed thermal analysis revealed that endothermal transitions due to the melting of MP and BM alone occurred at 203 and 152°C , respectively (d.s.c. diagram noted 1 and 9 in Figure 3). The melting points of the two monomers were very different and the difference observed probably resulted from several factors. In general, the melting point of a compound increases with its molar mass, although this is apparently not the case for MP and BM. This is consistent with believing that intermolecular Van der Waals interactions⁷ remain more important between neighbouring MP molecules to explain the much higher melting temperature of this compound. This hypothesis is supported by the fact that the intrinsic structure of MP is more rigid because of its small size (central group having only one aromatic ring). This rigidity leads to greater cohesion by interposed Van der Waals bonds and so mutual sliding of the molecules occurs with much more difficulty.

The addition of large quantities of BM to the mixtures, i.e. concentrations of X_{BM} equal to 0.1, 0.25 and 0.35 resulted in the appearance of two melting points. The first remained around 135°C and corresponded to the melting temperature of the eutectic (T_e) that remained independent of the BM/MP composition. The intensity of this first endothermal peak, however, depended on the BM concentration. The second endothermal transition corresponded to MP, i.e. the monomer with the higher melting point. The area of the second endotherm also varied with concentration, but above all was reduced to the point of furnishing a single and homogeneous melting signal with the first endotherm. This unique melting corresponded to the so-called eutectic composition zone, in which the molar fraction of BM (X_{BM}) in the mixtures was 0.5, 0.65 and 0.75.

As the proportion of BM was increased, two other endotherms again appeared (d.s.c. diagram noted 8 in Figure 3) at the BM proportion of 0.9. As before, the first was the melting of the eutectic whose temperature

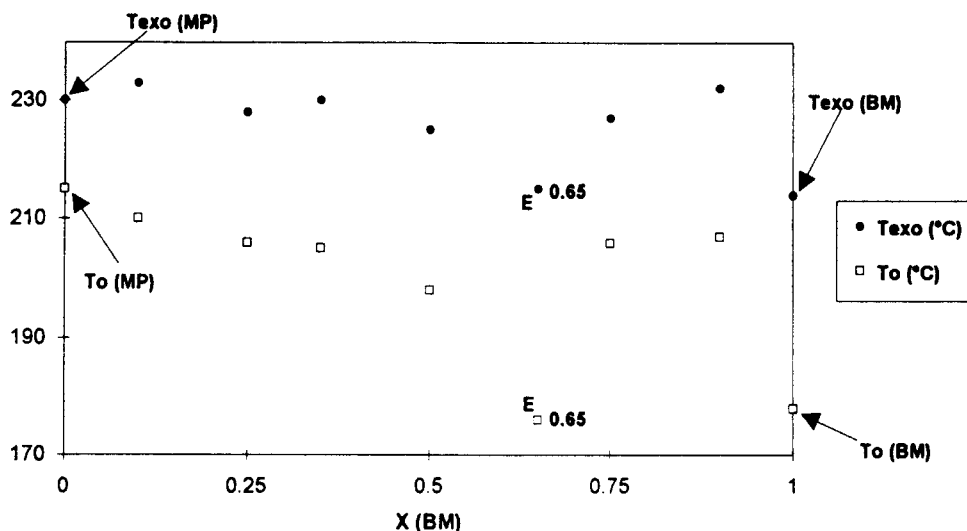


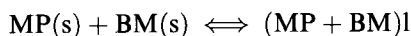
Figure 5 Changes in temperatures T_o and T_{exo} as a function of the molar fraction of BM in the mixtures

T_e remained unchanged, and the second signal was characteristic of BM monomer melting.

These experimental data are consistent with the results of Varma *et al.*⁶, who also obtained a significant decrease in melting points as a function of mixture stoichiometry when BM was added in high proportions. On the other hand, this author observed a double melting only in the case of the equimolar mixture. Nagai *et al.*⁷ reported that the maximal decrease corresponded to the melting of a eutectic (E) whose minimal temperature (noted T_e) could be determined both by calorimetric determinations and theoretical calculations with good correlation.

Processing melting data (T_{m_1} and T_{m_2}) as a function of the composition of the mixture (Table 2) enabled a phase diagram to be constructed (Figure 4). In this representation, a relationship between melting and the solubility of each component of the binary BM/MP system can be shown via different liquid–solid phases, while retaining the concept of eutectic introduced by Nagai *et al.*⁷. In the present case of a eutectic and in terms of melting equilibria, there are four particular zones, specific for each state, whether it be liquid, solid or both at the same time. These domains are delimited by three curves passing through E (eutectic point) characterized by a unique temperature T_e for a well determined composition of BM and MP ($X_{BM} = 0.65$).

The eutectic point is the only point at which the equilibrium between the three phases MP(s), BM(s) and binary liquid is possible:



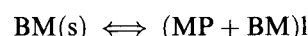
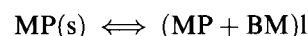
s: solid state

l: liquid state

It is noted that the mixture of the two monomers remains liquid at point E , at a temperature much lower than the melting temperature of the compound with the lower melting point. In addition, the four zones (Figure 4) are specific to one or another of the states:

- domain 1 corresponds to BM and MP in the liquid state,
- domain 2 concerns the two compounds in the solid state,

— and domains 3 and 4 correspond to (binary solution + solid MP) and (binary solution + solid BM) equilibria, i.e.



An equilibrium between the binary solution and MP(s) is possible between 203°C (T_m of MP alone) and 135°C (eutectic temperature) and the composition of the liquid phase for a given temperature can be read off the liquidus curve, noted AE. The same is true between 152°C (melting of pure BM) and T_e , where another equilibrium between the binary solution and BM(s) is also possible. When both phases were present, processing the EB liquidus curve enabled the composition of the liquid phase to be determined. Finally, at temperatures lower than T_e , an equilibrium forms only between the two compounds in the solid state that constitute two totally distinct solid phases.

The thermal studies also showed an effect of the composition of mixtures on the polymerization temperatures T_o , as well as on T_{exo} noted at the maximum of the exothermic peaks (Table 2). In order to better understand this effect, we plotted (Figure 5) the results of changes in T_o and T_{exo} as a function of the concentration of BM monomer in each binary mixture. The polymerization onset temperature decreased as the proportion of BM in the mixture was increased, and this decrease became maximal for concentrations corresponding to the eutectic composition zone. The result was most significant at point E , since at this eutectic concentration ($X_{BM} = 0.65$) T_o was the lowest (176°C) and of the same order as that noted for BM alone (178°C), considering the temperature gradient chosen for the study (5°C min⁻¹).

The same comment pertains to the T_{exo} temperatures. As the concentration of BM in the mixtures was increased, there was a significant decrease that became maximal at the eutectic point ($X_{BM} = 0.65$). When the proportion became higher than that at point E , reactivity changed with an increase in T_o and T_{exo} . These data are consistent with the results of Varma *et al.*⁶, who observed a low value of the exotherm maximum in a precise

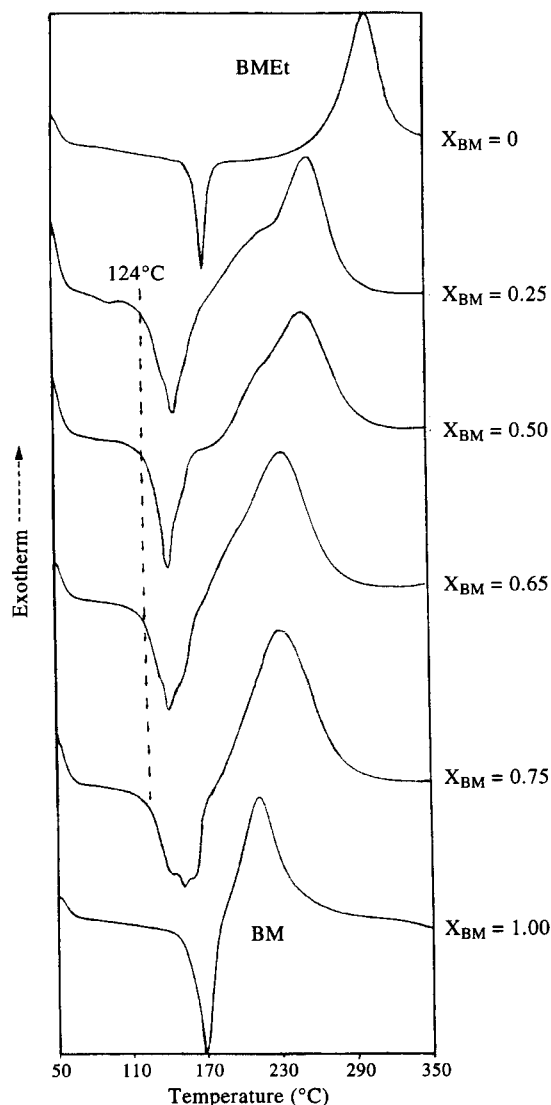


Figure 6 D.s.c. diagrams of BM and BMEt monomers alone and in mixture as a function of the molar fraction of BM

mixture, but are inconsistent with those of Nagai *et al.*⁷ who reported no change in the exothermal peaks in the eutectic mixture.

The same thermal study on another mixture, BM/BMEt (Figure 6) composed of the two monomers in Figure 1, confirmed the general shape of the melting curves and T_{exo} temperature. The T_m of these two maleimide systems were relatively close and practical conditions for preparing the different mixtures remained unchanged with reference to those prepared from BM and MP. Figure 7 shows the changes in T_m and T_{exo} as a function of the BM composition.

These differential thermal studies thus revealed a number of changes in the zones of reactivity of several binary mixtures that logically depend on the individual thermal characteristics of the constituents in question. Since the mixtures were consistently BM-based, the results show the fundamental role played by the other monomer in terms of thermal data. When the melting points of the two pure constituents were similar, e.g. in the case of BM (152°C)/BMEt (162°C) mixtures, the melting point of the mixture was consistently reduced as the proportion of the monomer with the lower melting point was increased, in this case (BM) (see Figure 6). This comment is valid for both the examples in this work and those of Varma *et al.*⁶ or Nagai *et al.*⁷.

In general, this decrease became maximal for the so-called eutectic composition, a result that was partially verified for the BM/BMEt-based mixture, where the minimal melting temperature was close to 124°C over a broad concentration zone (Figures 6 and 7). Figure 6 also shows a considerable difference between the beginning and end of the melting endotherms, undoubtedly due to complex melting. This indicates that in order to detect two well separated melting peaks in a defined mixture, two monomers with melting points relatively far apart should be used, as is the case of BM (152°C)/MP (203°C) where the temperature difference was about 50°C. The validity of this comment has been confirmed by the results of literature⁷.

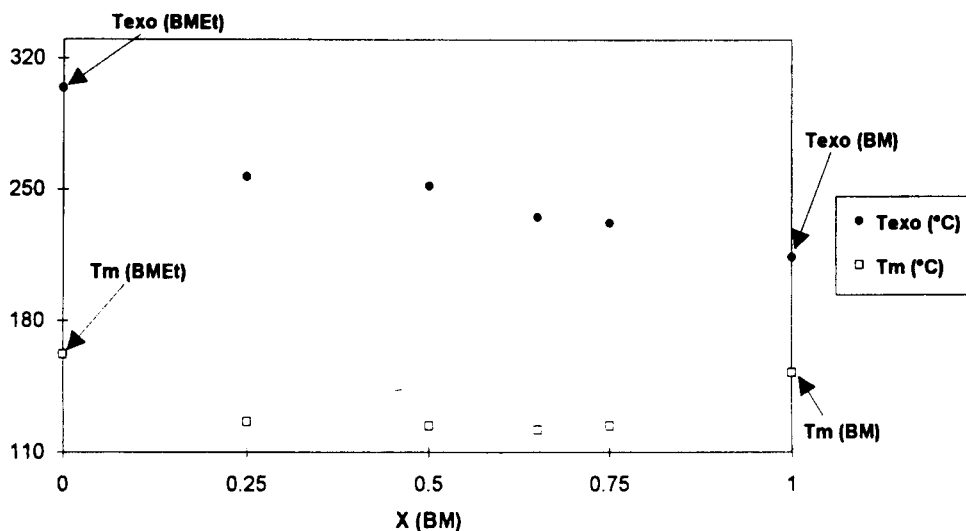


Figure 7 Changes in temperatures T_m and T_{exo} as a function of the molar fraction of BM in the mixtures

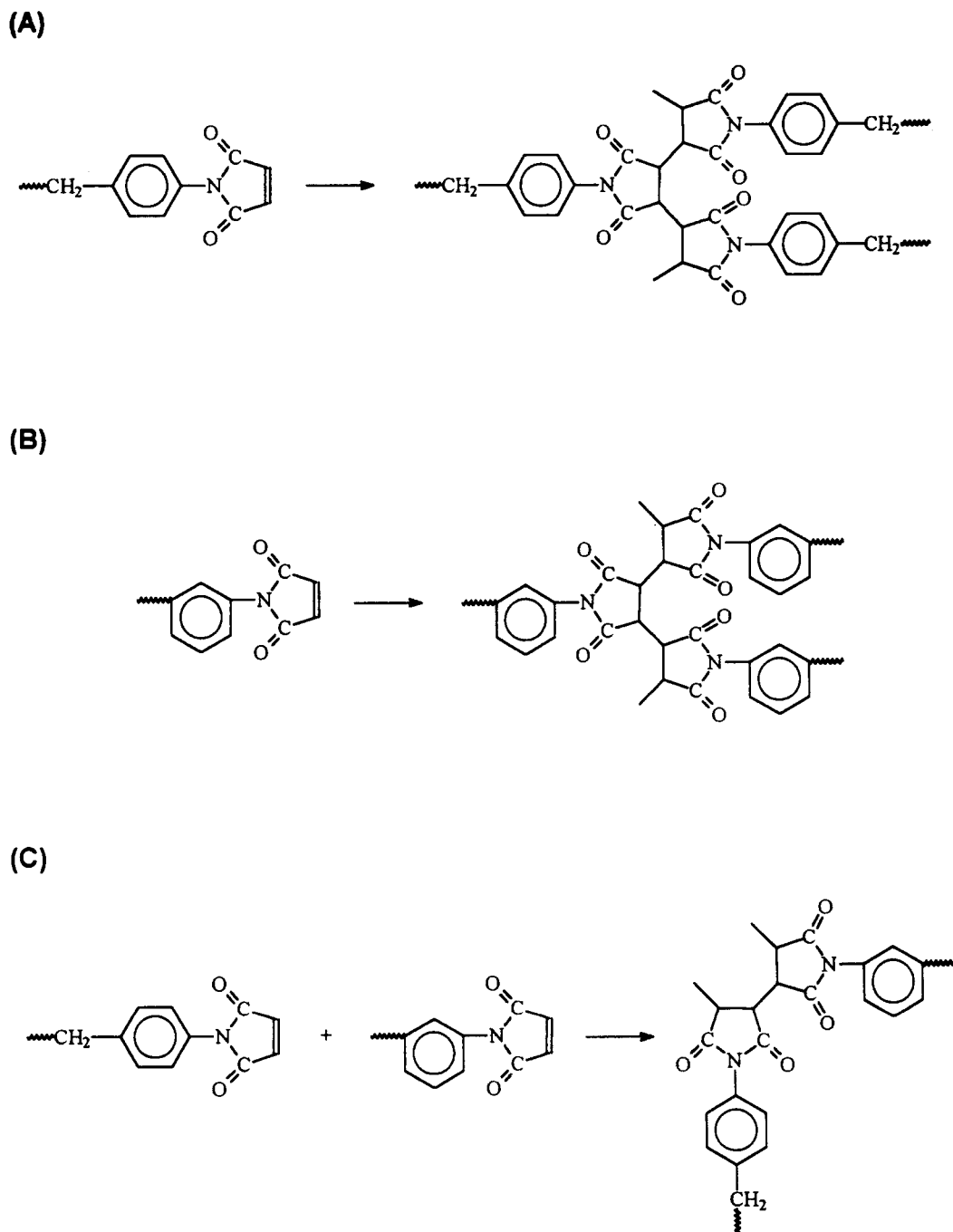


Figure 8 Expected reaction mechanisms for these systems in the molten state: (A) homopolymerization of BM; (B) homopolymerization of MP; (C) copolymerization of the BM/MP mixture

Based on these data, it becomes easier to understand the role of impurities in maleimide systems. In most cases, impurities lower the melting temperature and increase the difference with the end of the process. In the special case of a sample containing a single impurity in non-negligible quantities, the observed phenomena can be explained by a phase diagram of the binary mixtures, as shown in the BM/MP mixture. In this case of mixtures of bismaleimide monomers we introduced the concept of a eutectic previously used by Nagai *et al.*⁷

Changing the monomer concentrations in all these mixtures also affects the zones of reactivity of maleimide functions, except in the example considered by Nagai *et al.*⁷, where values noted at the maximum of exothermal peaks were invariant.

Overall conclusions cannot be easily drawn, since the data in this study varied depending on the two bismaleimide monomers used in the mixtures. Each mixture is in fact a special case and it is thus impossible to predict changes in the thermal parameters of binary mixtures based uniquely on thermal results (T_m , T_o and T_{exo}) of each constituent taken individually.

Mechanistic study

BM-based eutectic mixtures composed of two bismaleimide monomers have been the object of a number of unpublished industrial developments. Nonetheless, those published^{6,7} disagree with the reactivity of BMI monomers in binary systems. Thus, Varma *et al.*⁶ proposed a mechanism via the copolymerization of

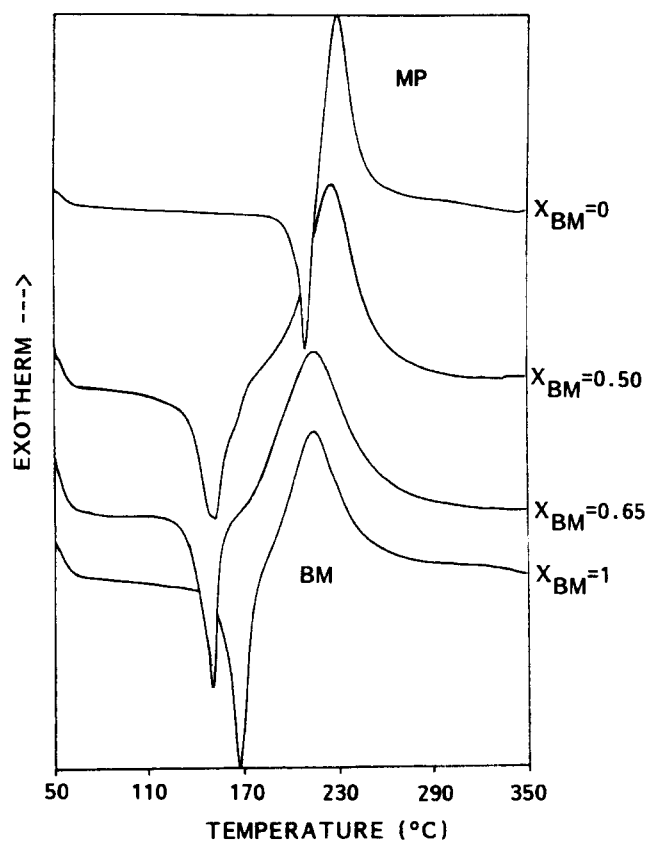


Figure 9 D.s.c. diagrams of BM and MP monomers alone and in the eutectic composition $X_{BM} = 0.50$ and 0.65

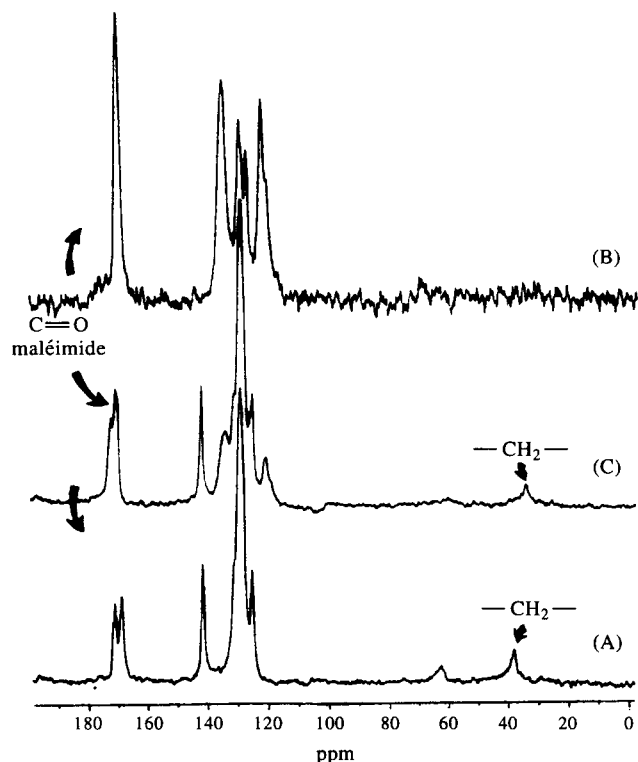


Figure 10 Solid state ^{13}C CP/MAS n.m.r. spectra at initial time $t = 0$: (A) BM; (B) MP; (C) mixture 1

bismaleimide molecules in the mixture at the minimal temperature of the exotherm maximum, T_{exo} . Inversely, Nagai *et al.*⁷ observed no change of T_{exo} in the eutectic mixture compared to the T_{exo} of each monomer alone

and concluded that the copolymerization reaction did not occur. Both of these conclusions, however, were not based on spectroscopic data and so the affirmations advanced were based only on thermal data. It was thus of interest to determine the reaction mechanism involved in polymerization by thermal priming of the binary BM/MP mixture. The study was conducted on two well defined mixtures corresponding to the zone of eutectic composition detected by d.s.c. (Figure 3). The mixtures used were:

- mixture 1 a molar fraction of BM equal to 0.50 ($X_{BM} = 0.50$, i.e. $X_{MP} = 0.50$);
- mixture 2 a molar fraction of BM equal to 0.65 ($X_{BM} = 0.65$, i.e. $X_{MP} = 0.35$).

Three reactions are possible in the case of BM/MP mixtures (Figure 8) in light of the molten state reactivity of MP and BM monomers alone or in the eutectic mixture. In the three proposed reaction pathways, the succinimide groups formed after chemical bridging and leading to the different three dimensional polymers have the same chemical composition after cross linking (hybrid saturated sp^3 carbons in each case). For this reason, it was expected that their differentiation would be difficult using classical solid state spectroscopic methods (^{13}C CP/MAS n.m.r. or FTi.r.). The resolution of these methods is insufficient to distinguish the slight wavelength variations in i.r. spectroscopy or chemical shifts in solid state ^{13}C n.m.r., as our results have shown. Figure 9 summarizes the d.s.c. results of the zone of reactivity of the two monomers alone and in the eutectic mixture.

The kinetic study of BM cross linking⁸ had shown the high reactivity of the compound that was totally unaffected by steric effects when isothermal kinetics were run at 165°C . Similarly, attention was paid to the reaction of MP alone and in mixtures. Pure MP is less reactive than BM as shown by the d.s.c. diagrams of reactivity zones (Figure 9). This system homopolymerizes after melting at a relatively high temperature (200°C), that depends on the chemical nature of the central group between the two cross linkable maleimide functions.

In mixture 2 ($X_{BM} = 0.65$), BM and MP were present in a single liquid phase with a eutectic composition, specific for a homogeneous molten state. As a result of this, the eutectic mixture melted sharply at a temperature T_c close to 135°C , lower than that of the compound with the lower melting point (BM), exactly as each of the basic substances, pure BM or MP. In these conditions, it is probable that at the level of the zone of reactivity of the eutectic mixture after thermal priming, the energy released by the shock of the monomers can be captured by either the molecules (BM or MP) used as an initiator for network formation. The creation of the cross linked network would thus depend on the relative proportion of each monomer, but also on molten state reactivity, i.e. the reactivity of their respective radicals, a hypothesis which remains to be confirmed and for which we will try to provide an answer in this study.

Study of mixture 1 ($X_{BM} = 0.50$, i.e. $X_{MP} = 0.50$)

Mixture 1 was analysed by solid state ^{13}C n.m.r. The spectra of monomers alone or in the mixture at initial time ($t = 0$) (Figure 10) show that mixture 1 presents signals characteristic of the carbons of each monomer in three different and characteristic zones:

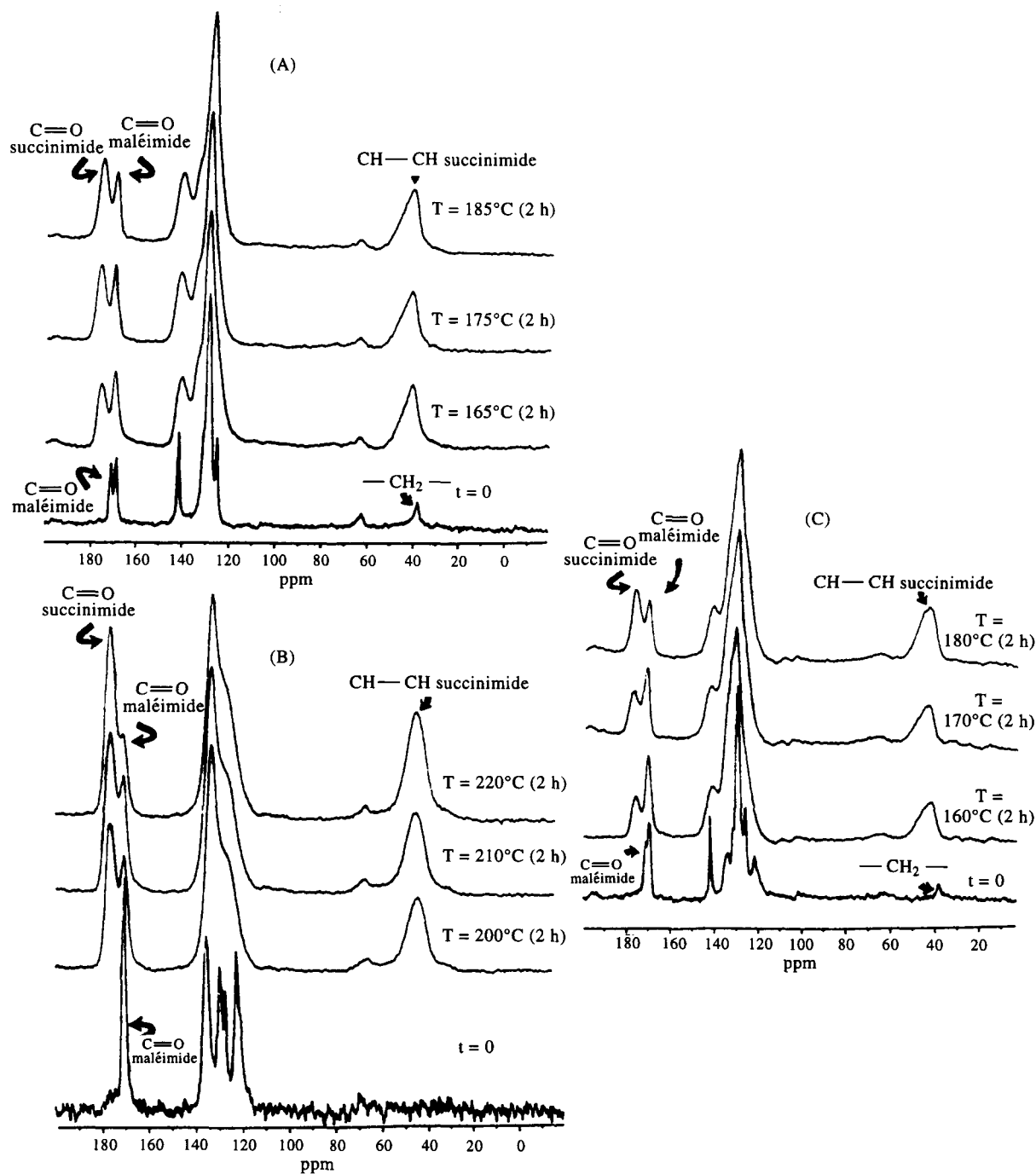


Figure 11 Solid state ^{13}C CP/MAS n.m.r. spectra after 2 h heat treatment: (A) homopolymerization of BM at $T = 165^\circ\text{C}$, 175°C and 185°C ; (B) homopolymerization of MP at $T = 200^\circ\text{C}$, 210°C and 220°C ; (C) polymerization of mixture 1 at $T = 160^\circ\text{C}$, 170°C and 180°C

- 30–50 ppm, resonance of carbon of the $-\text{CH}_2-$ pivot connecting the two aromatic rings of BM;
- 110–150 ppm, resonance region of aromatic carbons, as well as those of the maleimide double bond in each molecule, BM and MP;
- 160–180 ppm, resonance zone of maleimide carbonyl groups of both compounds. In this spectral zone it was impossible to differentiate the carbonyl carbons of the two monomers, since they resonated at the same frequency and furnished a unique signal in the mixture. This is not surprising, since in solution there was only a small difference in chemical shifts (Table 1) and considering the even lower resolution of solid state ^{13}C n.m.r., each carbonyl group cannot be differentiated. The resonance signals from

the carbons of each maleimide double bond were also masked by those of BM and the aromatic carbons.

These observations were confirmed by analysing the spectra obtained after thermal priming of mixture 1 (Figure 11), but it was not possible to quantify the individual disappearance of BM or MP. When the solid state ^{13}C n.m.r. spectra of the homopolymerization of the two monomers, pure and in the mixture are compared, the superimposition of signals does not enable one of the reactions (Figure 8) to be chosen. The only conclusion possible from this work is that there was indeed formation of a three-dimensional system characterized by the appearance of saturated carbons between 30 and 50 ppm, corresponding to succinimide

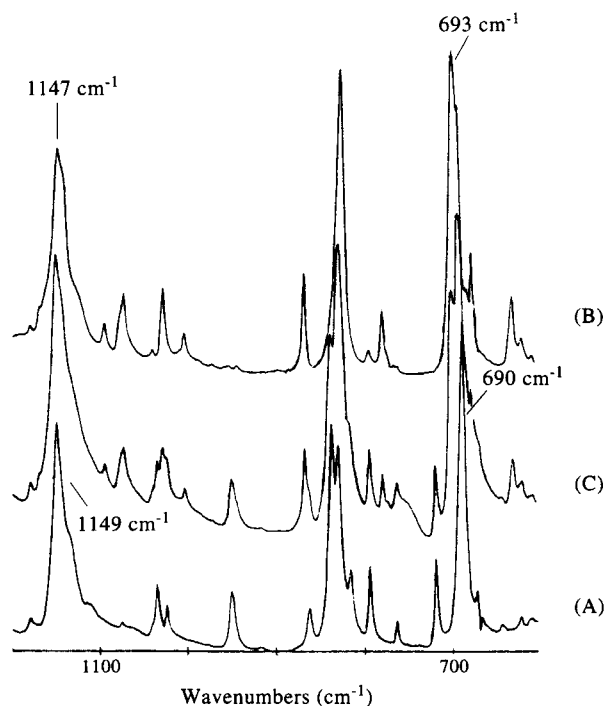


Figure 12 FTi.r. spectra at initial time $t = 0$: (A) BM; (B) MP; (C) mixture 1

fragments (CH-CH) created when the network was formed. These new entities are responsible for the resonance of carbonyl carbons at lower fields.

In order to determine reaction advancement (quantitation of the results), the broad bands between 160 and 180 ppm were deconvoluted^{14,15}. The quantity of residual maleimide double bonds was defined with reference to the total C=O surface of non-polymerized and polymerized maleimide functions. The surface of the line centered at 170 ppm is thus proportional to the number of carbonyl groups of residual maleimide functions in the case of BM and MP. That centered at 176 ppm would be proportional to the number of carbonyl groups of succinimide functions created during the polymerization reactions. The third line detected would be from small, slightly crosslinked molecules involving BM and MP, at least concerning the carbonyl detected and its immediate environment¹⁶. The results show that, depending on the temperature chosen (160, 170 or 180°C), crosslinked systems with transformation of maleimide functions can be obtained up to 70% advancement. The values of maleimide double bond conversion rates will be discussed at the same time as the results of the i.r. spectroscopy study.

Samples were also examined by i.r. absorption spectroscopy in the solid state, dispersed in a solid KBr matrix. Spectra (at $t = 0$) recorded in the range of 600–1200 cm^{-1} before heat treatment are shown in Figure 12. Similarly, i.r. examination of the monomers at the level of reactive maleimide functions, alone and in mixtures before polymerization did not provide differences that after thermal treatment could be used to differentiate the different reactions occurring. The reference spectrum of the mixture (Figure 12) contained a superimposition of bands characteristic of the maleimide vibrator in the two molecules. The $\nu\text{C-N-C}$ band of BM at 1149 cm^{-1} was thus superimposed on the same vibration band of MP around 1147 cm^{-1} . The same comment is applicable to

the $\delta\text{C=C-H(cis)}$ line of BM and MP at 690 and 693 cm^{-1} . These results were confirmed in the study of heat treated samples (Figure 13) in which both bands changed and broadened during the different heat treatments, so that it was impossible to quantify the individual disappearance of each monomer in mixture 1. Only an overall estimation of residual maleimide functions could be carried out (as in solid state ^{13}C n.m.r.) by assaying the $\nu\text{C-N-C}$ and $\delta\text{C=C-H(cis)}$ lines, whose intensity decreased in comparison to the reference band at 1511 cm^{-1} (aromatic ring aromatic untouched by the cross-linking mechanism).

Quantitation of residual maleimides after 2 h of heat treatment at 160, 170 and 180°C by ^{13}C CP/MAS n.m.r. and FTi.r. are listed in Table 3. In FTi.r. and depending on the wavelength chosen, the results diverged from those of solid state ^{13}C n.m.r. by up to 10%. When the $\delta\text{C=C-H(cis)}$ line was processed, the percentage of residual maleimide was overestimated in comparison to n.m.r. In addition, this i.r. band was dispersive (see the infrared spectrum of mixture 1 treated at 170°C for 2 h), which became a non-negligible factor in the evaluation of peak height.

Although not absolute, these values furnish an order of magnitude for changes in the cross-linked material. Regardless of the technique used, results follow the same changes as a function of the cycle (time/temperature) applied, as a result of their consistency.

Study of mixture 2 ($X_{\text{BM}} = 0.65$, i.e. $X_{\text{MP}} = 0.35$)

In the study of mixture 1 it was found that solid state techniques were difficult to apply to assay the individual disappearance of monomers and to conclude on the polymerization reaction involved in the eutectic composition zone. A fresh approach was adopted for mixture 2 that has enabled a reaction mechanism to be proposed. The experimental procedure involved separating the soluble part of mixture 2 after a 160°C heat treatment at several times (15 min, 30 min, 1, 2 and 7 h). The insoluble part (network formed) was separated from the soluble part of each heat treated sample by extracting in boiling dimethylsulfoxide and ultrasound treatment. For each sample taken, liquid state ^{13}C n.m.r. spectra of the solubilized portion were recorded in DMSO- d_6 (Figure 14). Special attention was paid to the zone around 170 ppm, corresponding to the carbonyl groups of residual maleimide functions.

Comparison with the initial reference spectrum ($t = 0$) showed that the soluble portion contained all the lines characteristic of the two starting bismaleimides, which thus did not react during the thermal process in question. Liquid state ^{13}C n.m.r. is a method reserved for structural analysis because of the quality of the data it furnishes, but it can also be used to study and quantify the composition of mixtures. This is possible when the surfaces of the signals from each constituent can be measured separately. This is why the zone of 170–175 ppm was chosen, which is well separated from the resonance of other carbon atoms. In this spectral region, BM and MP present the same number of carbonyl groups in their chemical structure. The percentage of one with relation to the other can be determined based on the relative intensity of the resonance lines of the carbonyl groups of the two systems in all soluble samples. After extraction, ^{13}C n.m.r. spectra (Figure 14) showed that the relative

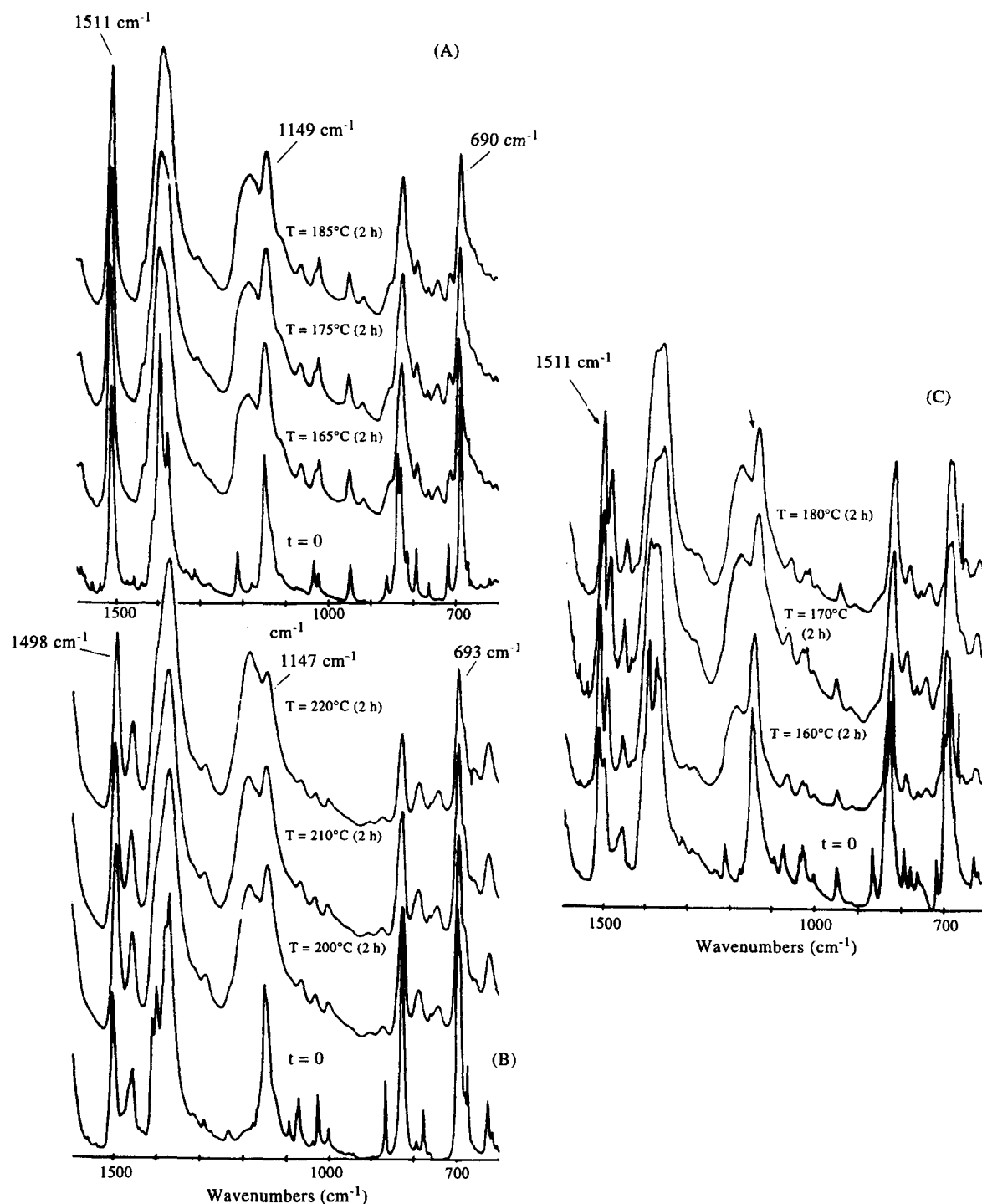


Figure 13 FTi.r. spectra after a 2 h heat treatment: (A) homopolymerization of BM at $T = 165^{\circ}\text{C}$, 175°C and 185°C ; (B) homopolymerization of MP at $T = 200^{\circ}\text{C}$, 210°C and 220°C ; (C) polymerization of mixture 1 at $T = 160^{\circ}\text{C}$, 170°C and 180°C

Table 3 Quantitation of residual maleimide functions in % after assay by solid state ^{13}C CP/MAS n.m.r. and FTi.r. in mixture 1

Cycle time (h)/temperature ($^{\circ}\text{C}$)	Residual maleimide functions (%)		
	Solid state ^{13}C n.m.r.	FTi.r.	
		$\nu\text{C}-\text{N}-\text{C}$	$\delta\text{C}=\text{H}(\text{cis})$
2/160	59	49	52
2/170	46	37	54
2/180	33	34	49

percentages of BM and MP monomers calculated by integrating the two $\text{C}=\text{O}$ signals varied little in the heat treated samples in comparison to the $t = 0$ sample, except for the $t = 15$ min sample. This would tend to indicate that the two monomers in the eutectic mixture disappeared simultaneously and in the same proportions during the thermally primed reaction. Thus, the reaction process involved the consumption of both molecules. The principal reaction in the eutectic mixture would preferentially be that of copolymerization (Figure 8).

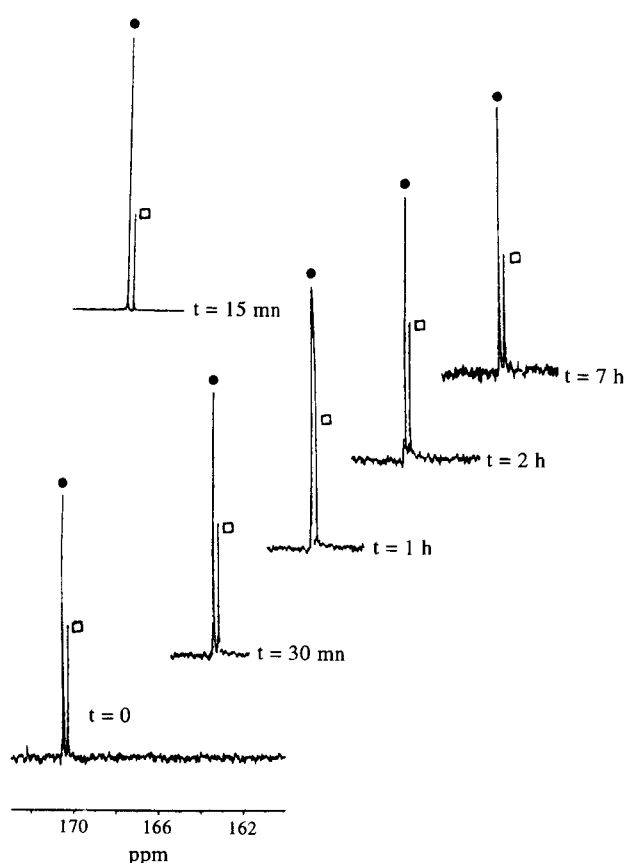


Figure 14 Mixture 2: liquid state ^{13}C n.m.r. spectra of each soluble portion (160–175 ppm region): ● carbonyl groups of BM monomer; □ carbonyl groups of MP monomer

In this type of copolymerization reaction, the networks formed at the beginning of the reaction are most often richer in one of the monomers in comparison to those formed at the end of the reaction; this finding can be correlated with our results. In the first extraction carried out after 15 min of heat treatment, the MP monomer apparently disappeared in the cross linking reaction more rapidly than BM (refer to the relative signal intensities in *Figure 14*). Several repeated experiments provided the same result and so the three-dimensional system was richer in MP monomer at the onset of its formation. Subsequently, monomer consumption remained stationary and both molecules disappeared simultaneously in the proportions initially present after the first 30 min. These data reflect a reactivity difference between MP and BM radicals. Once created, the more reactive MP radical reacted to form a network that is richer in MP monomer at the very beginning of copolymerization.

We next sought to determine the effect of the chemical structure of the monomers and radicals in an attempt to explain this hypothesis and confirm reactivity conditions¹². The specific reactivity of a monomer is generally determined by the resonance effect: if the radical resulting from addition of the monomer to the initial radical is strongly stabilized by resonance (for example, as a result of the presence of an aromatic substituent), the monomer will have a high tendency to add to the initial radical and the monomer will be highly reactive. In general, monomers containing conjugated double bonds will be more reactive than non-conjugated monomers.

BM and MP monomers both contain conjugated maleimide double bonds. Conjugation is greater in the case of MP and is delocalized on the entire aromatic ring, since the molecule lacks the $-\text{CH}_2-$ pivot. The presence of the methylene bridge in BM could be responsible for a weakening of electronic delocalization on the aromatic substituents, since delocalization does not occur over the entire molecule. In these conditions, MP radicals formed will be stabilized to a greater extent and will thus be more reactive.

Taking into account the interpretation proposed by Varma *et al.*⁶, these electronic effects can be considered differently. The MP molecule contains a single aromatic structure that has little or no effect on the reactive maleimide double bond that retains a relatively neutral character. Once the proportion of BM is increased, i.e. the molecule with the central $-\text{CH}_2-$ pivot, an $+I$ electron donating effect results, that can affect the electron density of the double bond by increasing it. As the proportion of BM in the BM/MP mixture increases, polymerization is initiated at lower cross linking temperatures. Copolymerization now becomes the reaction that takes place in the eutectic mixture, with both monomers being initially in the molten state in a single, perfectly homogeneous phase before reacting. This reaction is facilitated and favoured by electronic effects that go in the same direction, neutral on one hand (MP) and donating on the other (BM).

CONCLUSION

This work has presented results obtained on the reactivity of bismaleimide systems in the molten state. The d.s.c. study of the BM/MP mixture enabled a phase diagram to be prepared, containing a eutectic in which a relationship between the melting and solubility of each constituent, BM and MP, could be described. Using mixtures with well defined compositions, it was possible to considerably reduce the melting points and zones of reactivity of the monomers, which is of genuine interest for managing these systems. Reduction was generally maximal in the eutectic composition, where there was a single melting point and thus a single and perfectly homogeneous liquid phase. In this eutectic phase, monomers BM/MP could combine to form a three-dimensional network by copolymerization. After network formation, MP radicals were stabilized to a greater extent by resonance and so it was the most reactive molecule, at least at the onset of copolymerization.

Classical methods for the solid state physicochemical characterization of these systems, i.e. FTi.r. and ^{13}C CP/MAS n.m.r., did not lead to the precise identification of the chemical microstructure of the network that formed in the eutectic mixture during heat primed copolymerization. Since the crosslinking links created (succinimide $\text{CH}-\text{CH}$) were practically the same, it was not possible to quantify the individual disappearance of MP and BM in the binary mixture. It was, however, possible to determine the overall advancement of the cross-linking reaction in relation to the parameters of time, temperature and concentration of the two monomers.

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