

Influence of steric hindrance on the reactivity and kinetics of molten-state radical polymerization of binary bismaleimide–diamine systems

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Isothermal kinetic results were obtained for reactions between aromatic diamines with variable steric hindrance and two bismaleimide monomers, one with a structure hindered α from the two maleimide functions (BM α) and the other not (BM). In the temperature range 120–200°C it was found that these two reactions competed in the mixtures. It was thus possible to establish an order of molten-state reactivity of the diamines as a function of the steric hindrance of alkyl groups on NH₂ functions in binary systems with monomer BM. At 173°C, increasing hindrance on the diamine reduced the extent of the addition reaction and favoured the homopolymerization reaction of BM in the molten state. The same result was obtained in the hindered BMI–non-hindered diamine system. Because of the coexistence of steric hindrance of alkylated substituents on maleimide double bonds and steric hindrance of the diamine on reactive amine functions, some molten-state reactions are largely disfavoured.
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INTRODUCTION

Requirements of space technology and thermal protection of materials has led to the development of several series of polymers with good stability at high temperature in conditions of continuous service¹. In the field of aeronautics, the polymers most often used to prepare composite parts are based on epoxy resins, but they have limited thermal stability²: 150–180°C depending on the chemical system chosen. Within the past few years, aromatic polyimides have appeared, obtained by polycondensation. The structure of the polymer results from reactions between a diamine and a dianhydride in a polar proton-free solvent such as dimethylformamide or *N*-methylpyrrolidone. Viscous solutions of acid polyamide are obtained that are chemically or thermally transformed to the polyimide^{3–5}. However, these thermostable polymers obtained by condensation are relatively costly to produce and there are process problems related primarily to the elimination of water or volatile matter^{6,7}. During chemical transformation, the release of water or volatiles can in fact create porosity that impairs the mechanical properties and ageing characteristics of the materials.

Among the most widespread cross-linking functions currently used (acetylene, maleimide and nadimides, etc.), maleimide functions have undergone the most rapid development, for several reasons. First, the characteristics of bismaleimide resins (BMI) are intermediate between those of epoxy and nadimide resins (with vitreous transition temperatures $T_g \approx 300^\circ\text{C}$), which permits continuous service at temperatures between 200 and 250°C. These systems also have the dual advantage of polymerizing after

thermal priming without releasing volatiles, which reduces deleterious porosity. In addition, the use of BMI is also favoured by the fact that the products required for the synthesis of precursor monomers of these polymers are accessible and relatively inexpensive. The general synthesis process for BMI derivatives involves reacting aromatic diamines with maleic anhydride to yield initially an acid-amide intermediate, followed by BMI in a second step, having the desired central chemical skeleton. At this time, maleimide functions can undergo a homo- and/or copolymerization resulting from thermal and/or ionizing excitation⁸. In the case of the polymerization of BMI alone after thermal treatment, the cross-linked material is very heat-stable, but its resistance is mediocre because of a high density of cross-linking nodes. In order to improve and increase the stability and flexibility of the network, a comonomer (we will consider only aromatic diamines in this study) is systematically added. The structure of the polymer thus results from reactions of addition and polymerization into higher masses after first obtaining low-molar-mass, soluble and meltable prepolymers which are transformed into a three-dimensional, cross-linked and unmeltable system by a heat treatment. The diamine comonomer, a nucleophilic agent, then reacts on reactive maleimide functions via a Michael addition reaction^{9–11} (Figure 1) at the same time as allowing chain elongation (polyaspartimide) that depends on the stoichiometry chosen. The homopolymerization reaction of residual maleimide groups can then occur by simply raising the temperature.

In-house work at Rhône-Poulenc⁹ has shown that the addition reaction on the maleimide function is in fact thermoreversible. In spite of this, a number of resins involving maleimides are under development. The conclusion drawn from this is that when this type of reaction

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occurs and the resulting chains are embedded in a polydimensional network resulting from the cross-linking of maleimide double bonds, the reverse reactions cannot occur and the thermostability of the cross-linked materials is preserved¹². The resin that forms is initially at least a linear prepolymer having a certain degree of plasticity, which undergoes cross-linking after heat treatment. This chemical transformation sometimes limits the time during which the mixture can be used. In addition, it is important to determine cross-linking kinetics because of the time limits imposed when manipulating.

The aim of the present work was to determine the reactivity of several chain extenders, diamines with an aromatic structure tetra-substituted by different alkyl groups with variable steric hindrance, towards two aromatic bismaleimide monomers, one hindered, the other not. The techniques involved the molten-state kinetics and mechanisms of two reactions characteristic of each of the steps shown in *Figure 1*. It was expected that the results of this study would lead to a better understanding of molten-state mechanisms, in particular, competition between chain elongation and/or cross-linking reactions of the maleimide double bond during hardening of BMI-diamine systems as a function of several factors: stoichiometry of the binary mixtures, reactivity and above all steric hindrance created

by chemical groups as a function of the thermal treatment applied. These parameters could affect either of the two principal reactions or even both at the same time.

EXPERIMENTAL

Description and origin of products. The BMI-diamine systems studied are shown in *Figures 2 and 3*. In these binary systems, aromatic diamines tetra-substituted by methyl (Me), ethyl (Et) and isopropyl (iPr) groups ortho to the two reactive amine functions are commercially available (Aldrich). In this work with the two bismaleimides (BM and BMEt), they were used directly with no additional purification.

BM was obtained from a commercial batch provided by OUV Chemie Linz, which was used directly in the mixtures after checking purity by chromatography. The second monomer, BMEt, with a hindered chemical structure, was synthesized in the laboratory¹³ with chromatographic purity > 98%.

Experimental techniques

FTi.r. absorption spectroscopy. Spectra were recorded with a Bruker IFS 45 spectrometer in the following conditions: spectral bandwidth 4000–400 cm⁻¹, 32

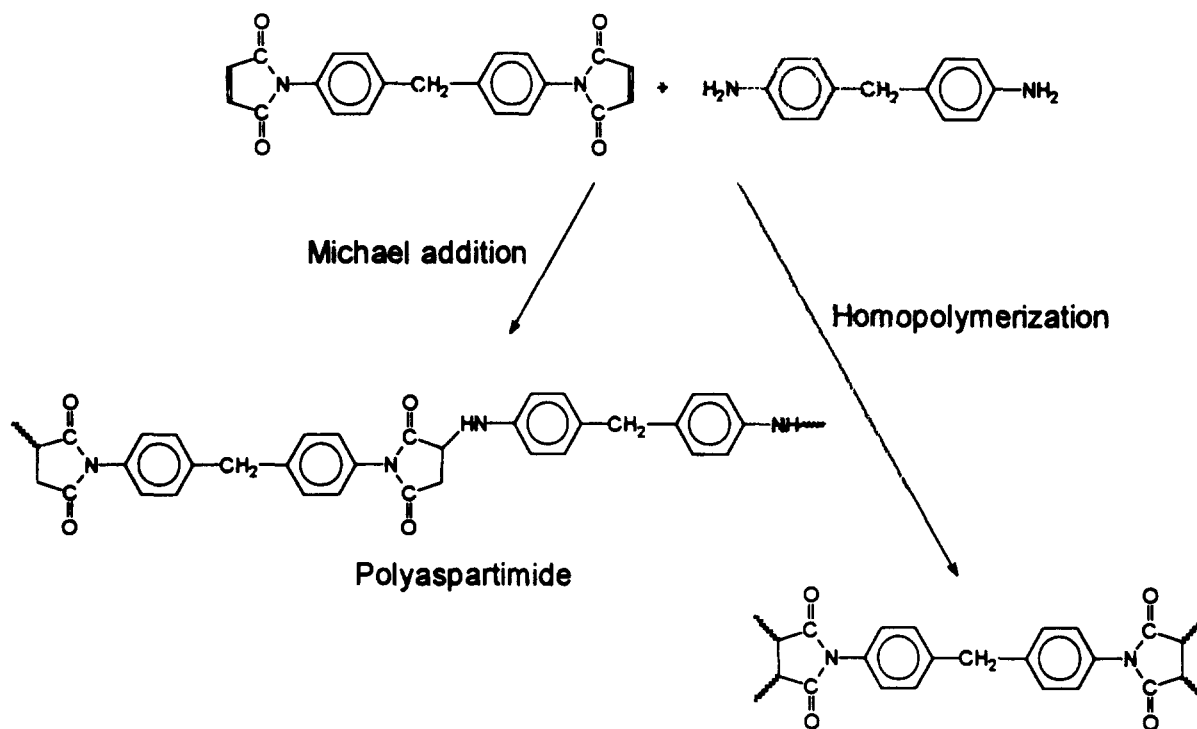


Figure 1 Principal reactions in bismaleimide-aromatic diamine systems

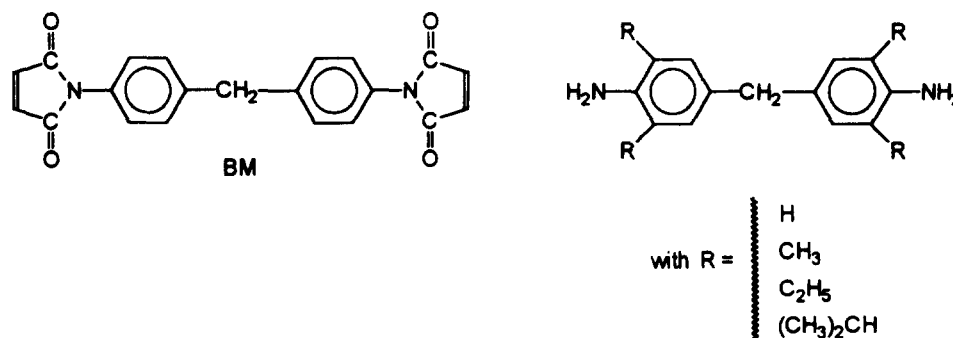


Figure 2 Monomer BM and aromatic tetra-substituted diamine comonomers examined in mixtures

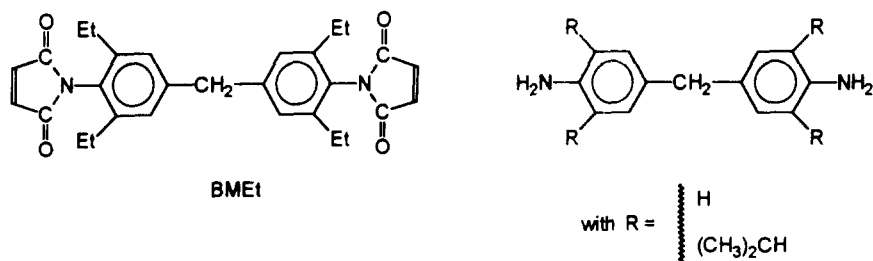


Figure 3 Monomer BMEt and diamine aromatic tetra-substituted comonomers examined in mixtures

accumulations, resolution 2 cm^{-1} , signal processing by triangular apodization. All solid samples were recorded as a potassium bromide pellet.

High-performance liquid chromatography

The chromatographic purity of BM and BMEt monomers was determined from analyses carried out with 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 spectroscopy

High-resolution liquid-state ^1H and ^{13}C n.m.r. spectra were recorded with a Bruker AM 400 spectrometer in the following conditions: pulse angle 90° ($7\ \mu\text{s}$ for ^1H and $4.2\ \mu\text{s}$ for ^{13}C), digital resolution 0.122 Hz/point (^1H) and 0.375 Hz/point (^{13}C) corresponding to a spectral width of 4 kHz (^1H) and 20 kHz (^{13}C) for a memory space of 64 K (^1H) and 128 K (^{13}C). Chemical shifts were calculated with tetramethylsilane (TMS) as internal standard.

Differential scanning calorimetry

D.s.c. diagrams were recorded with a SETARAM DSC 111 G differential calorimeter in conditions of programmed temperature gradient at 5°C min^{-1} for all samples studied.

RESULTS

Physicochemical characterization of diamine comonomers

The skeleton of the diamines (Figures 2 and 3) contained different alkyl R substituents at each position ortho to NH_2 functions, which probably play a dual role in terms of amine reactivity via electronic and steric effects. The steric effect-electronic effect duality described for maleimide functions¹³ remains valid in the case of the diamines studied.

When the electronic factor is considered, it is known that the nucleophilic character of amines increases with the electron-donating effect + I of alkyl groups, which reinforces the basicity of the amine function. This electron-donating effect preferentially enriches the non-bonding doublet on nitrogen by the presence of a higher

electronic density, reflecting higher reactivity. This increased reactivity evidently varies with the electron-donating effect of these R substituents. This was verified by a liquid-state ^1H n.m.r. study (solvent CDCl_3). Table 1 lists the chemical shifts of the amine protons in each structure.

Based on these results, it is seen that if the electron-donating character of the R substituents increases and the inductive effect + I along with it, then there will be an unshielding of the protons on the nitrogen atom. Thus, when hydrogen atoms are considered, slight chemical shifts signify low electronic density. In the case of nitrogen, however, this results in a higher electron density, and thus higher reactivity (Figure 4). Even though this electronic effect favours the reaction, there is another, more important effect that is unfavourable: the steric effect that preferentially orients the diamine towards reduced reactivity¹⁴. It is then expected that the addition reaction giving rise to chain elongation and which results from nucleophilic attack by NH_2 functions on the maleimide double bond will not be favoured, because of strong steric interactions induced by the R groups on these amine functions.

FTi.r. data from Di Giulio *et al.*¹⁵ for diamine DDM (R = H) indicate that several absorption frequencies in the infrared are characteristic of amine functions (NH_2). Figure 5 shows the infrared absorption spectra of the diamines examined, taking into account these attributions. Table 2 lists the principal infrared bands of the NH_2 function in the spectral zone $3500\text{--}1500\text{ cm}^{-1}$. In general, all primary amines are characterized by two valence vibration bands νNH_2 in the spectral range $3500\text{--}3300\text{ cm}^{-1}$ and by one deformation vibration line δNH in the spectral zone of $1650\text{--}1550\text{ cm}^{-1}$.

Reactivity of BM with diamine DDM

The molten-state polymerization of BMI resins with chain extenders is governed by two reactions. The first involves copolymerization of the aromatic diamine with the double bonds of maleimide functions via the Michael addition reaction and the second involves homopolymerization of maleimide functions by a thermally induced radical opening of maleimide double bonds (Figure 1).

As a result of the instantaneous insolubility of products after heat treatment, the molten-state cross-linking kinetics of polymers, i.e. chain extension and cross-linking, can be examined using different solid-state techniques (FTi.r. and/or ^{13}C CP-MAS n.m.r.), since these two reactions are

Table 1 Liquid-state ^1H n.m.r.^a; chemical shifts of NH_2 protons of the amine function in tetra-substituted aromatic diamines

R	Chemical shift (ppm)
H	3.1 ₇
CH_3	3.3 ₇
C_2H_5	3.5 ₀
$(\text{CH}_3)_2\text{CH}$	3.5 ₉

^aSolvent, CDCl_3 ; reference, TMS.

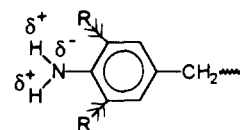


Figure 4 Electron density on the amine function

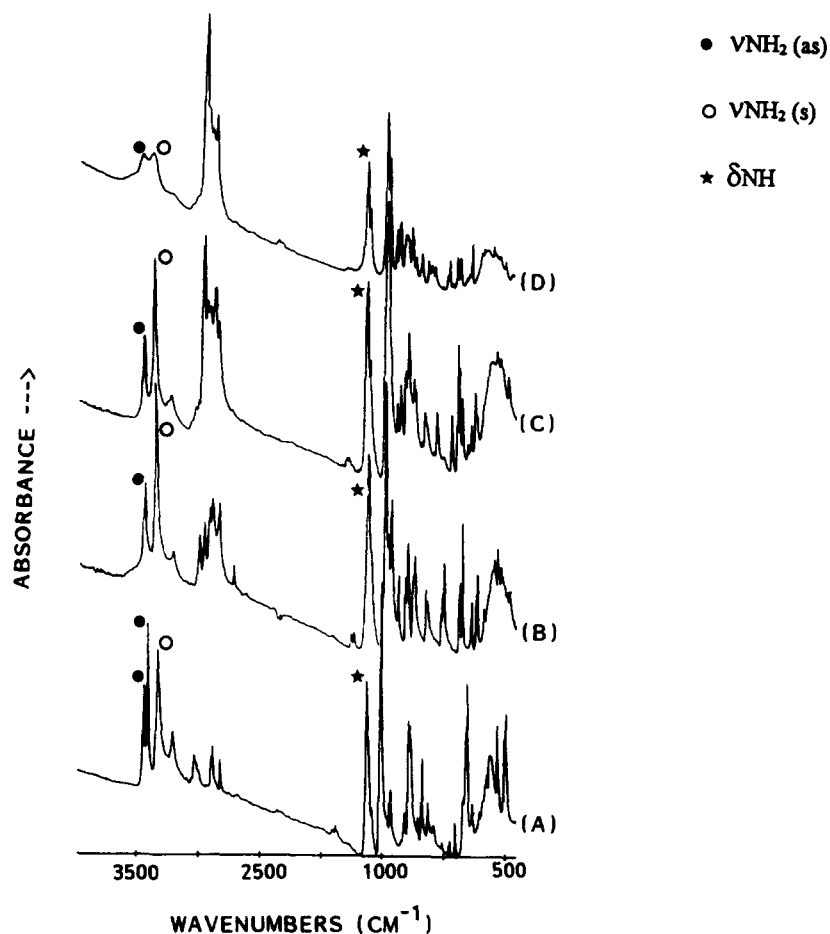


Figure 5 FTIR spectra of aromatic tetra-substituted diamine comonomers: (A) R=H; (B) R=CH₃; (C) R=C₂H₅; (D) R=(CH₃)₂CH

favoured during heat treatment. Published data¹⁵ have shown the advantage of using infrared absorption spectroscopy in the reaction between BM and aromatic diamine DDM.

Using this method, Di Giulio *et al.*¹⁵ followed the cross-linking kinetics of this type of resin by observing the disappearance of bands of νNH_2 functions at 3470 cm^{-1} of those corresponding to maleimide $\nu\text{C-H}$ vibrations at 3100 cm^{-1} , and the reduced intensity of the $\nu\text{C-N-C}$ line of the maleimide function at 1145 cm^{-1} . The intensity of the latter band was proportional to the appearance of the succinimide band around 1190 cm^{-1} . These authors showed that addition of the diamine was rapid and practically total, whereas the polymerization of the maleimide double bond depended essentially on reaction temperature.

Using the same method and the same type of resin, Grenier *et al.*¹⁶ reported that the diamine disappeared more rapidly than bismaleimide in the reaction mixture heated to 150°C . At this temperature, the addition reaction of the diamine on maleimide groups was best monitored with

infrared absorption spectroscopy after measurement of the intensity of vibrations characteristic of the succinimide functions created at 1180 cm^{-1} , and of residual maleimide and primary amines at 1145 cm^{-1} and 3338 cm^{-1} with reference to the standard band of aromatic rings at 1512 cm^{-1} . The results were consistent with expected kinetics, since equilibrium was shifted towards the addition product.

Several authors^{15,16} have thus examined the cross-linking of the binary mixture of BM and aromatic diamine DDM (R=H), with an unhindered structure. It was shown that the Michael reaction occurred in the molten state at temperatures between 120 and 140°C , whereas the homopolymerization of maleimide functions occurred at higher temperatures, $\sim 200^\circ\text{C}$.

These data from the literature were the starting point for the present study on the reactivity of BM with different tetra-substituted diamines. We chose several diamines, all containing electron-donating substituents with variable steric hindrance, located ortho to the two reactive amine functions. This steric effect could have a non-negligible influence on the molten-state behaviour of BMI-diamine binary systems, and on the kinetics of the two principal reactions, addition and homopolymerization.

Thermal studies of binary BM-hindered diamine systems

The d.s.c. study (5°C min^{-1} rise) of monomer BM alone (1:0 ratio) furnished a melting point close to 152°C with a zone of reactivity corresponding to the homopolymerization of maleimide functions that started around 170°C . Similarly, the melting temperatures (T_m) of diamines alone were

Table 2 Tetra-substituted diamine comonomers: infrared vibration frequencies characteristic of the amine function (NH₂)

R	Wavenumber (cm ⁻¹)		
	$\nu_{\text{as}}\text{NH}_2$	$\nu_{\text{s}}\text{NH}_2$	δNH
H	3443 3411	3334	1629
CH ₃	3443	3362	1624
C ₂ H ₅	3443	3362	1623
(CH ₃) ₂ CH	3467	3383	1624

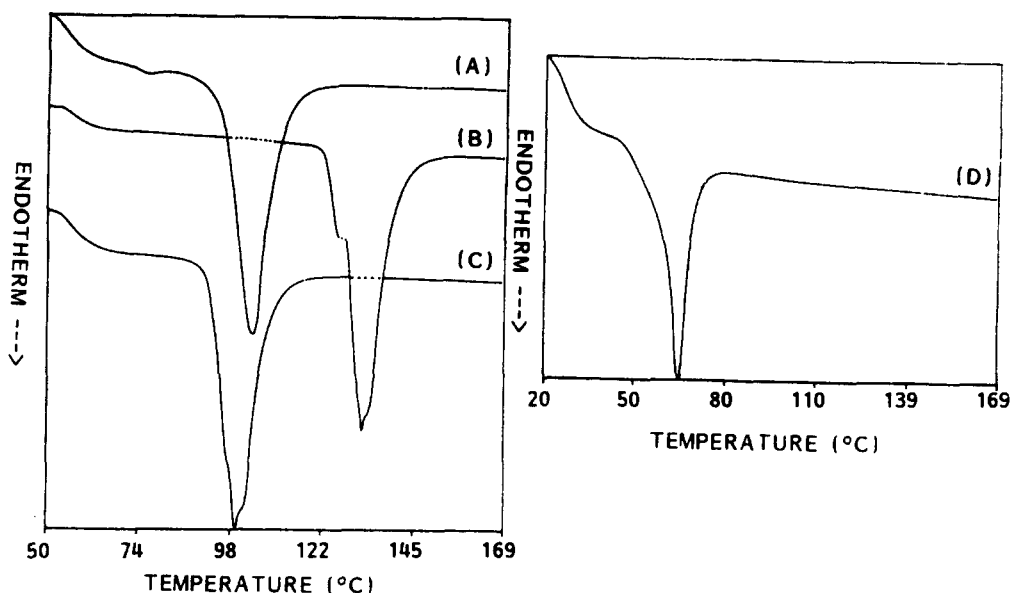


Figure 6 Thermal diagrams of aromatic tetra-substituted diamine comonomers (rise $5^{\circ}\text{C min}^{-1}$): (A)–(D) as in Figure 5

determined by d.s.c. using the same temperature gradient and in the range $50\text{--}170^{\circ}\text{C}$ for tetra-substituted diamines with $\text{R}=\text{H}$, CH_3 and C_2H_5 and in the range $20\text{--}170^{\circ}\text{C}$ for the most sterically hindered diamine, $\text{R}=(\text{CH}_3)_2\text{CH}$ (Figure 6). Based on these data (Table 3), it is seen that the melting temperatures of pure diamines were all lower than that of monomer BM alone. In addition, depending on the chemical structure of the diamine in question, but above all depending on the steric hindrance generated by the alkyl groups, there were disparities in T_m values.

Mixtures prepared with monomer BM and diamines $\text{R}=\text{H}$, CH_3 , C_2H_5 or $(\text{CH}_3)_2\text{CH}$ are denoted BM–RH, BM–RMe, BM–REt and BM–RiPr respectively in this paper. The mixtures were prepared by simple mechanical grinding (mortar and pestle) of BM at room temperature with the different diamines at BMI:diamine stoichiometric ratios of 1:1 and 1.5:1, i.e. an equimolar mixture and one with an excess of maleimide double bonds. All samples were homogeneous powders which could be easily analysed by d.s.c.

The d.s.c. diagram of BM alone in each case led to the determination of the effect of adding amines on the zones of melting and reactivity of the systems. Thus the differential enthalpic analysis study of all the binary systems (Figure 7) under the same temperature gradient conditions ($5^{\circ}\text{C min}^{-1}$) showed in all cases that the effect of the diamine in the medium was to decrease significantly both the melting point of monomer BM and that of each amine. This result can be directly correlated with published data^{17,18} on eutectic mixtures of bismaleimide monomers. In the case of BMI–diamine systems, we have a binary mixture in which the melting point of one constituent (diamine) is much lower than that of the other (BM). Thus, when the proportion of the compound with the lower melting point (diamine) increases in the mixture, the melting point of BM is substantially reduced. In the special case of the BM–RH system at equimolar ratio (1:1), melting even became homogeneous and unique for a decrease of $> 70^{\circ}\text{C}$.

Table 3 Melting temperatures of tetra-substituted aromatic diamines

R	H	CH_3	C_2H_5	$(\text{CH}_3)_2\text{CH}$
T_m ($^{\circ}\text{C}$)	92	123	92	50

Considering the diagrams in Figure 7d pertaining to the (1.5:1) and (1:1) BM–RiPr mixtures, the range used for the thermal study started at room temperature (20°C). This slight difference from all the other systems arose from the fact that the hindered aromatic diamine $\text{R}=(\text{CH}_3)_2\text{CH}$ before mixing has a very low melting point, $\sim 50^{\circ}\text{C}$ (Table 3). Above the T_m temperatures of the two compounds, an exotherm started at different temperatures (T_o) depending on the concentration and the skeleton of the aromatic diamine. This exotherm was reduced only in the case of the BM–RH system, i.e. when the diamine DDM with unhindered chemical structure was used. In the case of other systems using tetra-substituted diamines, zones of reactivity were observed at temperatures much higher than the cross-linking temperature of BM alone. Table 4 lists all thermodynamic data obtained, leading to a better understanding of the results by comparison, characterized by melting temperature (T_m), exotherm onset temperature (T_o) and exotherm peak temperature (T_{exo}). These values are not rigorous, since the tangent plot is difficult to evaluate in all cases, but the thermal data nevertheless enable a number of comments to be formulated.

First, in the case of all binary mixtures, the effect of adding the diamine comonomer resulted in the appearance of two melting endotherms (denoted T_{m1} and T_{m2} in Table 4) except for BM–RH (1:1), the only system in which melting remained perfectly homogeneous. At each stoichiometry considered, the first endotherm consistently remained around $73\text{--}74^{\circ}\text{C}$ for the BM–RH system, $97\text{--}99^{\circ}\text{C}$ for BM–RMe, $82\text{--}85^{\circ}\text{C}$ for BM–REt and $26\text{--}29^{\circ}\text{C}$ for BM–RiPr. The temperatures noted thus remained independent of the mixture ratio. Considering results obtained in the study of mixtures of two bismaleimide monomers¹⁷, this initial endotherm could correspond to the melting of a eutectic characteristic of each system. The melting point of the eutectic mixture would logically be lower than that of the most meltable compound (the diamine in all cases). In addition, and referring to that work¹⁷, the eutectic would be composed of the binary solution, i.e. a portion of the bismaleimide with the diamine, both in the molten state in an initial homogeneous liquid phase. The second melting point would correspond to BM, the compound with the higher melting point. Because of this, the addition of the

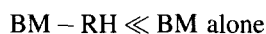
Table 4 BM-diamine systems: d.s.c. thermal characteristics^a

System	BM: diamine ratio	T_m (°C)		T_o (°C)	T_{exo} (°C)
		T_{m1}	T_{m2}		
Pure BM	1:0	152	—	178	214
Pure RH	0:1	92	—	—	—
BM-RH	1:1	73	/	126	170
	1.5:1	74	113	141	182
Pure RMe	0:1	123	—	—	—
BM-RMe	1:1	97	^b	180	229
	1.5:1	99	131	180	226
Pure REt	0:1	92	—	—	—
BM-REt	1:1	85	121	185	261
	1.5:1	82	124	186	258
Pure RiPr	0:1	50	—	—	—
BM-RiPr	1:1	29	127	189	261
	1.5:1	26	133	193	249

^a Rise 5°C min⁻¹^b Shoulder

comonomer to the medium would lower the second melting point in all binary mixtures in comparison with the melting of pure BM (152°C). This is of practical interest for utilization, since there is a 20°C gain in temperature in all cases.

Considerable differences were observed in the reaction onset temperatures (T_o) as a function of the system and at both molar ratios (1:1 and 1.5:1). All the systems can thus be arranged in the following order of increasing T_o :



Reaction onset temperatures (T_o) increased as the steric hindrance created by R groups in proximity to terminal reactive NH₂ functions became large. Nevertheless, the differences were in the temperature range 180–200°C with hindered diamine-based systems, a temperature zone in which bismaleimide (BM) can also react with itself by cross-linking double bonds. Monitoring of the kinetics of BM alone by infrared absorption spectroscopy showed that after 6.5 h at 173°C (Figure 8), more than half the maleimide functions had disappeared. If only BM reacted in this temperature interval, it is probable that the two principal reactions of addition and homopolymerization competed in the BM-hindered diamine reaction mixtures.

Whereas the exotherm was symmetrical for pure BM (Figure 7), those in hindered diamine-based systems were binodal with a wide range of reactivity. The study of these mixtures at different stoichiometries revealed binodal polymerization exotherms with different T_o and broad temperature ranges, which would tend to indicate that the two principal reactions expected from these systems occurred at different temperatures. Thus, it is interesting to utilize the diagrams (Figure 7) to determine the temperature ranges in which these two reactions occurred. The reaction exotherm of the BM-RH system effectively started well before the polymerization exotherm of BM alone, showing that the Michael addition reaction occurred at low temperatures, i.e. 120–140°C (Table 4). This result is consistent with published data^{16,19}. In the BM-RMe system however, the exothermic signal was symmetrical with a slight shoulder starting at higher temperatures, around

180°C in the zone of maleimide bond opening. This shows that the addition reaction probably occurred at the same time as the cross-linking reaction of maleimide functions.

In the other two systems investigated, BM-REt and BM-RiPr, the exothermal signals were unsymmetrical and began in the zone of reactivity of the BM group alone. This is consistent with the maleimide cross-linking reaction occurring first and then, as the temperature increased, the addition reaction becoming favoured. This hypothesis was confirmed by the thermal study of the BM-REt (1:1) mixture. Infrared spectral data on the product polymerized after heat treatment in the temperature range 50–350°C (rise 5°C min⁻¹) indicate the practically total disappearance of the lines of maleimide double bonds in BM and the persistence of the δNH band at 1623 cm⁻¹, characteristic of residual NH₂ in unreacted diamine $\text{R} \rightleftharpoons \text{C}_2\text{H}_5$. The cross-linking reaction of BM thus predominated at the beginning of the exotherm.

In addition, a third reaction, described by Varma and Tiwari²⁰, may occur in the reaction mixture. In the course of chain elongation reactions, a secondary diamine group is created which, in the presence of excess BMI and/or free BMI as yet unreacted, could again participate in a new nucleophilic addition with the maleimide double bond, leading to the formation of a cross-linked product (Figure 9). This reaction would be situated in the zone of reactivity of maleimide functions.

If we consider all the reactions possible between a bismaleimide and an aromatic diamine with the chemical structures shown in Figure 9, it is seen that two other parasitic reactions (aminolysis and cross-linking reaction on the secondary amine) may occur in parallel. They are responsible for the consumption of bismaleimide, with the concomitant formation of small proportions of side-products in the medium^{10,19,21,22}.

In conclusion, the differential enthalpic analysis of binary mixtures of BM and diamines provides valuable results on the melting temperatures and zones of reactivity of each system. First, it is the diamine comonomers that have the lowest melting points. As a result, the addition of the comonomer to the medium will result in the immediate general reduction of melting temperatures, the first in all cases remaining lower than melting of the diamine alone

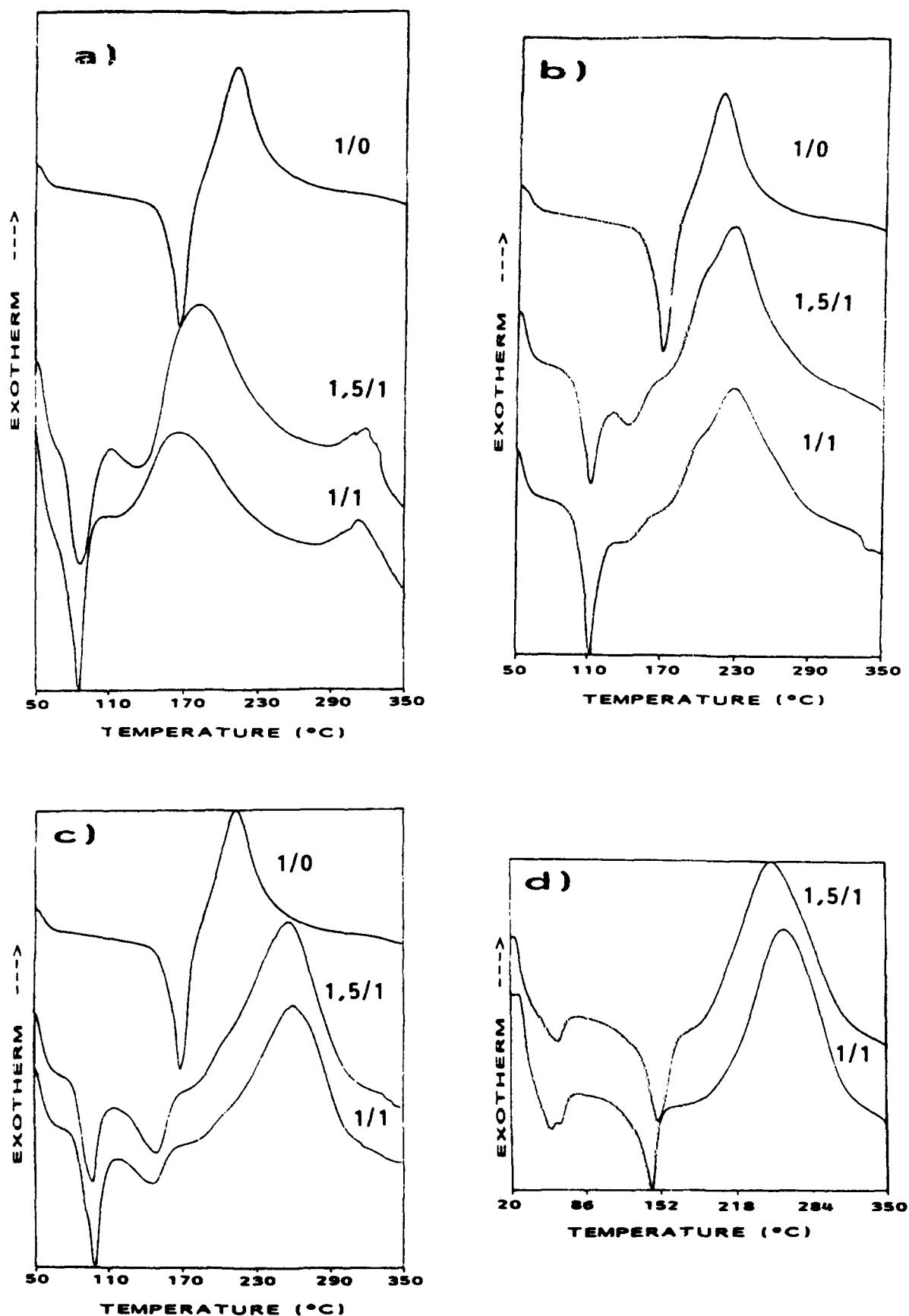


Figure 7 Thermal diagrams of binary systems at different stoichiometric ratios (rise $5^{\circ}\text{C min}^{-1}$): (a) BM-RH; (b) BM-RMe; (c) BM-REt; (d) BM-RiPr

(the most meltable compound) and the second much lower than that of the bismaleimide monomer alone. Furthermore, mixing these two chemical entities causes a variation in the temperatures of polymerization onset (T_o) and of the

exotherm peak (T_{exo}). These variations thus depend on the comonomer used, in particular on steric hindrance caused by R alkyl groups ortho to reactive amine functions. When there is no hindrance ($R \rightleftharpoons H$), the zones of reactivity are

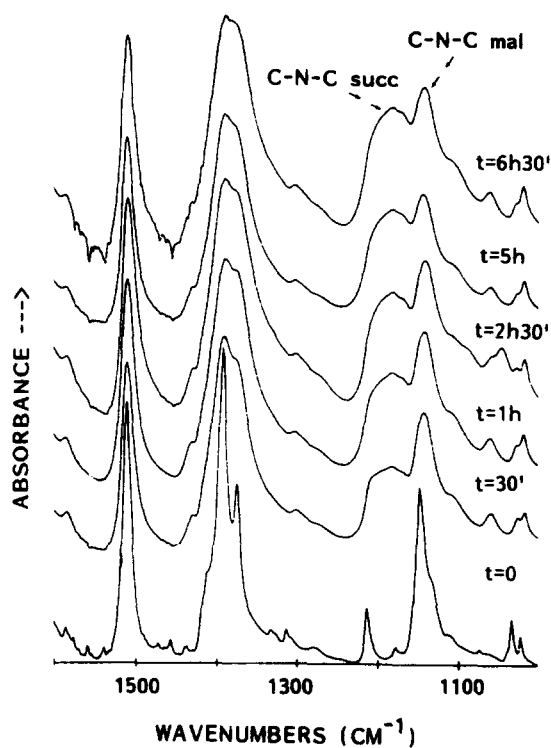


Figure 8 FTi.r. monitoring of cross-linking of BM alone at 173°C

reduced in comparison with the reactivity of the bismaleimide compound alone. These data are consistent with published results^{16,19} indicating that the addition reaction occurs at low temperatures (130–150°C) and that homopolymerization reactions are initiated at higher temperatures. When steric hindrance increases, on the other hand, d.s.c. shows the occurrence of the reverse phenomenon, i.e. T_0 and T_{exo} are shifted to higher values. This shift to higher temperatures is proportional to the volume occupied by the alkyl substituents. The T_0 values observed are then in the region of 180–193°C (Table 4). At these temperatures, the bismaleimide monomer (BM) can also react with itself by homopolymerization: the two principal reactions described above (addition and homopolymerization) probably compete.

FTi.r. study of the reaction medium of BM-hindered diamine systems

As an indication, the infrared absorption spectrum from the thermal study of three systems at 173°C, i.e. BM-RMe (1:1), BM-REt (1:1) and BM-RiPr (1.5:1) are shown in Figures 10–12. The FTi.r. spectra of the binary systems thus confirm that the addition of the primary amine by nucleophilic attack of NH_2 functions on the BMI double bond indeed occurred, with the formation of the addition product in the mixtures. During each thermal treatment, the different νNH_2 bands disappeared (see Table 2) and there

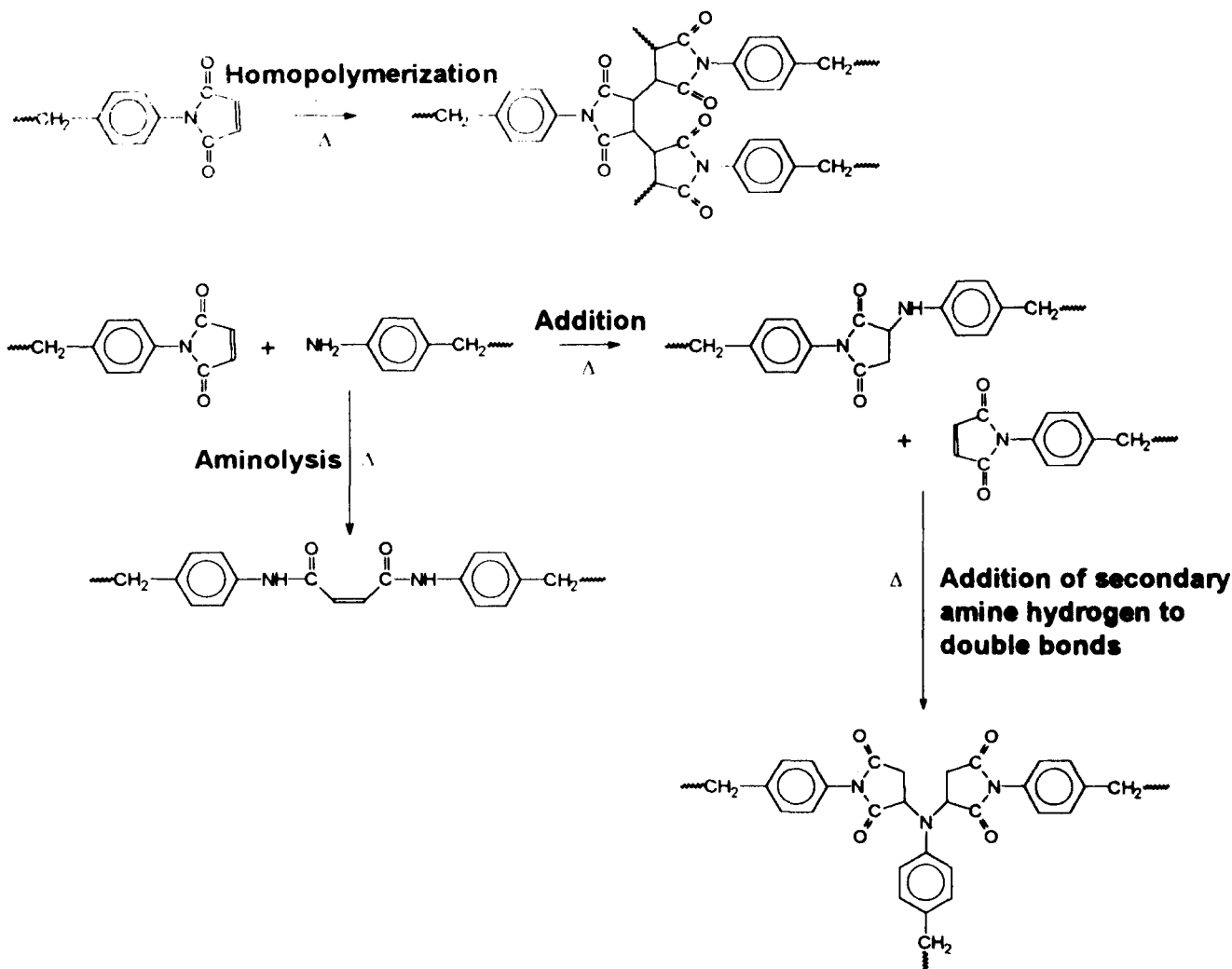


Figure 9 Overall reaction path (reactions and secondary reactions) in bismaleimide–aromatic diamine systems

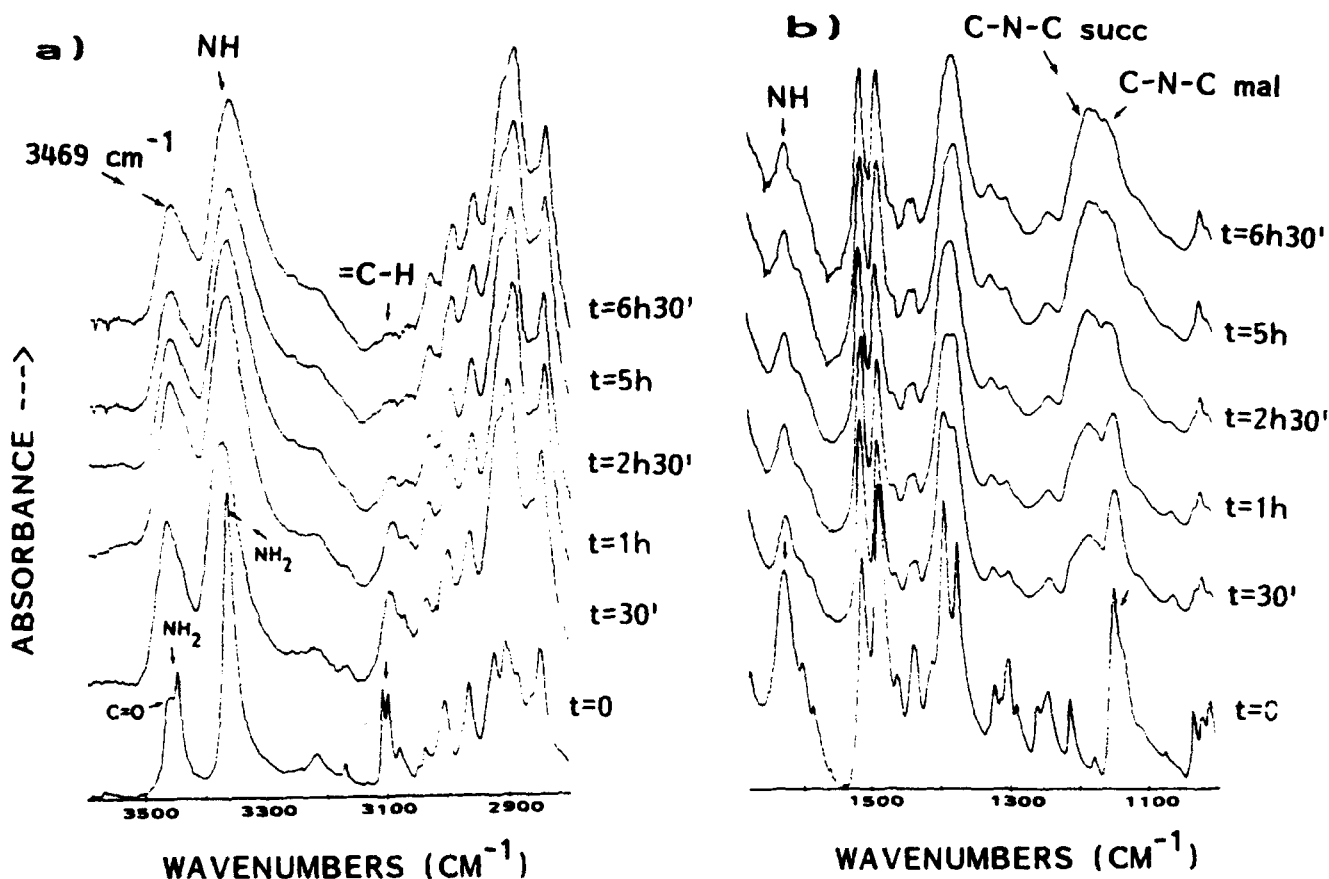


Figure 10 FTIR spectra of the BM-RMe (1:1) system after isothermal treatment at 173°C: (a) 3600–2800 cm^{-1} ; (b) 1700–1000 cm^{-1}

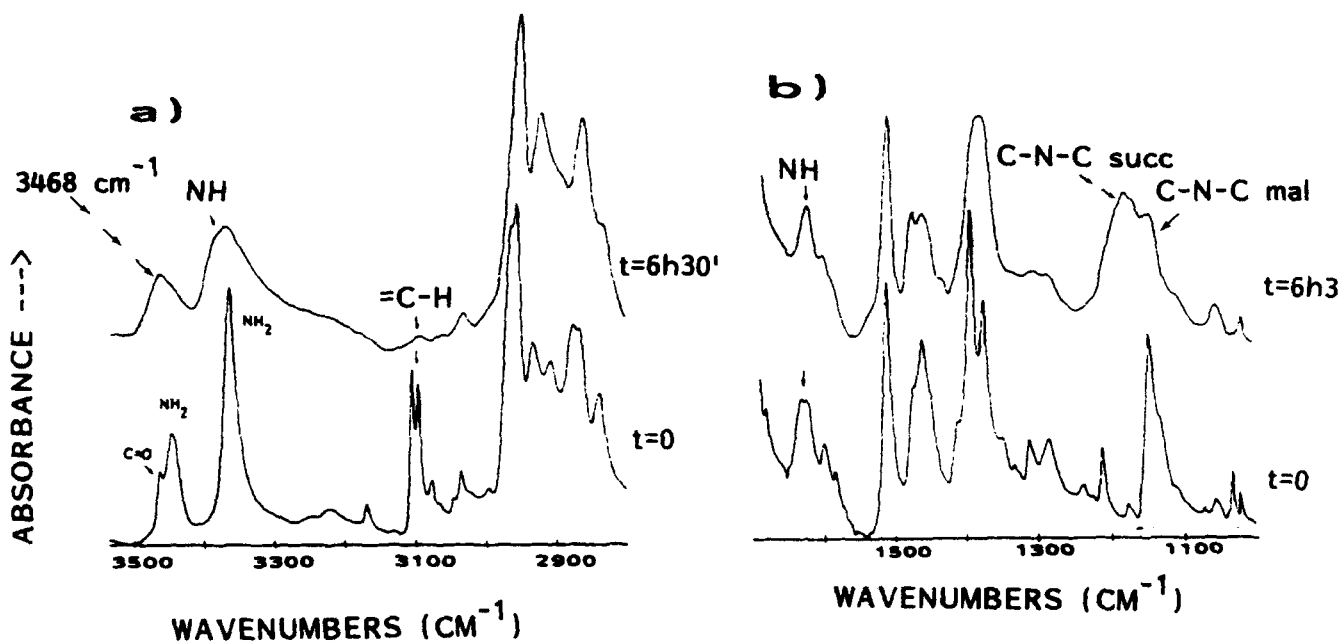


Figure 11 FTIR spectra of the BM-REt (1:1) system after isothermal treatment at 173°C: (a), (b) as in Figure 10

was a decrease in the intensity of the δNH band between 1650 and 1600 cm^{-1} , depending on the primary diamine in question. The maleimide double bond with $\nu\text{C}=\text{H}$ bands at 3100 cm^{-1} and $\nu\text{C}-\text{N}-\text{C}$ at 1150 cm^{-1} also disappeared during polymerization. There was a simultaneous increase in the intensity of peaks corresponding to the formation of the addition product in the mixtures, in particular with the appearance of two new NH bands in the three systems, at:

- 3469 and 3374 cm^{-1} for the BM-RMe system (Figure 10)
- 3468 and 3388 cm^{-1} for the BM-REt system (Figure 11)
- 3472 and 3394 cm^{-1} for the BM-RiPr system (Figure 12). In the third of these it was the most difficult to determine precisely the exact position of the two bands, because of the linewidth at half-height. But based on published data^{10,15}, a single NH band characterizes the presence of a secondary amine in the mixture, in the region 3500–3300 cm^{-1} . A second band may sometimes

appear at lower frequencies²³ when high concentrations of diamine are present, as a result of intramolecular hydrogen bonds (associated NH). In these systems however, the two lines had a broad envelope that also encompassed the NH₂ bands of primary diamines that had not reacted during the thermal treatment. To explain the presence of the highest frequency (3469, 3468 and 3472 cm⁻¹ for the BM-RMe, BM-REt and BM-RiPr systems respectively), another hypothesis is tenable: it could also envelop the νC=O harmonic signal characteristic of residual bismaleimide and of the prepolymer formed in the molten medium, based on published results¹⁵. In the 1700–1000 cm⁻¹ zone of each FTi.r. spectrum, there was a new broad νC–N–C succinimide band (νC–N–C succ) around 1180 cm⁻¹ and characteristic not only of the addition product formed but also of the three-dimensional network created during the homopolymerization of maleimide functions²⁴. In the BM-RMe (1:1) system (Figure 10), the reaction of maleimide BM was practically complete after 6.5 h of treatment at

173°C, whereas in the other two systems (Figures 11 and 12) at the same temperature there was slightly more residual maleimide.

FTi.r. kinetics of BM-hindered diamine systems

The BMI-hindered diamine systems were followed at 1:1 and 1.5:1 stoichiometries for 7 h at 173°C. Based on the above results, the two principal reactions, Michael addition by chain elongation and homopolymerization of maleimide functions of monomer BM would occur preferentially at this temperature. The kinetics were followed with FTi.r. by measuring the relative intensity of bands characteristic of maleimide νC–N–C (1149 cm⁻¹) and amine δNH functions (1629 to 1624 cm⁻¹, depending on the substitution on the aromatic ring of the diamine). These two lines accounted for the disappearance of one or other of the molecules in the reaction mixture with reference to a standard band unaffected by the reaction process, at 1511 cm⁻¹: vibration of aromatic rings which remained constant throughout the process, as indicated elsewhere²⁴.

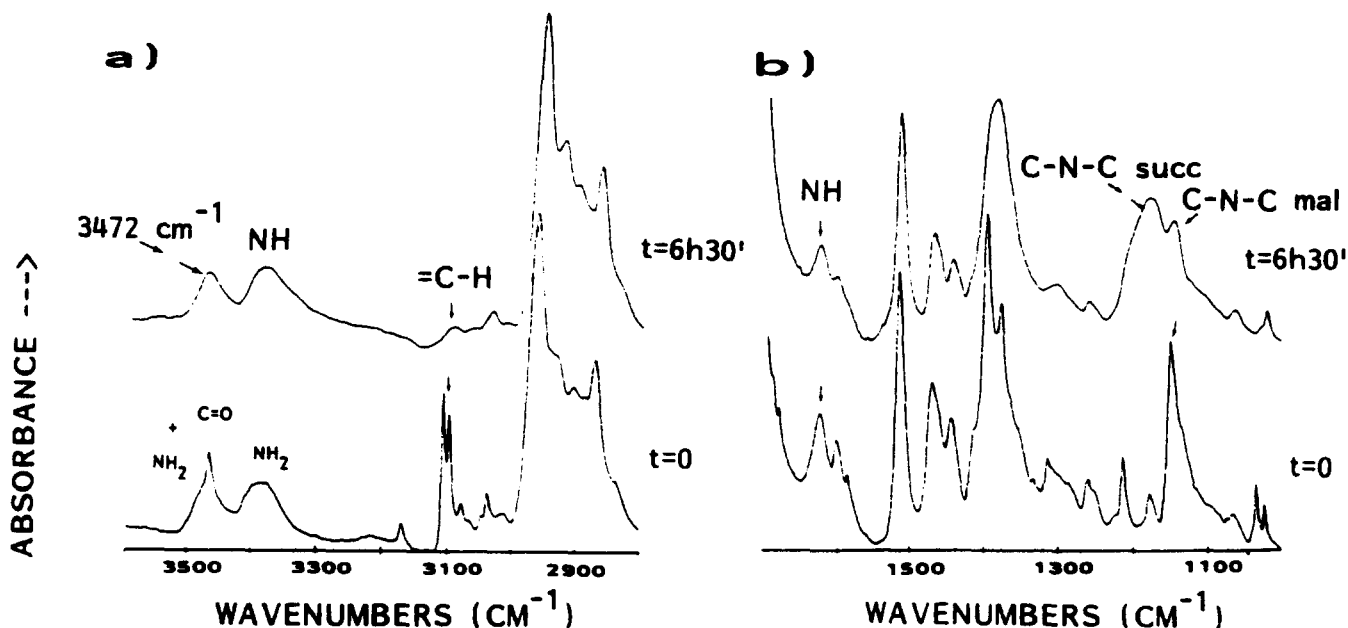


Figure 12 FTi.r. spectra of the BM-RiPr (1.5:1) system after isothermal treatment at 173°C: (a), (b) as in Figure 10

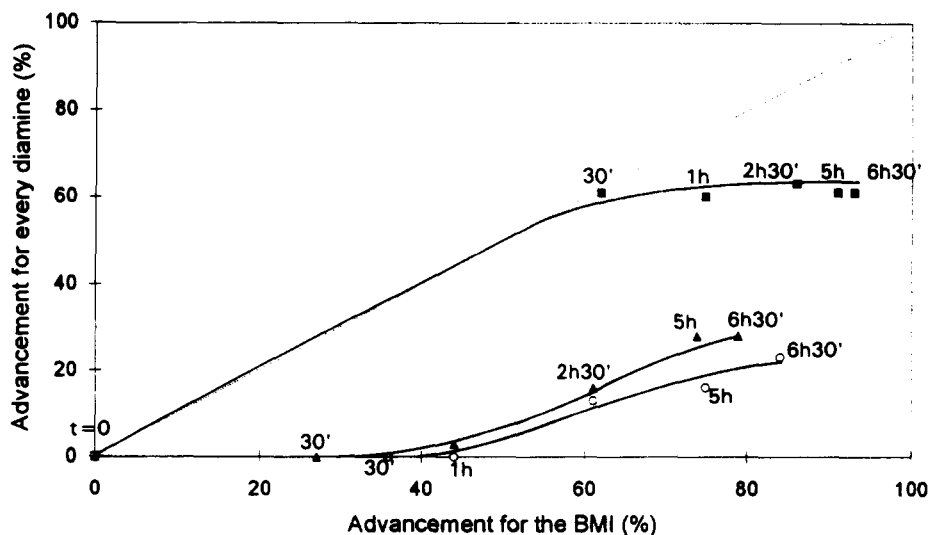


Figure 13 Representative curves of the advancement of monomer BM and different diamine comonomers in binary BM-hindered diamine (1:1) systems (T = 173°C): ■, BM-RMe; ○, BM-REt; △, BM-RiPr

At 173°C, the curves resulting from the simultaneous disappearance of the two compounds from the reaction mixture of each system are shown in Figures 13 and 14 for the 1:1 and 1.5:1 stoichiometries respectively. In each curve, the percentage advancement of BM is on the x-axis and that of diamines on the y-axis. Times of exposure to heat in isothermal conditions (30 min, 1 h, 2 h 30 min, 5 h or 6 h 30 min) are given above or below the points representing the states of advancement of the two compounds in the reaction media of the three binary systems.

The results (Figure 13) show that the disappearance of bismaleimide monomer (BM) occurred simultaneously with that of the diamine R=CH₃ in the binary mixture during the first half-hour. Consumption of the amine after that time remained unchanged, while the disappearance of BM continued. This dual advancement pattern confirms the competition between the two molten-state reactions. Initially, the addition reaction predominated in the mixture and then abruptly ceased, to the benefit of the polymerization of BMI alone.

In addition, when hindrance of the amine functions

became greater (BM-REt and BM-RiPr systems), the kinetics were considerably different from those of the preceding system. This is not surprising, in view of the steric effect which decreases the molten-state reactivity of the diamine. During the initial moments of the heat treatment at 173°C, the two diamines tetra-substituted with ethyl and isopropyl groups lost reactivity, and were totally devoid of reactivity during the first hour. The maleimide double bonds of BM on the other hand disappeared rapidly due to the homopolymerization reaction. After this and at a given level of conversion to BMI, the most sterically hindered diamines again disappeared, but to only a very slight extent (residual diamine content $\geq 70\%$ in both cases after 7 h of heat treatment).

These data were confirmed by the results obtained for systems with excess BMI (1.5:1) (Figure 14): BM disappeared from the molten binary mixture regardless of hindrance on the diamine, indicating that the homopolymerization reaction of BM competed with the addition reaction at this temperature.

The percentage of residual maleimide functions was

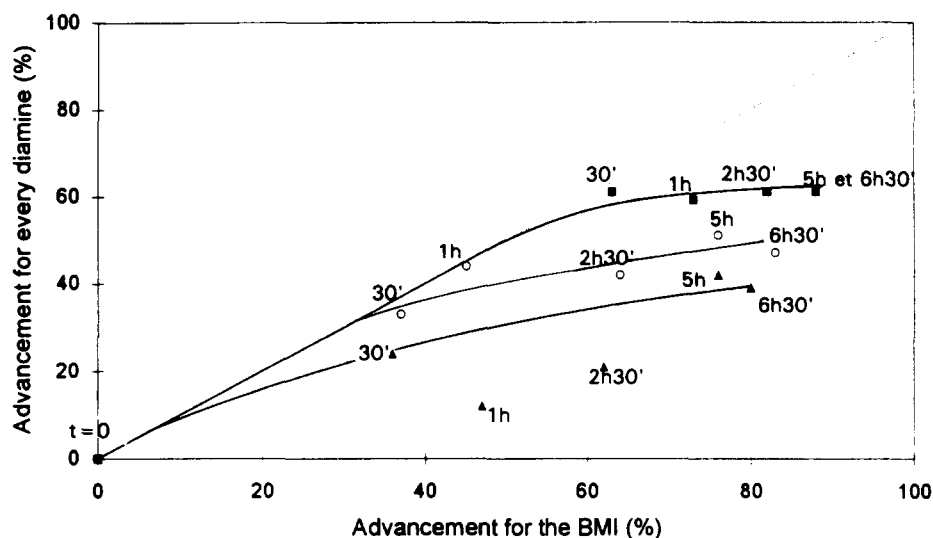


Figure 14 Representative curves of the advancement of monomer BM and different diamine comonomers in binary BM-hindered diamine (1.5:1) systems ($T = 173^\circ\text{C}$). Symbols as in Figure 13

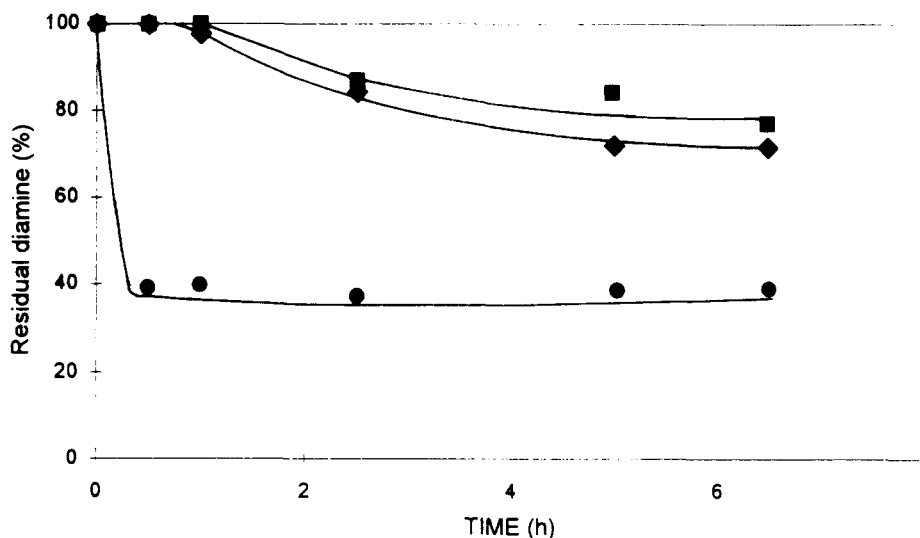


Figure 15 FTIR kinetics of the disappearance of diamine comonomers in BM-hindered diamine (1:1) systems: ●, Me; ■, Et; ◆, iPr

relatively low in all the cases studied: after a 6 h isothermal heat treatment at 173°C, it was < 30%. This is consistent with kinetic data on the cross-linking of BM alone at the same temperature for > 6 h and where there was ~40% residue at the end of reaction (Figure 8). Of course, steric hindrance of NH₂ functions decreased amine reactivity by slowing addition of the comonomer at BMI double bonds.

For a clearer comparison of the results obtained with the three systems at the two stoichiometries used, and after heat treatment at 173°C, the disappearance of the different diamine comonomers with time is shown in Figures 15 and 16 and the disappearance of bismaleimide monomer (BM) is shown in Figures 17 and 18. The kinetic curves (Figures 15 and 16) clearly show that the reactivity of diamines depended on the steric hindrance created by R substituents on amine functions. The decreasing reactivity of the diamines is logically R=CH₃ > C₂H₅ > (CH₃)₂CH. Thus, in the case of low hindrance (R=Me), reactivity was high and when hindrance was more voluminous (R=Et and iPr), reactivity which was initially nil began after a lag of > 1 h in the 1:1 systems (Figure 15). This lag period for the most

hindered amines can be correlated with the parallel homopolymerization reaction that always occurred (Figures 17 and 18). This polymerization reaction apparently initiated the addition reaction via a priming phenomenon after a lag, but this remains a hypothesis that could not be confirmed.

In 1.5:1 systems with an excess of maleimide functions (Figure 16), consumption started as early as the onset of heat treatment and comonomer disappearance followed the above logical order of hindrance.

The consumption of monomer BM in the 1:1 and 1.5:1 systems (Figures 17 and 18) varied with the diamine used. BMI disappeared rapidly from the BM-RMe system. When the system included diamines with a greater degree of hindrance (BM-REt and BM-RiPr), however, the kinetics of BMI consumption in the course of the two chemical processes, addition and homopolymerization, were slower. Residual BMI in the latter two systems varied in practically the same manner as a function of time of heat treatment, explaining the two kinetic curves rather than three expected (Figures 17 and 18). Even so, residual maleimide was ~20% after 7 h of isothermal treatment at 173°C. Note that

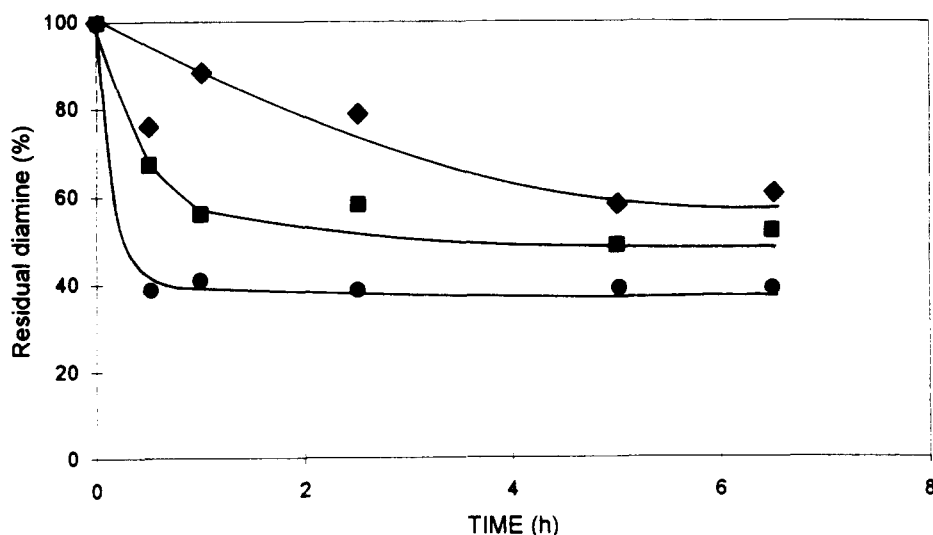


Figure 16 FTi.r. kinetics of the disappearance of diamine comonomers in BM-hindered diamine (1.5:1) systems. Symbols as in Figure 15

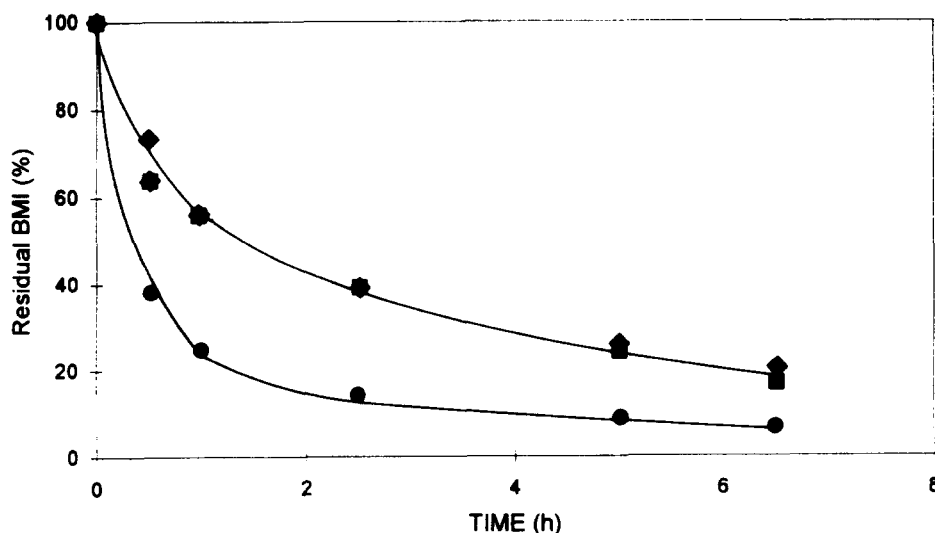


Figure 17 FTi.r. kinetics of the disappearance of monomer BM in BM-hindered diamine (1:1) systems: ●, BM-RMe; ■, BM-REt; ◆, BM-RiPr

the precision of kinetic measurements by infrared absorption spectroscopy is at best 5%.

The thermal study of binary BM-diamine mixtures has shown the importance of the steric hindrance of aromatic diamines in determining the polymerization temperatures of BM-RMe, BM-REt and BM-RiPr systems. In the presence of bismaleimide (BM), the polymerization kinetics of diamines at the temperature selected (173°C) strongly depended on the steric effect caused by R substituents on the amine functions. Based on the infrared spectral results and kinetic studies conducted, there is competition between the principal reactions described above. Depending on the volume occupied by R, ortho to the amine functions, the kinetics are quite different in terms of the disappearance of the monomer and comonomer. Overall, the order of decreasing reactivity of the diamines is logically $R=CH_3 > C_2H_5 > (CH_3)_2CH$.

In all the cases, the percentage of residual diamine

remained high, whereas that of residual BM was relatively low at the end of kinetic monitoring (7 h), indicating that the largely predominant homopolymerization reaction occurred simultaneously in the mixtures containing hindered diamines.

Study of BMEt-diamine binary systems

This is complementary to the above, in that the BMI-diamine binary systems used were composed of a bismaleimide with a hindered chemical skeleton ($R=C_2H_5$) and one of two primary aromatic diamines, one hindered, $R=(CH_3)_2CH$, the other with no substituent on the aromatic ring (DDM with $R=H$). Each R group is α from the reactive functions, either maleimide or amine (Figure 3).

In view of the preceding data, the steric hindrance caused by the R substituents should play a major role by reducing diamine reactivity in these systems. In addition, it was of interest to determine if substitution on BMI would prevent

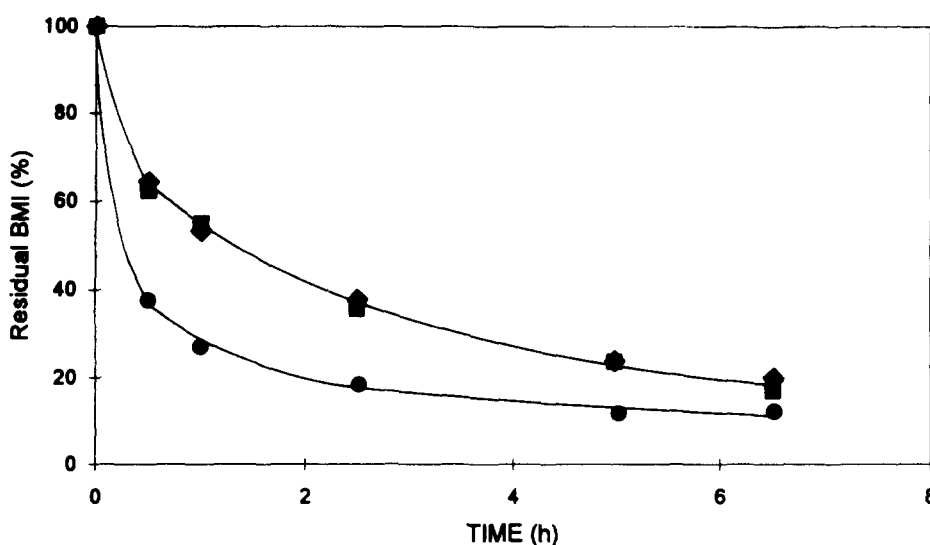


Figure 18 FTIR kinetics of the disappearance of monomer BM in BM-hindered diamine (1.5:1) systems. Symbols as in Figure 17

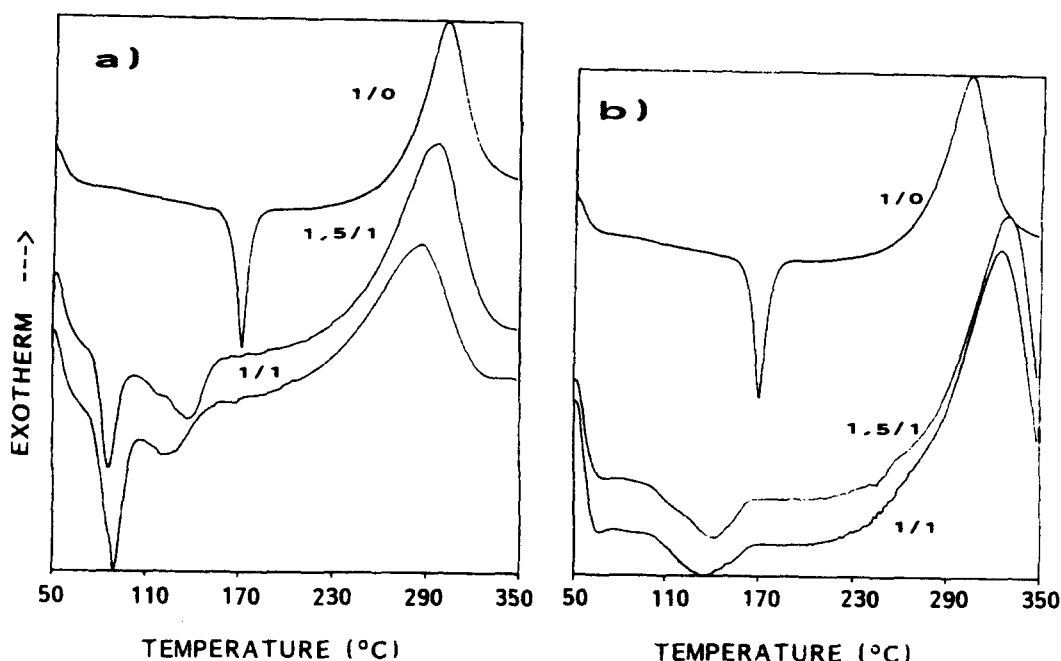


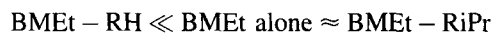
Figure 19 Thermal diagrams of binary systems at different stoichiometric ratios (rise 5°C min⁻¹): (a) BMEt-RH; (b) BMEt-RiPr

access of the double bonds to the amine functions of the diamine comonomer DDM. The d.s.c. study of BMEt alone and the two diamines alone was carried out using the procedure described for the above systems. The thermal results with pure BMI (1:0) (Figure 19) show that the melting point was $\sim 160^\circ\text{C}$ with temperatures T_o and T_{exo} of 267 and 304°C respectively. Bismaleimide is thus characterized by a broad window of utilization.

In the case of mixtures containing BMEt, the two systems examined were BMEt–RH for the mixture with diamine $\text{R}=\text{H}$, and BMEt–RiPr for that with diamine $\text{R}=(\text{CH}_3)_2\text{CH}$, with BMI–diamine molar ratios of 1:1 and 1.5:1. Each sample was heat-treated as above (Figure 19) and the results are listed in Table 5. In each binary system, there were two endothermic transitions (T_{m1} and T_{m2}). The addition of the diamine to BMEt–RH and BMEt–RiPr mixtures thus led to a considerable reduction in the melting point of both bismaleimide BMEt and the amine. This reduction is a phenomenon specific to binary systems with two different melting points¹⁷, allowing access to mixtures that overall have much lower melting points than that of the monomer or

comonomer. In addition, melting was never unique and the first (T_{m1}) corresponded to that of a eutectic composed of the comonomer with a portion of the monomer BMEt in the liquid state. The second endotherm would correspond to the melting of BMEt, the compound with the higher melting point¹⁷.

It must be remembered that the thermal results (Table 5) obtained by the method of tangents is not rigorous, because the curve is difficult to evaluate on each thermal diagram. There is nevertheless a trend which reinforces the effect of steric hindrance, a consistent factor in this work. The zones of reactivity of systems at the ratios of 1:0, 1:1 and 1.5:1 are characterized by T_o values that increase in the following overall order:



The addition of unhindered diamine thus significantly reduced the reactivity in comparison with pure BMI, whereas the presence of a diamine with a hindered chemical skeleton favoured an increase in the zones of reactivity, which is logical in view of the hindrance of the structures.

Table 5 BMEt–diamine systems: d.s.c. thermal characteristics^a

Systems	BMEt: diamine ratio	T_m ($^\circ\text{C}$)		T_o ($^\circ\text{C}$)	T_{exo} ($^\circ\text{C}$)
		T_{m1}	T_{m2}		
Pure BMEt	1:0	162	—	267	304
pure RH	0:1	92	—	—	—
BMEt–RH	1:1	75	110	213	289
	1.5:1	77	107	232	298
Pure RiPr	0:1	50	—	—	—
BMEt–Ri- Pr	1:1	<i>b</i>	102	259	327
	1.5:1	<i>b</i>	97	269	330

^a Rise 5°C min^{-1} .

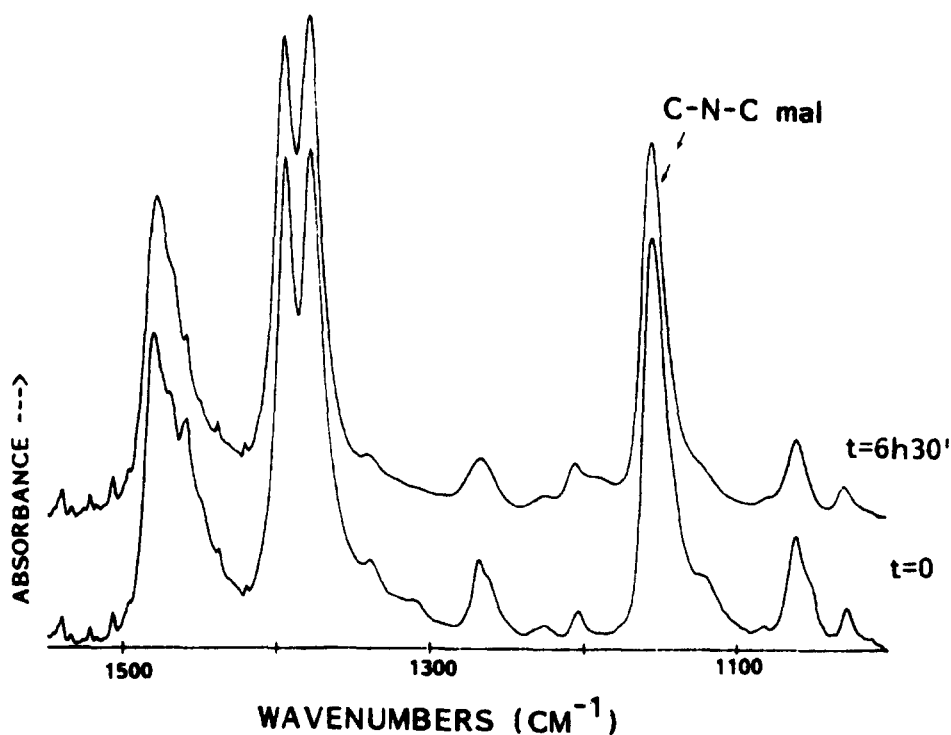


Figure 20 FTIR spectra of the BMEt–RH (1.5:1) system after isothermal treatment at 173°C : (a) $3600\text{--}2800\text{ cm}^{-1}$; (b) $1700\text{--}1000\text{ cm}^{-1}$

The polymerization kinetics expected for these systems (addition and/or homopolymerization) are clearly very different in the molten state, depending on the type of diamine. The reactivity difference between the two diamines was

confirmed by the infrared spectral study of the 1.5:1 BMEt-RH and BMEt-RiPr systems heated at 173°C for several hours (Figures 20 and 21). It was decided to determine whether or not the bismaleimide BMEt alone could

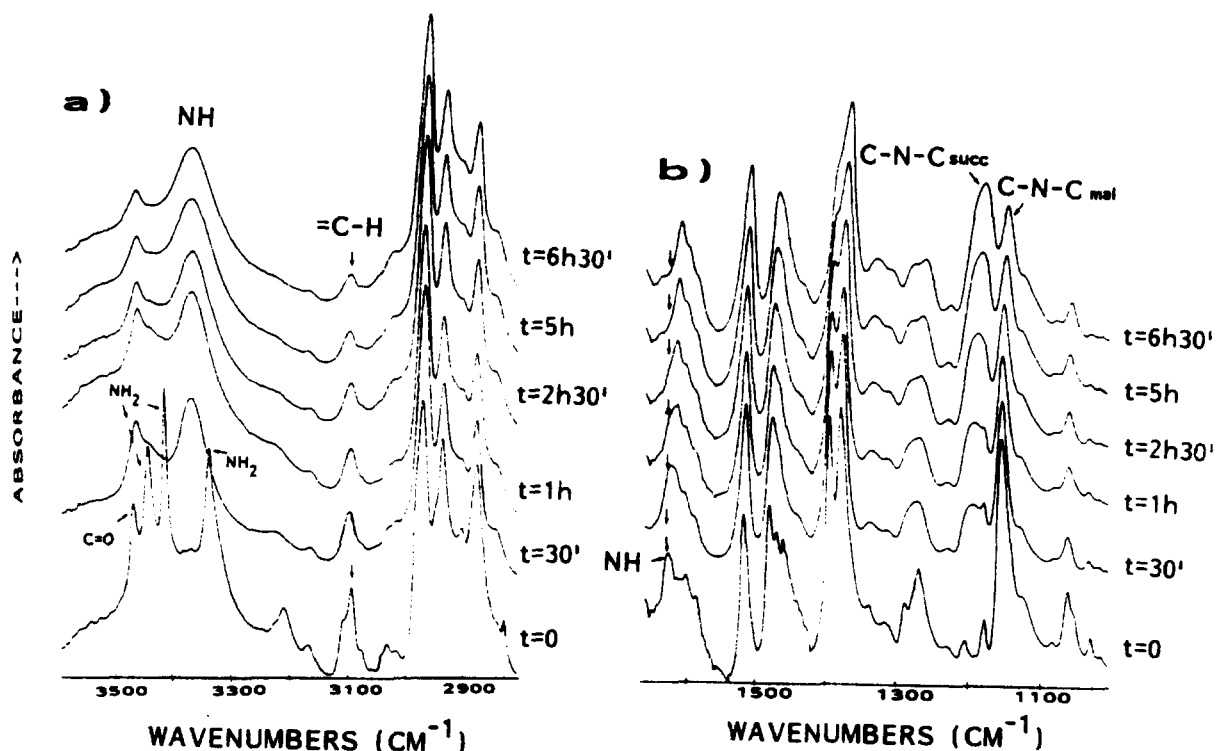


Figure 21 FTIR spectra of the BMEt-RiPr (1.5:1) system after isothermal treatment at 173°C: (a), (b) as in Figure 20

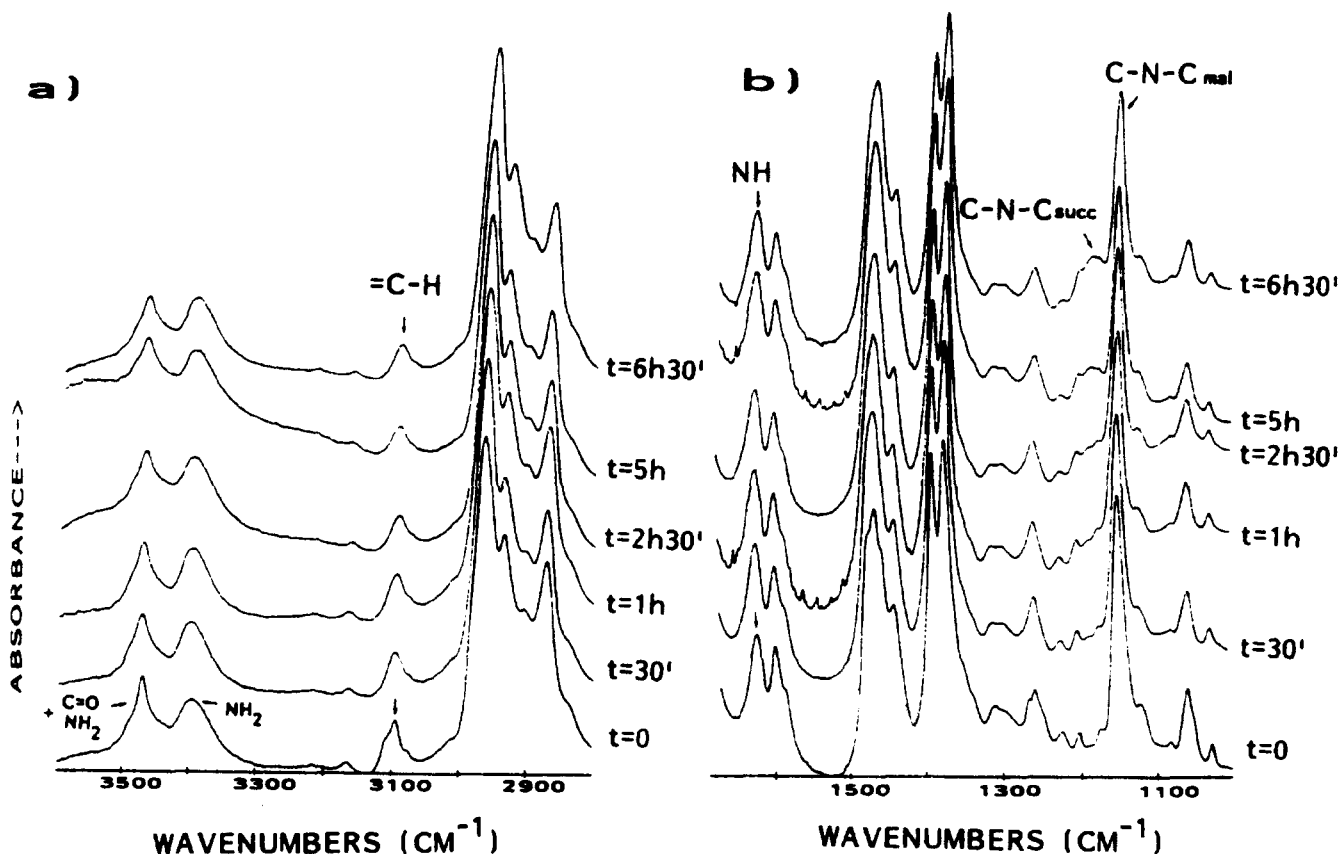


Figure 22 FTIR monitoring of cross-linking of BMEt alone at 173°C: (a), (b) as in Figure 20

react by homopolymerization at this temperature. A response was furnished by the infrared absorption spectrum of pure BMEt recorded after heat treatment at 173°C for > 6 h (Figure 22): there was no change in the intensity of the maleimide $\nu\text{C-N-C}$ band, indicating that the double bond was not reactive at this temperature. If BMI did not react in this temperature range, it is unlikely that this reaction occurred in the binary mixtures studied. On the other hand, it was noted that the Michael reaction occurred in the BMEt-RH system (Figure 20) and that the addition product formed very rapidly in the reaction medium. After 30 min, the NH line appeared at $\sim 3368\text{ cm}^{-1}$, characteristic of a secondary amine, with a concomitant decrease in the intensity of νNH_2 bands ($3334, 3411$ and 3443 cm^{-1}), indicating the consumption of DDM. In the spectral zone $1700\text{--}1000\text{ cm}^{-1}$, disappearance of the amine was also verified by the intensity of the δNH line at 1629 cm^{-1} , which decreased with time. Even so, it was difficult to follow its kinetics since it was not well individualized in the mixture. The disappearance of the maleimide (decreased intensity of $\nu\text{C-N-C}$ mal and $\nu\text{C-H}$ lines) evidently occurred in parallel in the molten BMEt-RH system.

The same heat treatment at 173°C applied to the BMEt-RiPr mixture (Figure 21) showed little or no modification during the first few hours of heating. Thus the intensities of the νNH_2 and δNH bands underwent no variation during heat treatment, even after 6.5 h in isothermal conditions. There was only a very slight decrease in the intensity of the $\nu\text{C-N-C}$ line at 1153 cm^{-1} and of $\nu\text{C-H}$ at $\sim 3095\text{ cm}^{-1}$, characteristic of reactive maleimide functions. This decrease was barely perceptible after 5 h of heat treatment.

These results are important for two reasons:

- the reactions are favoured only when the bismaleimide and aromatic diamine used are both hindered (BMEt-RiPr system);
- the reactions nevertheless occur when hindered BMI is used with an unhindered aromatic diamine (BMEt-RH system).

CONCLUSIONS

This study of binary BMI-diamine systems conducted in the molten state has shown the importance of steric hindrance caused by the aromatic diamine or the bismaleimide in the context of the two principal reactions of addition and homopolymerization expected in these systems. In each mixture studied, the addition of diamine changed the melting points, with a general decrease, the first in all cases remaining lower than that of the diamine alone (the more meltable compound) and the second much lower than that of the pure bismaleimide monomer considered.

Depending on the diamine used, there were changes in the zones of reactivity, which were very strictly dependent on the steric hindrance caused by the alkyl R group α to the

amine functions (NH_2). In BM-based systems, there is a logical order of diamine reactivity as a function of the steric hindrance of the alkyl groups on NH_2 functions. This was established by differential enthalpic analysis and infrared absorption spectroscopy. In addition, at the temperature selected (173°C) and using systems composed of bismaleimide BM with tetra-substituted diamines $\text{R}=\text{CH}_3, \text{C}_2\text{H}_5, (\text{CH}_3)_2\text{CH}$, infrared spectral kinetics showed that the two principal reactions of the bismaleimide groups, chain elongation and homopolymerization, competed. As the steric effect of the diamine increased, the addition reaction tended to occur to a lesser extent, favouring the homopolymerization reaction of BM in the molten medium.

The logic of steric hindrance is also obeyed in the case of hindered BMI (BMEt) with two diamines, one unhindered ($\text{R}=\text{H}$) and one having an excessive steric effect [$\text{R}=(\text{CH}_3)_2\text{CH}$]. Because of the dual existence of steric hindrance of alkyl substituents of BMI on maleimide double bonds, and steric hindrance of the diamine on reactive amine functions, the reactions are disfavoured in the molten state, except in the case of diamine DDM ($\text{R}=\text{H}$).

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