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Study of molten-state polymerization of bismaleimide monomers by solid-state ^{13}C n.m.r. and *FT*i.r.

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The solid state cross-linking reactions occurring after the thermal priming of different bismaleimide monomers with variable steric hindrance were examined. As a result of the insolubility of the materials, monitoring reaction mixtures over time requires the use of techniques adapted to characterizing solids. After defining system reactivities by differential scanning calorimetry, most of the results could be obtained from spectral data furnished by *FT*i.r. and solid-state carbon-13 CP–MAS n.m.r. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: bismaleimide monomers; homopolymerization; spectroscopy)

INTRODUCTION

In contination of our work[1,2] on thermostable, thermohardening polymers, we have examined the molten-state radical polymerization of bismaleimide (BMI) systems using analysis techniques adapted to solids. Infrared absorption spectroscopy[3,4] has been used in the past to quantify new and/or residual chemical entities. In the light of the difficulties in using the method (poorly resolved broad bands, relatively small number of specific bands, etc.) however, we have undertaken parallel development of structural analyses using solid-state carbon-13 CP–MAS (cross-polarization with magic angle spinning) n.m.r.

The entities studied in this work were different bismaleimide monomers containing electron-donating alkyl substituents R with variable steric hindrance, situated ortho to the two maleimide functions on the aromatic rings. After synthesizing tetrasubstituted BMI in the laboratory[1], we examined changes in these heat-treated systems in the molten state, using two spectroscopic methods: *FT*i.r. and ^{13}C CP–MAS n.m.r. The comparative examination of the collated data has enabled structural information to be validated, residuals and/or new species to be quantified, and the final structure of the system formed to be elucidated.

EXPERIMENTAL

Synthesis

The BMI compounds denoted 1, 2, 3 and 4 in *Figure 1* were synthesized in the laboratory; the general synthesis process has been published previously[1].

Techniques

Infrared absorption spectroscopy (FT*i.r.*). Spectra were recorded with a Bruker IFS 45 spectrometer with the following conditions: spectral bandwidth 4000–400 cm^{-1}, 32 accumulations, resolution 2 cm^{-1}, signal processing by triangular apodization. All solid samples were examined as potassium bromide (KBr) pellets.

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 ^{1}H and ^{13}C n.m.r. spectra in liquid ($CDCl_3$) were recorded with a Bruker AM 400 spectrometer with the following conditions: pulse angle 90°, 7 μs (^{1}H) and 4.2 μs (^{13}C), digital resolution (Hz per point) 0.122 (^{1}H) and 0.375 (^{13}C) corresponding to a spectral width of 4000 Hz (^{1}H) and 20 000 Hz (^{13}C) for a memory space of 64K (^{1}H) and 128K (^{13}C).

Solid-state ^{13}C CP–MAS n.m.r. spectra were recorded with a Bruker ARX 300 spectrometer in quadrupole detection. Solid samples (powder) were placed in a boron nitride sample holder. A contact time of 1000 μs 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 bismaleimide monomers were recorded with a Setaram DSC 111G differential calorimeter with a programmed temperature gradient of 5°C min^{-1}.

RESULTS AND DISCUSSION

Reactivity of the maleimide double bond

This work considered only molten-state radical polymerization with thermal priming[1,5]. To determine the zone

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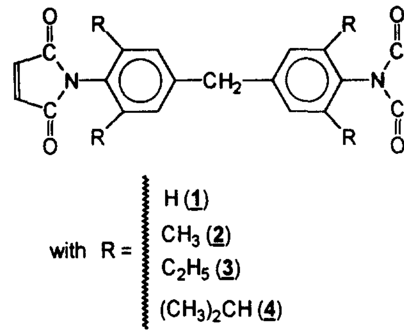


Figure 1 Bismaleimide monomers studied

Table 1 D.s.c. thermal data[a] for compounds 1, 2, 3 and 4

Compound	T_f (°C)	T_o (°C)	T_{exo} (°C)
1	152	178	214
2	210	250	285
3	162	267	304
4	221	262	340

[a] Heating rate 5°C min^{-1}

of reactivity of the four BMI monomers, we initially analysed all the products by dynamic d.s.c. (*Figure 2*). Under these experimental conditions, the thermal data obtained, i.e. melting temperature (T_f), polymerization onset temperature (T_o) and maximum exotherm temperature (T_{exo}), are listed in *Table 1*. It can be seen that there is an initial endothermal transition due to melting for all four monomers, followed by a cross-linking exotherm corresponding to the homopolymerization of maleimide groups according to the mechanism shown in *Figure 3*. The expected mechanism of cross-linked resin formation after heat treatment was the same regardless of the steric hindrance of the systems, and this structure is characteristic of thermohardening polymers. The mobility of molecules remained limited in all cases, since the mechanism of radical polyaddition causes the formation of a cross-linked, unmeltable and insoluble system having all the physico-chemical characteristics of succinimide groups, as shown in *Figure 3*.

Next, the thermal data showed the extent and influence of the steric effect caused by the alkyl substituents R: methyl, ethyl and isopropyl (monomers 2, 3 and 4) on system reactivity in comparison with the unhindered maleimide compound 1. The presence of voluminous substituents caused greater steric hindrance in proximity to the maleimide double bond and thus reduced molten-state reactivity[1].

Thermal polymerization is particularly difficult to study owing to the need for rigorous purification of the monomer. This is because traces of impurities or of residual catalyst can play a priming and/or inhibitory role[6,7]. In spite of this, some electron paramagnetic resonance (e.p.r.) spectral data indicate a radical polymerization mechanism in bismaleimide systems. Based on an e.p.r. study of the unhindered monomer 1, Brown *et al.*[7] proposed a detailed mechanism for the polymerization of maleimide functions. The homopolymerization of 1 involves first an initiation or priming step in which there is thermally induced homolytic rupture of the double bond, with the formation of a biradical. The biradical then rapidly adds to another monomer, furnishing two additional radicals, one active, the other inactive. The initial active radical adds to another monomer molecule, playing the role of reaction intermediate in the formation and growth of the network by radical polyaddition. The inactive radical has been unambiguously demonstrated by e.p.r., and results from the loss of one proton from the central methylene group during the first step in propagation[7].

Study of BMI monomers

All the products examined were highly crystalline and perfectly defined chemically. Based on the attribution of the chemical shifts of carbons conducted in liquid-state ^{13}C n.m.r. (*Table 2*), we could attribute all the signals from

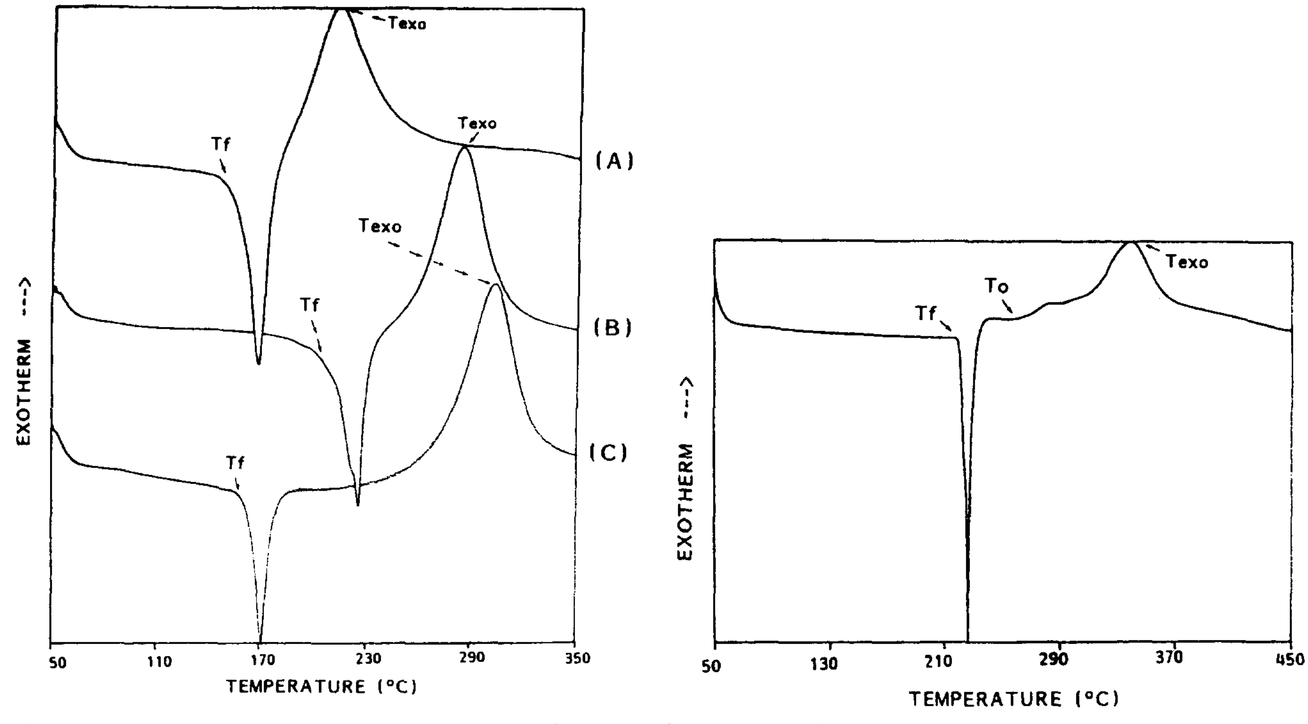


Figure 2 DSC diagrams: (A) monomer 1; (B) monomer 2; (C) monomer 3; (D) monomer 4

solid-state spectra by comparison of the liquid- and solid-state spectra (*Figures 4 and 5*). Liquid-state ^{13}C n.m.r. data correlated with solid-state spectra provide structural information (conformation, spatial structure) on the different monomers in the solid state.

In the absence of true crystalline structures determined by X-ray diffraction[8], we were led to interpret some line splittings as spatial conformational and structural effects, removing the degeneration of certain resonances caused by dissymetry in the molecule.

In the case of compounds 1 or 2 (*Figure 4*), the splitting of line 6 (carbonyl carbons) would seem to indicate that in the crystalline state, the carbonyl functions of the two maleimide rings are not equivalent in terms of the basic aromatic structure, as a result of a privileged spatial conformation. Solid-state spectra revealed that other lines were also split, undoubtedly due to phenyl and maleimide groups with a specific spatial environment. In particular, the carbons of maleimide ethylene bonds (C_7) and some aromatic carbons (those α and β to the central $-CH_2-$ group) are the most stereosensitive to the orientation of substituents on the skeleton. The carbons of the different alkyl groups also have preferential orientations in the crystalline space in the structure of the monomers, as shown by the splitting of carbon signals from $\underline{C}H_3CH_2$ and $(\underline{C}H_3)_2\underline{C}H$ (*Figure 5*).

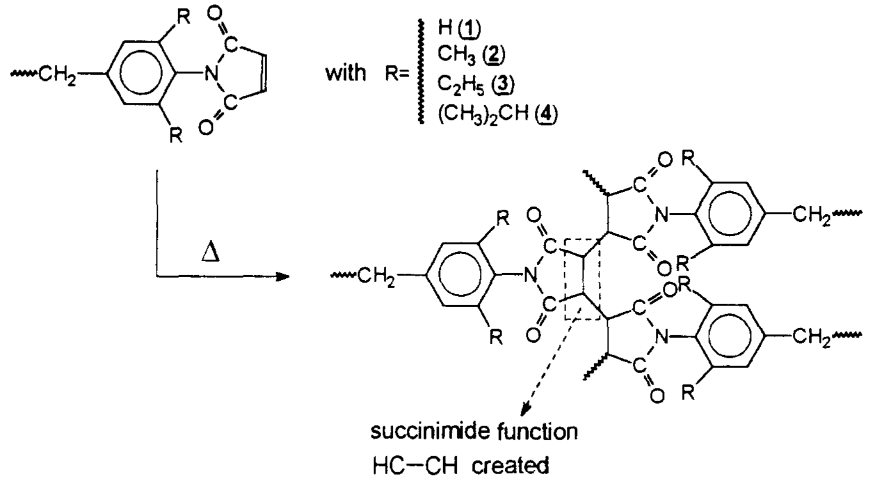
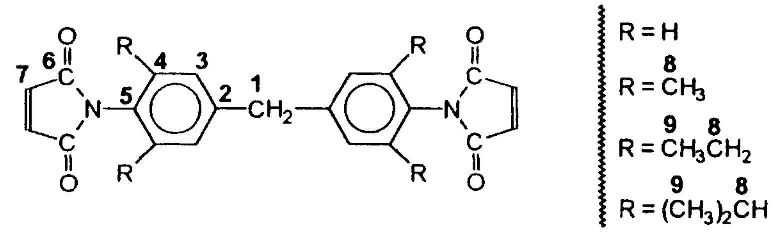


Figure 3 Homopolymerization mechanism of bismaleimide systems in the molten state

Table 2 Liquid and solid-state ^{13}C n.m.r. chemical shifts (ppm)[a]



Compound	R	State	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
1	H	liquid	41.0_9	140.3_9	129.7_3	126.2_0	129.4_3	169.5_6	134.2_2	—	—
		solid	38.7_6	141.7_9	129.3_4	125.6_5	129.3_4	171.1_4	shoulder	—	—
								168.8_2			
2	CH_3	liquid	41.0_9	141.7_4	129.1_9	136.9_1	127.1_9	169.6_0	134.3_5	17.9_0	—
		solid	41.3_4	142.7_5	129.4_7	138.8_1	127.2_6	172.3_5	133.8_9	17.2_1	—
				140.4_0		137.4_6		168.6_0			
3	C_2H_5	liquid	41.5_0	142.0_4	127.4_4	142.7_8	125.8_4	170.3_5	134.3_0	24.5_7	14.4_8
		solid	40.8_3	140.0_8	131.2_6	143.2_1	127.5_7	170.4_8	133.5_5	26.3_5	16.4_5
				138.1_9	129.7_8						15.3_2
4	$(CH_3)_2CH$	liquid	41.3_1	141.6_3	124.6_8	147.1_9	124.0_1	170.3_8	134.3_1	28.6_6	23.6_4
		solid	42.5_3	142.9_0	127.4_7	148.8_1	125.6_9	171.2_6	134.9_5	29.3_5	25.2_8
					126.4_2	147.6_9	124.0_6	170.6_4	131.9_2	27.0_4	23.4_0
								169.8_4			

[a] Solvent $CDCl_3$ and liquid reference TMS; solid reference polyoxymethylene (80 ppm)

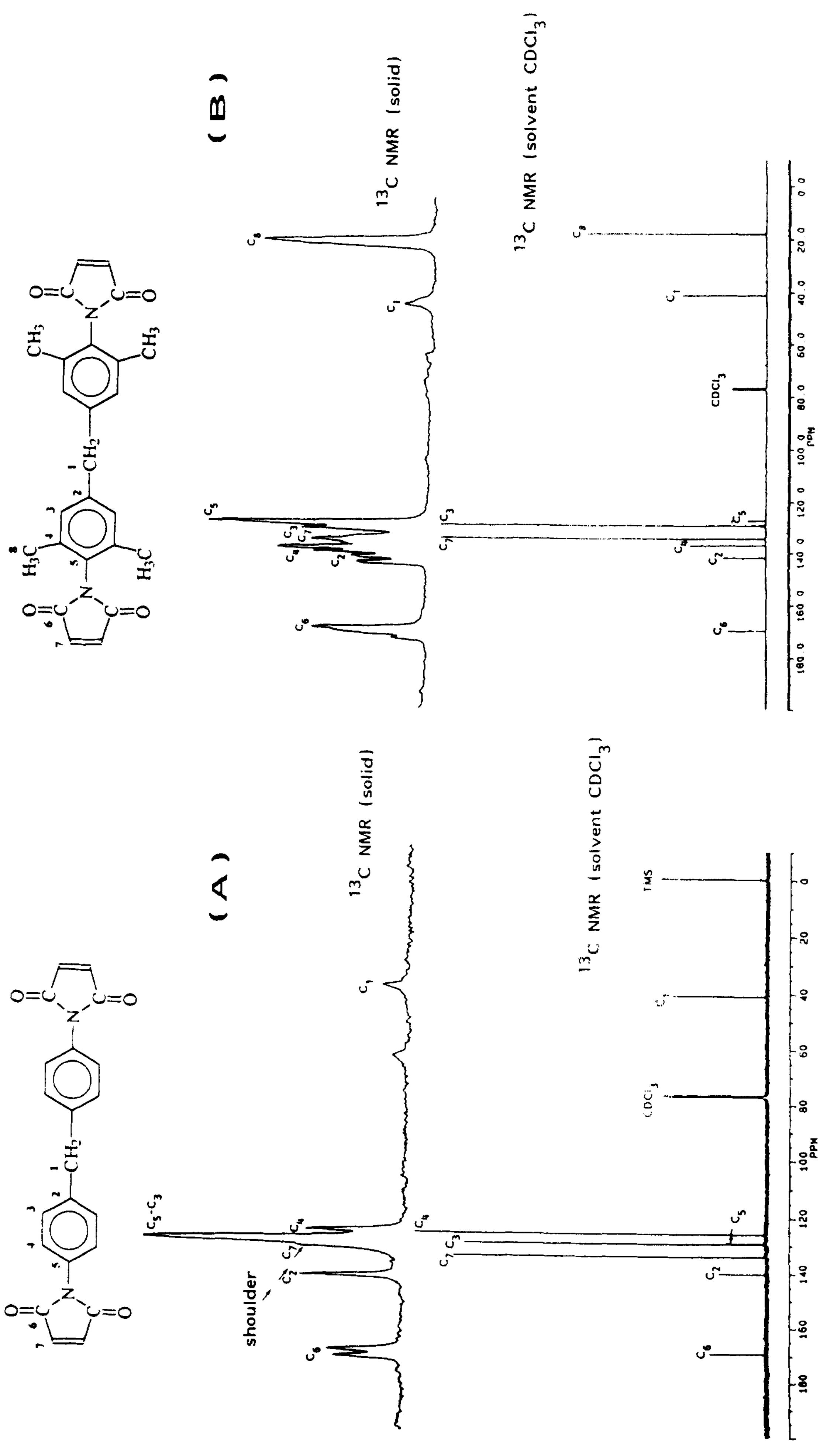


Figure 4 Liquid and solid-state ^{13}C n.m.r. spectra (0–180 ppm): (A) compound 1; (B) compound 2

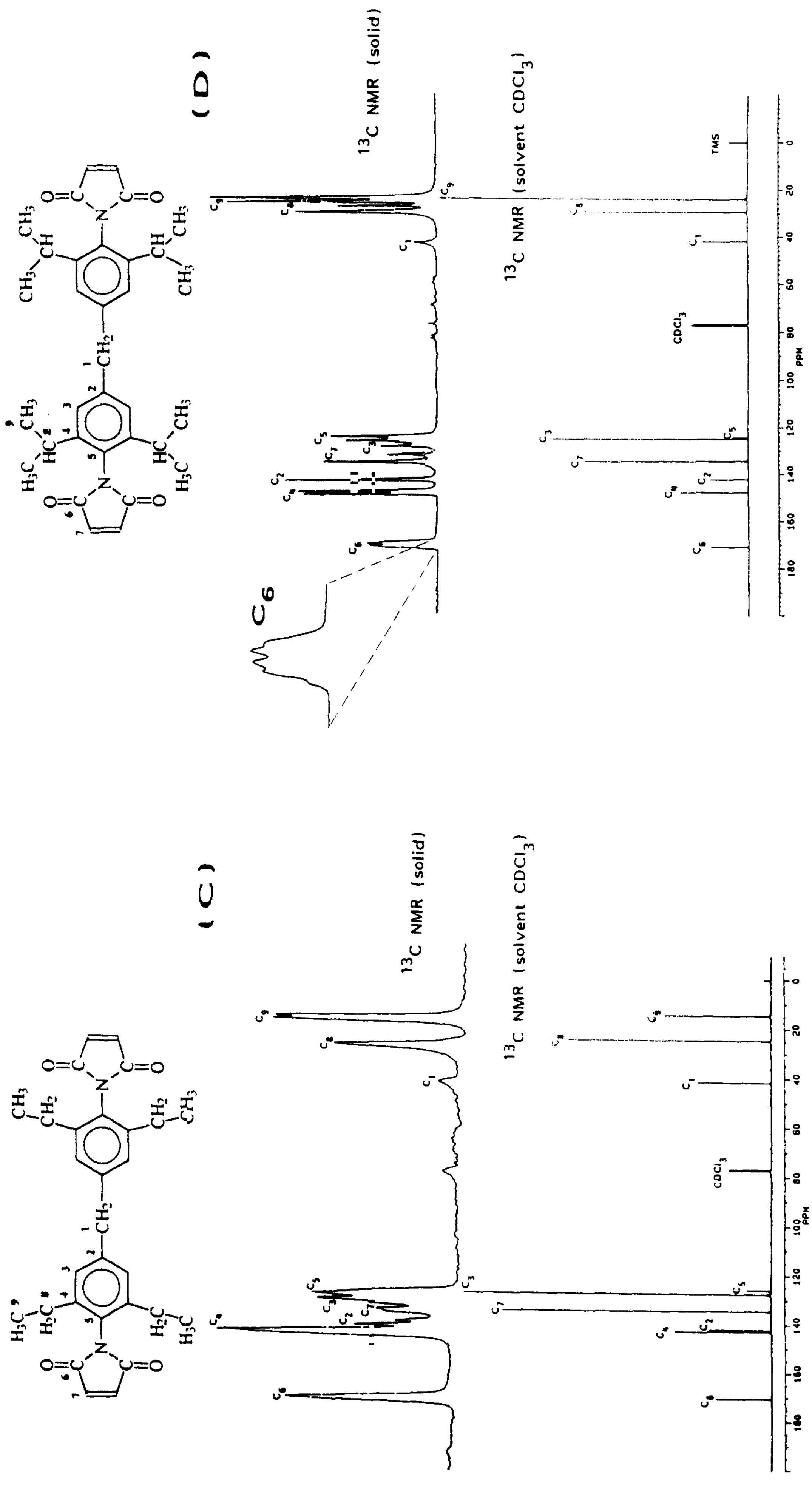


Figure 5 Liquid and solid state ^{13}C n.m.r. spectra (0–180 ppm): (C) compound 3; (D) compound 4

5h>The spectral zone around 160–180 ppm in the solid-state ^{13}C n.m.r. spectrum of compound 4 is broadened, indicating that the even more complex resonance signal of carbonyl groups is composed of several lines. The steric hindrance of isopropyl groups undoubtedly imposes several preferred conformations on the entire molecule in the crystalline state, but this hypothesis could not be confirmed in the absence of crystallographic data.

Study of molten-state homopolymerization

There are few methods for studying the chemical structure of heat-polymerized bismaleimide because of the very low solubility of the reaction mixture. This is why we developed solid-state ^{13}C CP–MAS n.m.r. as a complement to infrared absorption spectroscopy (*FT*i.r.), which are two techniques very well adapted to the structural analysis of cross-linked BMI.

The comparison of the results obtained using the two techniques allowed us to select the chemical shifts and wavelengths characteristic of the mechanism of homopolymerization of maleimide functions to succinimide functions. The specific spectral data of changes in the medium (*Table 3*) show among other things that tetra-substitution on the aromatic ring has little effect on these spectral parameters.

The solid-state ^{13}C CP–MAS n.m.r. spectra (*Figures 6* and *7*) of the monomers at initial time $t = 0$ exhibit three or four different and distinct spectral zones, depending on whether or not alkyl substituents are present ortho to maleimide functions:

- between 0 and 30 ppm: resonance signals from different aliphatic carbons $\underline{C}H_3$, $CH_3\underline{C}H_2$, $(\underline{C}H_3)_2\underline{C}H$;
- around 30–50 ppm: $-\overline{C}H_2-$ group of the methylene bridge between the two aromatic rings;
- 120–150 ppm: aromatic carbons and ethylene double bond carbons in the maleimide ring;
- between 160 and 180 ppm: carbons of the carbonyl groups of the two maleimide rings.

After the molten-state polymerization of all the maleimide systems, the following spectral changes were observed (*Figures 6* and *7*):

- between 30 and 50 ppm, appearance of signals from saturated sp^3 carbons of succinimide groups, resulting from the formation of cross-linking nodes that are superimposed on the resonance line of the central $-CH_2-$ group of the monomers, also present in this portion of the spectrum[5];
- around 134–135 ppm, disappearance of the resonance signals from maleimide double bond carbons, visible only in the case of compounds 3 and 4, which are the most hindered (*Figure 7*); these lines are not well individualized and are difficult to quantify because they resonate in the same region as aromatic carbons;
- shift of the resonance signals of carbonyl groups from 170 ppm (maleimide environment) towards 175–176 ppm (succinimide environment); this region is characteristic of carbonyl functions, is well separated from the other carbons of the skeleton, and in our study was found to be the most suitable for the identification and quantification of entities, either created (with a succinimide group) or residual (with a maleimide group) during heat polymerization.

*FT*i.r. spectroscopy of the same samples also provided interesting data on the reaction medium. As an example, there were several spectral changes in the region 3500–600 cm^{-1} after the polymerization of monomer 2 (*Figure 8*):

- disappearance of the bands characteristic of the maleimide function towards 3100 cm^{-1} ($\nu =$ CH), 1150 cm^{-1} (νC–N–C) and around 690 cm^{-1} [δC = C–H(*cis*)];
- attenuation of the intensity of the line around 830 cm^{-1} attributed to δC = C deformation vibration of the maleimide ring of these systems;
- appearance of a broad νC–N–C band towards 1185–1190 cm^{-1}, characteristic of the succinimide function created after the cross-linking reaction.

The two entities present simultaneously in the reaction mixture could thus be quantified by the two techniques used in this study. In the case of *FT*i.r. of each heat-treated compound 1, 2, 3 and 4, we decided to follow the disappearance of the lines centred at 1150 and 690 cm^{-1} (*Table 3*). The aromatic νC = C band localized between 1511 and 1473 cm^{-1}, depending on the monomer and unaffected by the reaction mechanism, was used as internal

Table 3 Wavelengths (*FT*i.r.) and chemical shifts (solid-state ^{13}C n.m.r.) of maleimide and succinimide groups

Compound	1		2	
Function	Maleimide	Succinimide	Maleimide	Succinimide
^{13}C n.m.r. δ (ppm)	170 (C = O)	176 (C = O)	170 (C = O)	175 (C = O)
		30–50 (CH–CH)		30–50 (CH–CH)
*FT*i.r. ν and δ (cm^{-1})	~3100 (ν = CH)		~3100 (ν = CH)	
	1149 (νC–N–C)	1185 (CH–CH)	1153 (νC–N–C)	1187 (CH–CH)
	832 (δC = C)		830 (δC = C)	
	69O [δC = C–H(*cis*)]		687 [δC = C–H(*cis*)]	
Compound	3		4	
Function	Maleimide	Succinimide	Maleimide	Succinimide
^{13}C n.m.r. δ (ppm)	170 (C = O)	176 (C = O)	170 (C = O)	175 (C = O)
		30–50 (CH–CH)		30–50 (CH–CH)
*FT*i.r. ν and δ (cm^{-1})	3095 (ν = CH)		3098 (ν = CH)	
	1153 (νC–N–C)	1184 (CH–CH)	1150 (νC–N–C)	1188 (CH–CH)
	832 (δC = C)		826 (δC = C)	
	693 [δC = C–H(*cis*)]		692 [δC = C–H(*cis*)]	

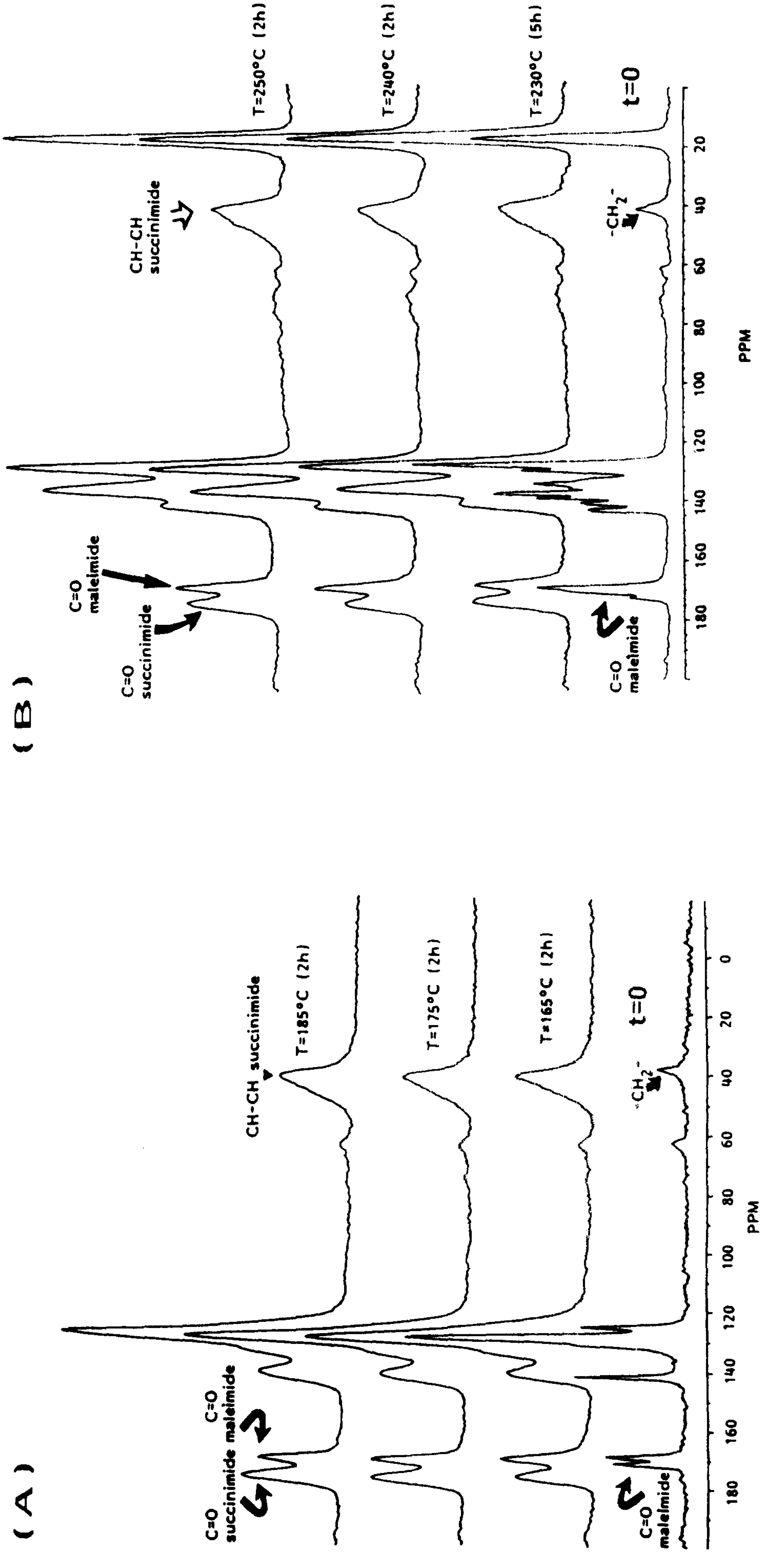


Figure 6 Homopolymerization followed by solid-state ^{13}C n.m.r. after heat treatment: (A) compound 1; (B) compound 2

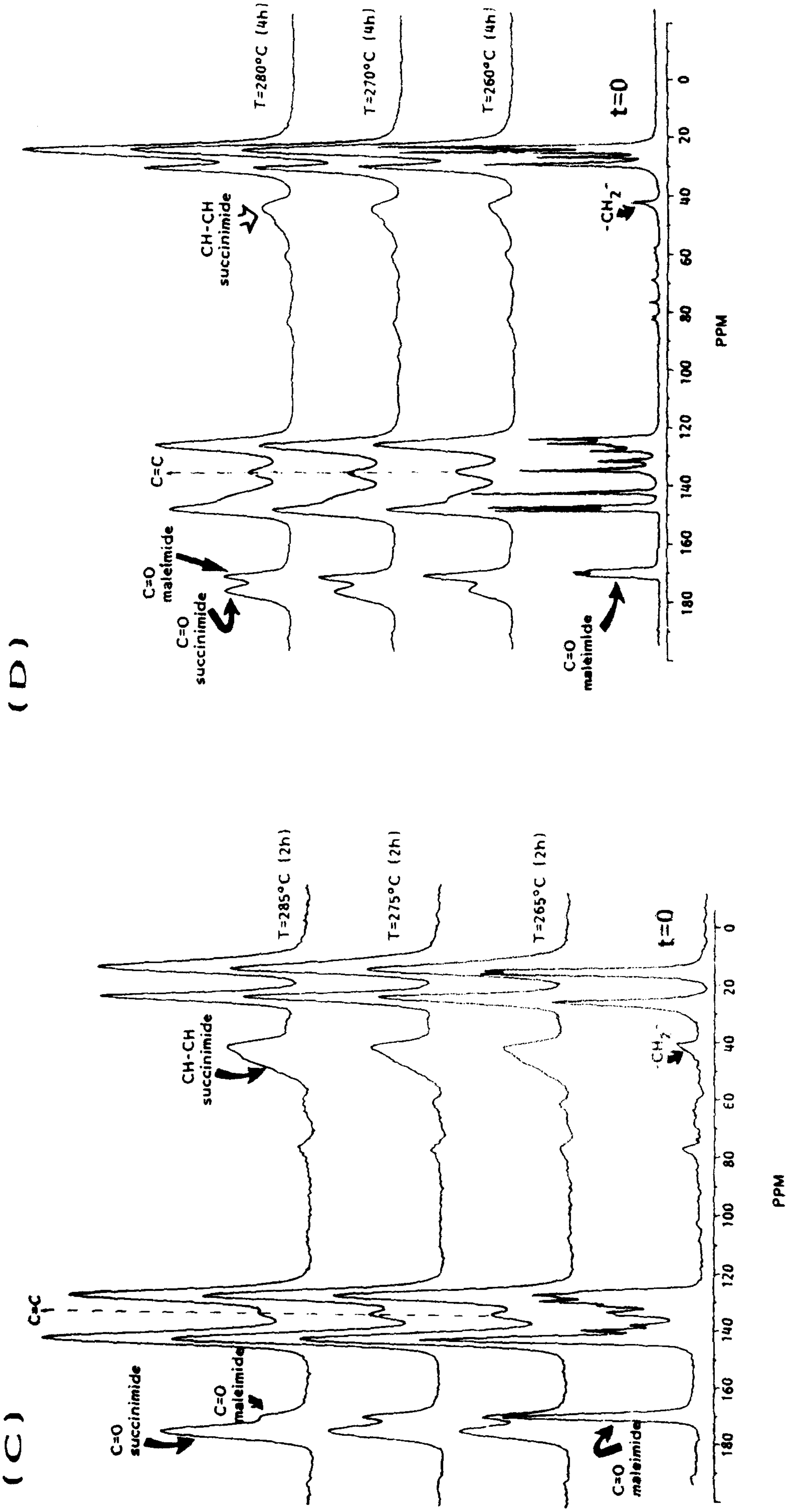


Figure 7 Homopolymerization followed by solid-state ^{13}C n.m.r. after heat treatment: (C) compound 3; (D) compound 4

standard for the four monomers, as reported elsewhere[9,10]. In solid-state ^{13}C n.m.r., prior work in our laboratory[9,10] showed that the region of carbonyl group resonance (160–180 ppm) was an ideal probe for monitoring thermal changes in these systems. The network is characterized by the presence of succinimide groups whose carbonyl carbons resonate at lower fields (unshielding $\geq$ 5 ppm for all the compounds). To quantify the two species, we therefore deconvoluted the broad band of resonance of carbons of the different carbonyl groups into basic lines.

The changes in the surface of the two deconvoluted bands after heat treatment enabled us to calculate the respective percentages of the maleimide and succinimide forms. As an example, *Figure 9* shows the deconvolution of monomer 1, obtained after 2 h of reaction at 165°C. The bands around 170 and 176 ppm correspond to residual maleimide functions and to newly arisen succinimide functions. Integration of these two lines furnishes the percentage of residual maleimide and thus the extent of progress of cross-linking reaction. In the course of these deconvolutions, a

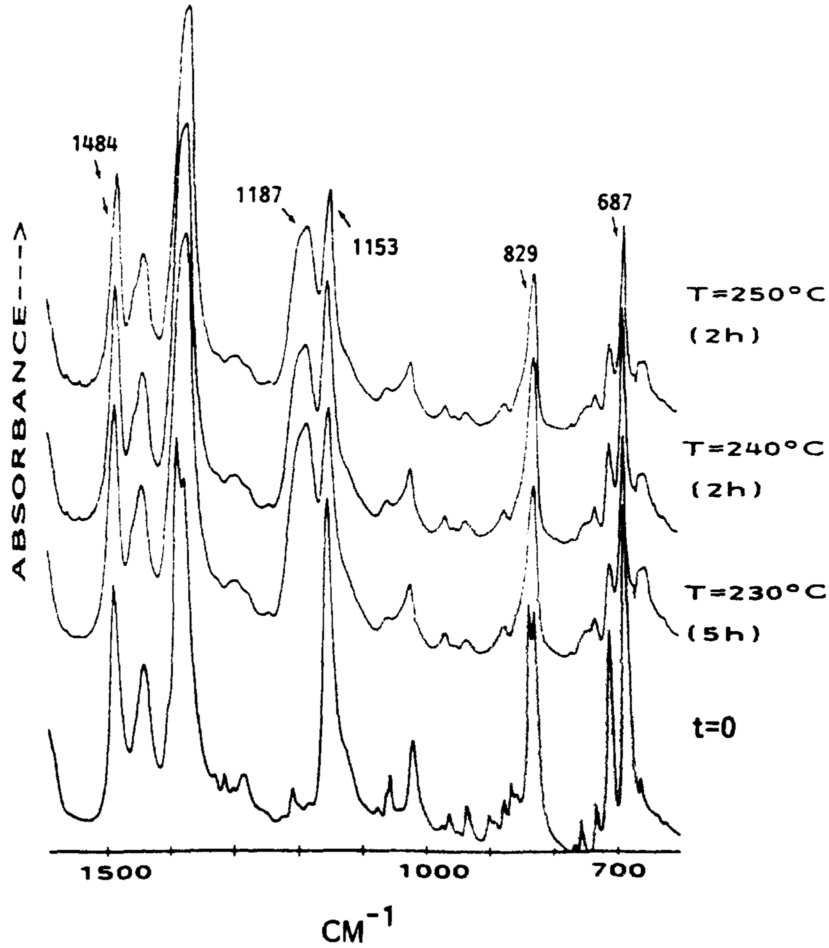


Figure 8 Homopolymerization of compound 2 followed by *FT*i.r. after heat treatment

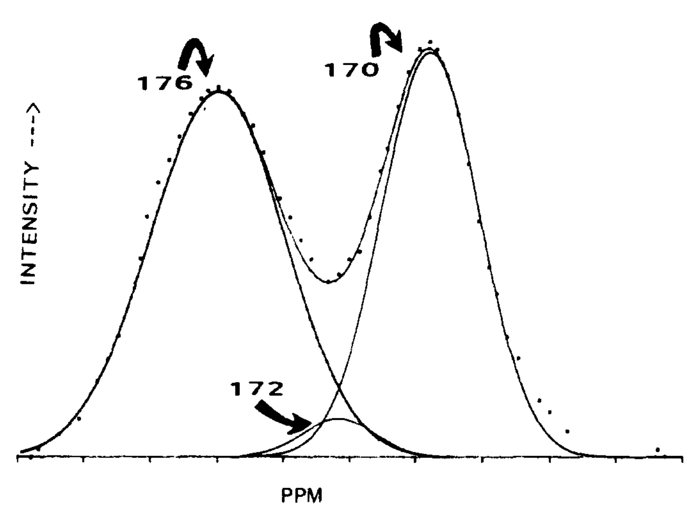


Figure 9 Deconvolution of the broad band at 160–180 ppm into basic lines (monomer 1, T = 165°C for 2 h)

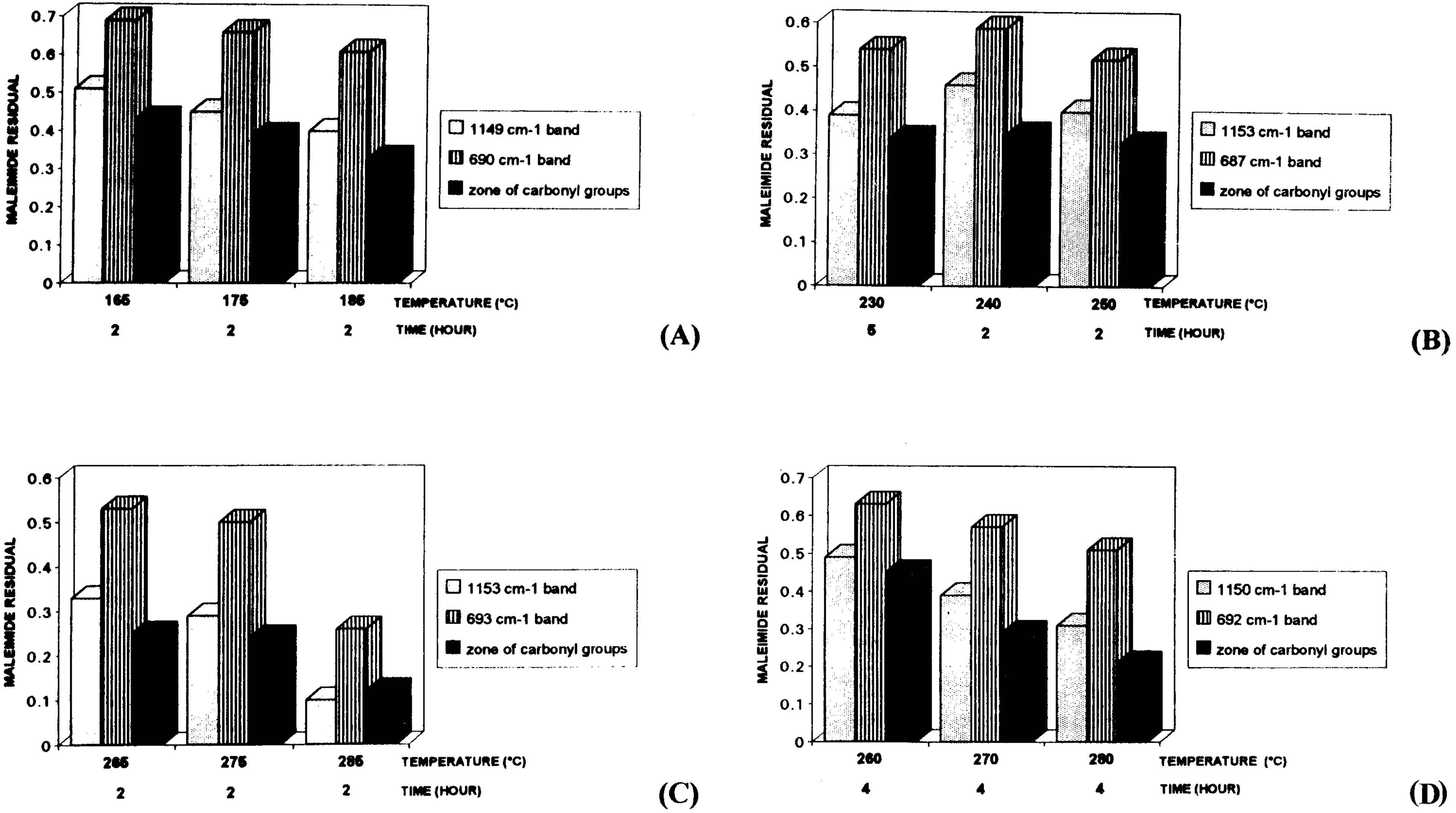


Figure 10 Quantitation of residual maleimides by solid-state ^{13}C n.m.r. and FTi.r.: (A) compound 1; (B) compound 2; (C) compound 3; (D) compound 4

third line around 172–173 ppm was revealed for all the monomers, of much lower intensity and which could be due to the presence of small, weakly cross-linked molecules in the medium, with a structure midway between that of the maleimide and succinimide forms. This result is consistent with other findings in the laboratory[9].

From quantitation of residual maleimides as a function of the heat treatment applied to the four systems 1, 2, 3 and 4 (*Figure 10*), it is seen that polymerization of maleimide double bonds depends essentially on reaction temperature and the duration of heat treatment, in agreement with the literature[3]. The unhindered monomer 1 reacted at the lowest temperature, starting at 165°C. The other BMI compounds started reacting at much higher temperatures, $\geq 250°C$, depending on structural hindrance.

Differences of up to 20% were observed when quantifying residuals in infrared absorption spectroscopy as a function of the wavelength chosen. This suggests that the integration method used (method of tangents) was responsible for these differences. After cross-linking, the band at $1150\ cm^{-1}$ became a shoulder of the succinimide band around $1185-1190\ cm^{-1}$ which appeared and increased as a function of the heat cycle applied. The examination of the band around $690\ cm^{-1}$ was more delicate, since the intensity could not be evaluated because the signal became dispersive at the end of heat treatment. Residuals calculated from the changes in this band were higher and there were more associated errors.

Overall, the use of the two assay methods shows that construction of histograms from residual maleimides determined by n.m.r. follows the same patterns of changes as those established by the use of *FT*i.r. In n.m.r., deconvolution of the broad band into basic lines is relatively simple and comparisons after quantitation are conducted on the same carbon class: sp^2 hybridization of the carbonyl carbon in maleimide and succinimide structures. The smallest difference ($< 10\%$) is attributed to the νC–N–C maleimide band with reference to n.m.r. data, indicating that the use of this frequency to process results is quite reliable for following the disappearance of maleimide double bonds.

CONCLUSIONS

The results presented indicate that solid-state reaction methods can be used to follow the homopolymerization reaction of molten-state bismaleimide systems. The polymerization of maleimide double bonds depends primarily on reaction temperature and the duration of the heat treatment.

We were also able to determine the limits of the n.m.r. and *FT*i.r.techniques used. Thus, some signals (chemical shifts and/or vibration frequencies) are weaker than others for the mechanistic and kinetic monitoring of these systems.

Data furnished by *FT*i.r. and solid-state ^{13}C n.m.r. follow the same overall changes as a function of the heat cycle applied.

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