Synthesis, mechanism and kinetics of radical polymerization of bismaleimide-type telechelic oligomers in solvent and in the solid state

Marie-Florence Grenier-Loustalot*, Frederic Gouarderes, Frederic Joubert and Philippe Grenier
Laboratoire de Chimie Organique Physique, URA CNRS 1494, Hélioparc Pau-Pyrénées, 2 rue du Président Angot, 64000 Pau, France
(Received 2 November 1992; revised 11 January 1993)

In order to characterize the various residual fragments or those created during the use and polymerization of bismaleimide prepolymers, different compounds characteristic of the expected fragments were synthesized and physicochemically characterized by Fourier-transform infra-red spectroscopy, nuclear magnetic resonance spectroscopy and differential scanning calorimetry. Thus, depending on heating temperature, the bismaleimide telechelic group gives rise to chain extension at 140–150°C in the presence of aromatic diamines, either by addition or by maleimide ring opening. At higher temperatures (200°C) it causes a crosslinking reaction, which forms a three-dimensional system.

(Keywords: telechelic oligomers; radical polymerization; bismaleimide; mechanism; kinetics; characterization)

INTRODUCTION

When bismaleimide (BMI) resins are used alone, they tend to form highly crosslinked networks that are very fragile. In order to control and avoid this defect, chain extenders are added to the resins to reduce crosslink density and improve mechanical properties. Chain elongation and crosslinking reactions occur during the heating cycle (*Figure 1*). In light of the competition between these two reactions, the structure of the resulting crosslinked network depends on the quantities of bismaleimides and chain extenders present in the mixture, as well as the heating cycle (time, temperature) used with these systems[1–6].

In order to follow the different reactions involved, model compounds were synthesized and characterized chemically and physicochemically, and their reactivity was studied in solvent or in the solid phase. These results were then applied to the study of bismaleimide polymerized in the absence of chain extenders (aromatic amines).

EXPERIMENTAL

Synthesis of products

The different model compounds used in this study are shown in *Table 1*.

Models of succinimide and maleimide amic acids (compounds 1–8). Compounds **1** through **8** were synthesized by adding 0.02 mol of amine dropwise to a solution of anhydride (0.02 mol in 20 ml of dimethylformamide (DMF)). After mixing at room temperature for 4 h, the product was precipitated in 60 ml of distilled water and recovered by filtration.

Models of imides: succinimides and maleimides (compounds 9–16). Compounds **9** through **16** were obtained by adding to the preceding reaction medium 40 ml of acetone, 6 ml of acetic anhydride and 0.5 g of molten sodium acetate. After mixing for 4 h at 60°C, the compound was precipitated in 400 ml of water, washed with a saturated solution of $NaHCO_3$ and then with water until neutral pH.

Succinimide model (compound 17). Compound **17** was synthesized by slowly pouring a solution of diaminodiphenylmethane (DDM) (0.02 mol in 15 ml of DMF) into a solution of succinic anhydride (0.04 mol in 40 ml of DMF). After mixing for 4 h at room temperature, 60 ml of acetone, 45 ml of DMF, 12 ml of acetic anhydride and 1 g of molten sodium acetate were added. The reaction mixture was heated at 60°C for 3 h, after which the product was precipitated with 500 ml of water, washed with a saturated solution of $NaHCO_3$ and then with water until neutral pH.

Aspartimide models (compounds 18–21). Compound **18** was synthesized from a solution of *p*-toluidine (0.01 mol in 10 ml of acetic acid), which was poured into a solution of bismaleimide (compound **21**, 0.005 mol in 20 ml of acetic acid). After reacting for 1 h at 110°C, the product was precipitated by cooling.

---

* To whom correspondence should be addressed

0032-3861/93/183848-12

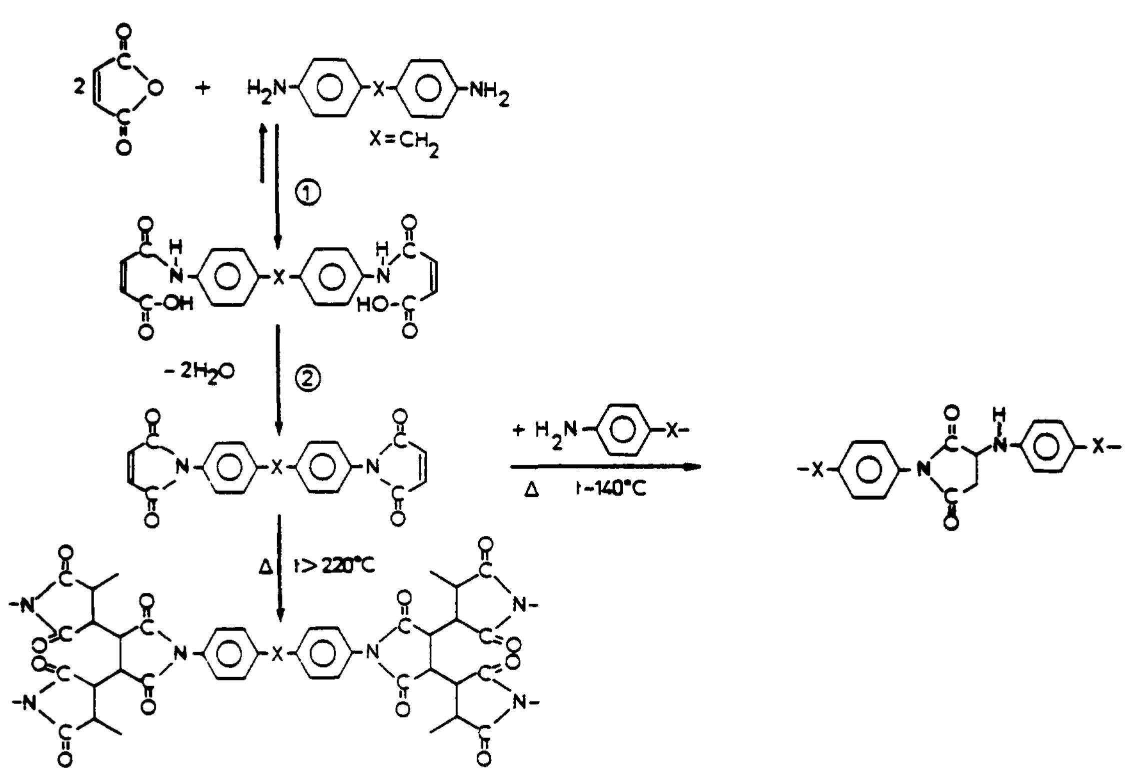


Figure 1 Reaction mechanism

Table 1 Characteristics of the model compounds

Anhydride	Amine	M.p. acid(°C)	Compound	M.p. imide (°C)	Compound
Succinic anh.	Aniline	152	**1**	158	**5**
Succinic anh.	*o*-Toluidine	154	**2**	103	**6**
Succinic anh.	*m*-Toluidine	138	**3**	114	**7**
Succinic anh.	*p*-Toluidine	182	**4**	158	**8**
Maleic anh.	Aniline	200	**9**	91	**13**
Maleic anh.	*o*-Toluidine	123	**10**	79	**14**
Maleic anh.	*m*-Toluidine	173	**11**	121	**15**
Maleic anh.	*p*-Toluidine	194	**12**	142	**16**

Synthesis	M.p. (°C)	Compound
Compound **21** + *p*-toluidine	232	**17**
Maleic anh. + MDA[a]	242	**18**
Compound **9** + *N*-methylaniline	175	**19**
Succinic anh. + MDA	214	**20**
Maleic anh. + diamine	157	**21**

[a] MDA = methylene dianiline (**22**)

Compound **19** was prepared by slowly adding a solution of diaminodiphenylmethane (0.01 mol in 10 ml of dichlorobenzene) to a solution of *p*-toluidine maleimide (0.02 mol in 20 ml of dichlorobenzene), followed by 8 ml of acetic acid. After mixing for 1 h, the product precipitated in the reaction medium and was recovered by filtration.

Compound **20** was obtained by pouring a solution of *N*-methylaniline (0.1 mol of *N*-methylaniline in 10 ml of acetic acid) into a solution of aniline maleimide (0.1 mol in 30 ml of acetic acid). After reacting for 2 h at 115°C, the reaction medium was chilled in ice, the product was precipitated and recovered by filtration.

Compound **21** was obtained by pouring a solution of diaminodiphenylmethane (0.02 mol in 15 ml of DMF) into a solution of maleic anhydride (0.04 mol in 30 ml of DMF). After mixing for 4 h at room temperature, 60 ml of acetone, 45 ml of DMF, 12 ml of acetic anhydride and 1 g of molten sodium acetate were added. The reaction mixture was heated under reflux for 3 h, after which the product was precipitated with 500 ml of water and washed with a saturated solution of $NaHCO_3$ until neutral pH.

Techniques

Fourier-transform infra-red absorption spectroscopy. A Bruker IFS 45 spectrometer was used to record spectra in the following conditions: 4000–400 cm^{-1} spectral band, 32 accumulations, resolution 2 cm^{-1}, signal processing by triangular apodization. Solid-state room-temperature spectra were recorded in KBr pellets.

Differential scanning calorimetry. Thermal measurements were recorded with a Setaram DSC 111G calorimeter with linear temperature programming (5°C min^{-1}).

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

Chemical shifts were given with tetramethylsilane (TMS) as internal standard. Classes of carbon atoms (quaternary, CH_2, CH_3, etc.) were attributed by the use of d.e.p.t. (distortionless enhancement by polarization transfer) selective pulse sequences.

Solid-state ^{13}C n.m.r. spectra (cross-polarization/magic-angle spinning (c.p./m.a.s.)) were obtained with a Bruker WM 250 spectrometer operating in quadratic detection and equipped with an Aspect 2000 computer (DISN 88 program). Samples of fine powder were placed in a boron nitride sample holder. A contact time of 0.8 s, a delay of 20 s between sequences and spinning between 5 and 6 kHz, as well as a mean of 1000 contacts were required to obtain an interpretable spectrum with a suitable signal-to-noise ratio. Chemical shifts were calculated from the polyoxymethylene (Delrin) line at 80 ppm (internal standard).

The comparison of solid and liquid spectra enabled the selection of lines characteristic of the different groups expected.

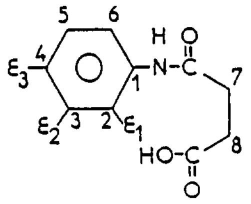
ANALYSIS OF THE RESULTS OF THE PHYSICOCHEMICAL STUDY OF COMPOUNDS 1–22

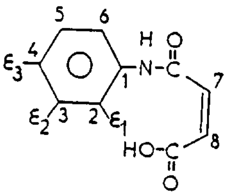
^{13}C n.m.r. study

Monofunctional succinimide and maleimide compounds (1-16). The data obtained by ^{13}C n.m.r. (*Tables 2* and *3*) led to the following conclusions.

Within the same series of compounds (succinimides or maleimides) ring dehydration reactions could be easily followed in four or five regions, respectively, depending on the chemical nature of the product. In particular, in the region of carbonyl groups at 165–180 ppm, there was considerable shielding of carbonyls in the case of the

Table 2 Chemical shifts and attributions of solid and liquid ^{13}C n.m.r. spectra of amic acids

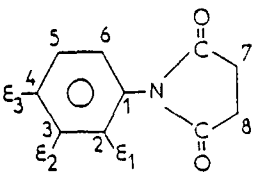


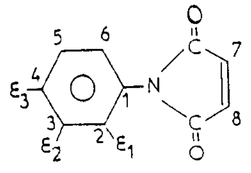


		Chemical shifts^a (ppm)										
Compound	State	1	2	3	4	5	6	7	8	CH_3	C=O amide	C=O acid
5	liquid	138.46	119.64	128.80	123.90	128.80	119.64	131.82	130.45	–	163.29	166.76
	solid	134.72	116.20	126.85	122.31	126.85	116.20	128.78	127.12	–	161.01	162.23
6	liquid	135.30	125.78	130.37	125.95	130.37	125.08	132.54	132.01	17.76	163.69	166.46
	solid	136.16	125.65	131.74	127.56	131.74	122.35	135.01	135.01	17.80	163.76	166.53
7	liquid	136.66	118.73	136.60	123.38	127.17	115.42	130.22	129.07	19.58	161.85	165.41
	solid	134.31	115.84	134.31	122.60	127.12	113.80	129.32	127.12	19.82	163.35	166.52
8	liquid	134.66	119.15	131.62	133.64	131.62	119.15	131.68	131.68	19.17	162.98	164.54
	solid	136.03	118.37	131.33	136.03	131.33	118.37	133.67	133.67	19.88	163.32	167.24
Compound	State	1	2	3	4	5	6	7	8	CH_3	C=O	
13	liquid	131.30	126.07	129.04	127.92	129.04	126.07	134.17	134.17	–	169.46	
	solid	131.40	125.62	129.71	128.24	129.71	125.62	135.24	135.24	–	171.65	
14	liquid	136.39	129.87	131.03	128.56	129.30	126.76	134.24	134.24	17.78	169.45	
	solid	137.81	129.80	131.21	128.10	129.35	125.68	134.95	136.09	20.15	170.38	
15	liquid	131.89	128.75	138.87	129.07	127.47	124.12	134.75	134.75	21.16	170.21	
	solid	134.21	128.11	137.41	128.35	125.81	123.80	131.17	131.17	21.28	170.68	
16	liquid	128.50	125.97	129.71	137.94	129.71	125.97	134.08	134.08	21.01	169.61	
	solid	126.12	122.82	127.12	134.50	127.12	122.82	132.50	132.50	18.87	168.51	

^{a} Solvent, DMSO-d_6; liquid reference, TMS; solid reference, polyoxymethylene (80 ppm)

Table 3 Chemical shifts and attributions of solid and liquid ^{13}C n.m.r. spectra of imides





Compound	State	Chemical shifts^a (ppm)										
		1	2	3	4	5	6	7	8	CH_3	C=O amide	C=O acid
1	liquid	139.95	119.39	123.52	123.59	129.52	119.39	29.46	31.71	-	170.78	174.39
2	liquid	136.88	124.89	130.79	126.10	130.38	124.20	31.03	29.07	17.30	170.83	173.63
	solid	136.85	125.32	131.89	126.16	130.31	123.95	29.22	29.32	16.16	171.40	181.45
3	liquid	138.39	119.95	139.50	124.08	128.64	116.52	31.35	31.30	20.77	170.29	173.76
	solid	137.36	119.67	140.78	123.66	129.37	119.67	28.96	29.02	20.07	171.35	182.15
4	liquid	137.16	119.31	132.51	132.51	132.51	119.31	31.39	31.29	19.88	169.96	173.48
	solid	135.15	122.09	128.65	126.65	128.65	122.09	28.10	28.20	18.84	166.72	178.98

Compound	State	1	2	3	4	5	6	7	8	CH_3	C=O
9	liquid	133.26	127.63	129.32	128.81	129.32	127.63	28.97	28.97	-	177.47
	solid	131.49	128.42	131.49	131.49	131.49	128.42	32.36	32.36	-	178.05
10	liquid	135.59	127.96	131.15	129.44	131.08	126.88	28.55	28.55	17.64	176.23
	solid	136.59	129.94	131.32	129.94	131.32	127.42	28.68	28.68	17.53	177.22
11	liquid	132.46	127.32	138.86	128.77	129.11	123.82	28.53	28.53	20.78	176.61
	solid	132.91	128.18	140.08	128.18	128.24	124.93	29.68	29.68	20.44	178.24
12	liquid	129.11	126.10	129.65	138.50	129.65	126.10	28.23	28.23	21.04	176.20
	solid	126.83	124.88	128.67	137.75	128.67	124.88	28.80	28.80	20.57	175.28

^{a}Solvent, DMSO-d_6; liquid reference, TMS; solid reference, polyoxymethylene (80 ppm)

acids ($\Delta\delta_{A-I} = -4$ to -7 ppm)*. The same was true for the region of quaternary carbons bearing a nitrogen group (carbon C1: 128–138 ppm). The carbon bearing the secondary (amic acid) or tertiary amine (imide) was stereosensitive to its chemical environment since it underwent considerable unshielding ($\Delta\delta_{A-I} = +2$ to $+6$ ppm). Finally, in the region of aromatic carbons α to the amic acid or imide function (carbon C2: 115–129 ppm), it underwent a shielding of -3 to -9 ppm in the case of the imide (tertiary amine) by a β effect (stereosensitive). This is a very important result, since in the case of chain elongation reactions, secondary and/or tertiary amines were created. These carbons could be used as molecular probes characteristic of this reaction. In the region of carbons characteristic of the alkyl substituent (16–21 ppm, $\Sigma = CH_3$), the methyl group could be used as a molecular probe for studying the ring dehydration reaction. It is stereosensitive to amide and imide groups located at four σ bonds, e.g. in the case of p-toluidine ($\Delta\delta_{A-I} = -2$ ppm). Since this carbon is unaffected by the polymerization mechanisms occurring, it can be used as a standard to quantify reaction kinetics. The region of 28–31 ppm is characteristic for succinic compounds (C7 and C8). The ring dehydration reaction could thus be followed with these carbons, since symmetry of the molecule in the case of the imide leads to an equivalent chemical shift of carbons C7 and C8 and an unshielding of the line by about +2 ppm.

When the spectra of compounds characteristic of succinimide and maleimide functions were compared, it was seen that the maleimide→succinimide crosslinking reaction could be followed in several spectral regions, in particular that characteristic of succinimide carbons: 28–31 ppm. As difficult as it is to follow the disappearance of the maleimide double bond (carbons C7 and C8 at 126–128 ppm), whose carbons resonate in the same region as those of the benzene rings, it is easy to follow the crosslinking reaction involving an $sp^2 \rightarrow sp^3$ carbon process, leading to the appearance of new lines in the region of alkyls (10–40 ppm). This is precisely what is seen, since the region of 28–31 ppm showed the appearance of new lines absent from maleimide models.

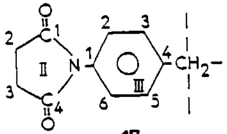
Case of bifunctional compounds (17–22). Liquid ^{13}C n.m.r. results (*Table 4*) obtained with compounds **17** through **22**, models of the different reactions shown in *Figure 1*, lead to several comments that will enable us to follow molten-state mechanisms in BMI–amine prepolymers.

In particular, in the region of 168–175 ppm, compound **21** (maleimide model) exhibited a carbonyl resonance around 168–170 ppm, and, when an addition reaction occurred in the presence of amines (aspartimide compounds **18–20**) or a homopolymerization reaction (succinimide compound **17**), this resonance was substan-

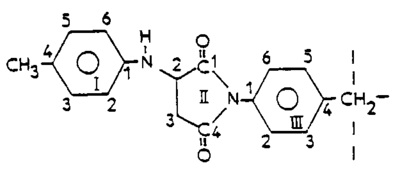
---

*$\Delta\delta_{A-I} = \delta_{acid} - \delta_{imide}$ for the same carbon

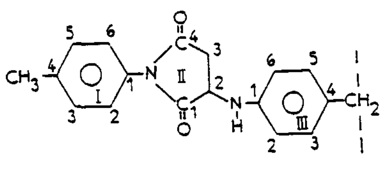
Table 4 Chemical shifts and attributions of solid and liquid ^{13}C n.m.r. spectra of compounds **17**–**22**



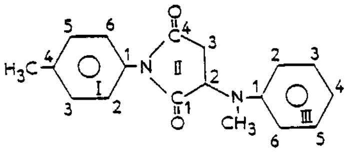
17



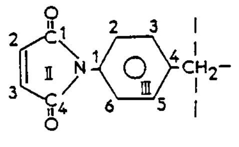
18



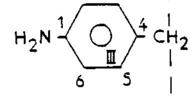
19



20



21



22

Compound	State	Chemical shift^a (ppm)																		
		Cycle II							Cycle II					Cycle III						
		1	2	3	4	5	6	CH_3	1	2	3	4	CH_3	1	2	3	4	5	6	CH_2
17	liquid	145.77	113.90	130.24	141.84	130.24	113.90	20.93	177.31	52.86	39.39	175.13		131.26	126.32	127.88	141.84	127.88	126.32	39.37
	solid	144.23	109.43	130.11	141.90	130.11	109.43	21.46	173.23	52.87	40.82	173.23		130.11	129.80	129.80	141.90	129.80	129.80	40.82
			116.43				116.34		177.15			177.15								
									180.05			180.05								
18	liquid	130.15	128.87	129.32	137.33	129.32	128.87	20.25	173.91	51.30	35.80	176.10		144.80	112.54	129.07	137.33	129.07	112.54	38.39
	solid	129.87	129.87	129.87	137.74	129.87	129.87	22.31	176.93	52.97	36.85	176.93		145.25	118.23	129.87	137.74	129.87	118.23	36.85
19	liquid	129.89	127.07	129.60	132.24	129.60	127.07	20.60	174.29	58.72	32.44	175.54	33.76	149.56	113.67	129.31	117.90	129.31	113.67	
	solid	131.97	128.81	130.97	133.39	130.97	128.81	24.40	174.73	61.52	32.08	174.73	32.08	148.50	113.13	130.97	117.56	130.97	113.13	
														150.35			118.87			
20	liquid								177.47	29.15	29.15	177.47		141.45	127.44	129.43	131.25	129.43	127.44	28.15
	solid								174.61	29.09	29.09	174.61		143.17	129.83	129.83	132.09	129.83	129.83	29.09
									176.96			176.96								
21	liquid								168.67	133.99	133.99	168.67		129.09	125.62	128.15	139.69	128.15	125.62	40.00
	solid								168.60	141.89	141.89	168.60		131.56	125.74	128.98	141.80	128.98	125.74	38.90
									168.68			168.68				129.42		129.42		
									170.99			170.99				130.11		130.11		
									171.94			171.94								
22	liquid													146.3	113.9	128.9	129.4	128.9	113.9	39.7
	solid													143	113	128	129	126	113	40.2
														145	114	126	132	128	114	
															117				117	

[a] Solvent, DMSO-d_6; liquid reference, TMS; solid reference, polyoxymethylene (80 ppm)

Table 5 *FTi.r.* wavenumbers characteristic of amic acid and imide groups

Wavenumber (cm^{-1})		Assignment
Acid	*Imide*	
3300/3200		ν(N–H)
	1770	ν(C=O) in-plane
	1710/1730	ν(C=O) out-of-plane
1560/1530		δ(N–H)
	1390	ν(C–N–C)
1270–1250		δ(N–H)
	700/740	δ(O=C–N)
650–630		δ(N–H)
Succinimide	*Maleimide*	
3060	3100	ν(=C–H)
1180	1150	ν(C–N–C)
810	830	δ(C=C) aromatic
670	690	δ(C=C) out-of-plane

tially unshielded. These carbons were sensitive to the chemical environment, since in compounds **18** and **19** there was a difference of about 3 ppm between a carbonyl carbon β or γ to a secondary amine.

The second region of interest is located between 110 and 120 ppm, in which aromatic ring carbon atoms β to an amine resonate. To our knowledge, this is the only region in which carbons specific to the Michael reaction can be unambiguously identified.

Finally, in the region of aliphatic carbons between 0 and 60 ppm, the chemical shifts of the CH_2 group in the pivot of the BMI prepolymer and in the diamine DDM in the initial mixture were very similar (40 ppm). It was very difficult to differentiate them in liquid ^{13}C n.m.r., even in high field. In addition, the study of the ^{13}C n.m.r. spectra of models **18** and **19** shows that the addition reactions led to the presence of two additional resonances (disappearance of carbons 2 and 3 of maleimide ring II and the appearance of carbons 2 and 3 of aspartimide ring II) at 37 and 52 ppm, the first merged with the CH_2 group of the pivot in solid-state ^{13}C n.m.r.

The addition reaction by a secondary amine (compound **20**) caused a shielding of the CH_2 carbon (C3) of $+5$ ppm and an unshielding of the methine carbon (C2) of -6 ppm in comparison to the addition of a primary amine.

When these results are summarized, it is seen that this region is a suitable molecular probe for mechanistically and kinetically following the different reactions expected in the BMI–primary amine systems shown in *Figure 1*.

Thus, in light of the insolubility of products after crosslinking, these model compounds were studied by solid-state ^{13}C n.m.r. (62–89 MHz) in CP/MAS. Comparing the solid- and liquid-state spectra enabled every line in the solid-state spectra to be attributed. Because of the good resolution (in some cases the lines split because of the presence of several crystalline systems), the conclusions reached concerning chemical shifts were also applicable to solid-state CP/MAS ^{13}C n.m.r. spectra, as will be seen below.

FT*i.r. study*

Since Fourier transform infra-red absorption spectroscopy is the most widely used technique in the literature[7], a detailed study was carried out with attributions of wavenumber maxima to pure and chemically defined model compounds, made possible by the high quality of the spectra. Attributions were made on the basis of published data[7] and by mutually comparing the spectra of our model compounds.

The data obtained from compounds **1–16** enabled the following conclusions to be drawn: the ring dehydration reaction of amic acid→imide can be followed with little difficulty, regardless of the initial anhydride. Similarly, the crosslinking reaction can be followed at the wavenumbers listed in *Table 5*: 1515 cm^{-1}, characteristic of the aromatic group common to both series, can be used as an internal standard in the mechanistic and kinetic study.

The study of the *FT*i.r. spectra of compounds **17** through **22** (*Figure 2*) confirmed results obtained with the monofunctional models. The spectra of the addition compounds also enabled certain conclusions to be reached concerning the fate of the different chemical functions present, transitory and/or created in the systems during polymerization by addition in the liquid state. The most significant wavenumbers are listed in *Table 6*.

These data show that it is possible to use infra-red absorption spectroscopy to follow the different overall reactions (disappearance of the amine from bismaleimide). On the contrary, it is difficult to identify unambiguously and to quantify the reactions leading to succinimide chains, without deconvoluting into basic lines different regions, e.g. 3500–2900, 1600–1450 and 1200–1100 cm^{-1}.

D.s.c. study

All the model compounds were subjected to a thermal study in order to determine their different zones of reactivity in the solid and molten states, in the temperature range of 50 to 350°C.

Succinic anhydride-based models (*1–8*). In the case of acids, only the ring dehydration reaction is expected, as shown in *Figure 3*. The results (*Table 7*) show that the melting points of the acids are higher than those of the imides (except for aniline). The presence of an alkyl substituent on the benzene ring has a non-negligible effect on the melting points of the acid and the imide: the loss of symmetry of the molecule (*ortho* and *meta* positions) reduced the melting points considerably. Ring dehydration reactions occurred just after the acid melted and most often the d.s.c. diagrams showed only the envelope of the two endothermic phenomena. Finally, the ring dehydration reaction occurred at high temperature in the liquid state, between 150 and 190°C.

Maleic anhydride-based models (*9–16*). In the temperature range studied in this work (50–350°C), several reaction mechanisms were expected: in the case of imides, only crosslinking was considered, while for the amic acid models, two reaction mechanisms were invoked. Thus, ring dehydration and crosslinking could be simultaneous or successive. The reaction temperatures obtained for the two products, amic acid and the corresponding imide, are listed in *Tables 8* and *9*.

Crosslinking reactions of the imide compounds began dynamically in the temperature range of 200–250°C. These reactions are exothermic with a maximum around 280°C, regardless of the carbon skeleton. In the case of the amic acid models, endothermic ring dehydration occurred simultaneously with the melting of the products, while the crosslinking reaction occurred at higher

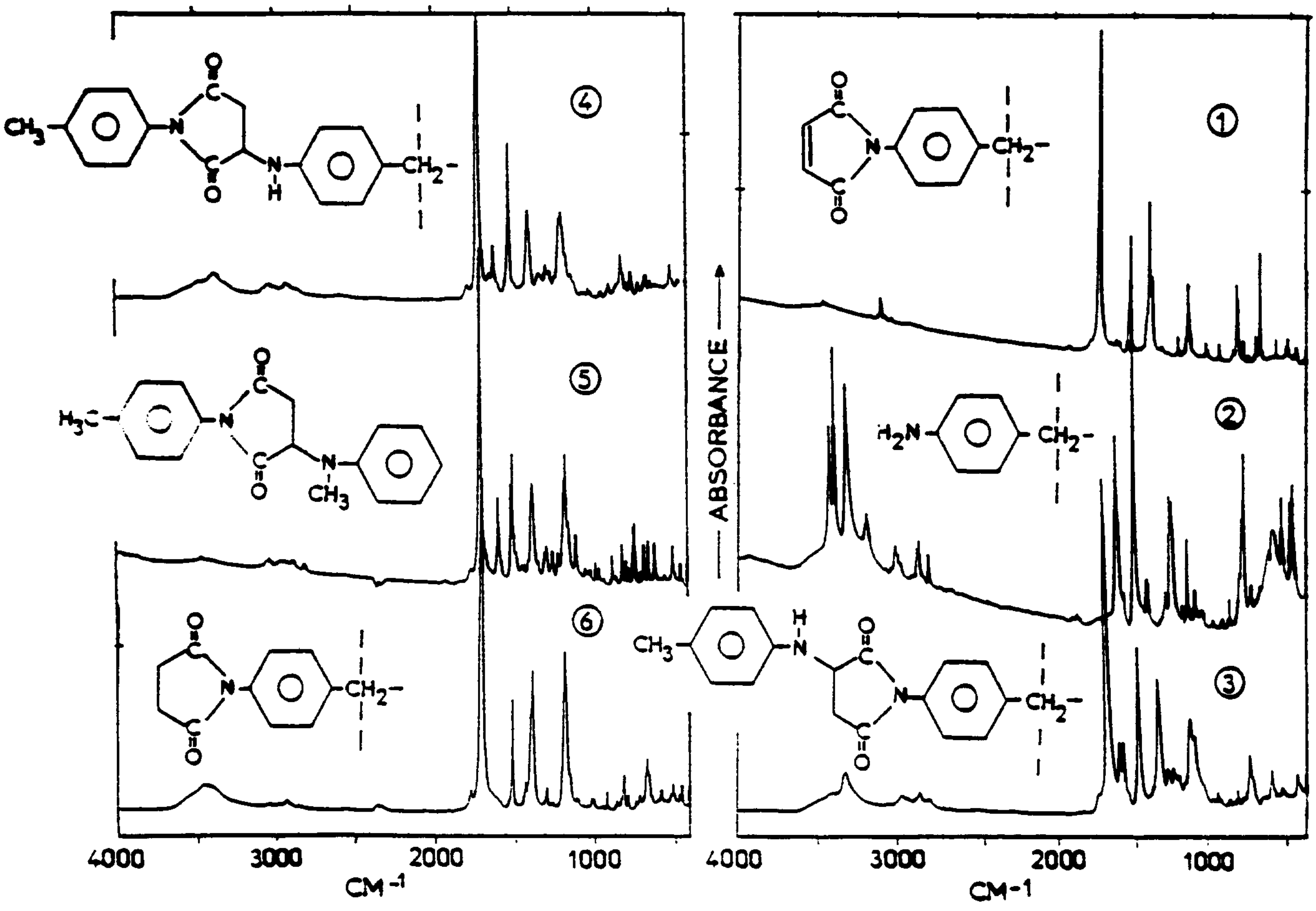


Figure 2 Infra-red spectra of model compounds **17**–**22**: (1) **21**, (2) **22**, (3) **18**, (4) **19**, (5) **20**, (6) **17**

Table 6 *FT*i.r. wavenumbers characteristic of succinimide and maleimide groups

Wavenumber (cm^{-1})	Assignment and compound
3450–3410	$\nu(NH_2)$ **22**
3380–3360	ν(N–H) **18**, **19**
3100–3090	ν(=C–H) (maleimide) **21**
1635	δ(N–H) **18**, **19**
1625	δ(N–H) **22**
1190–1180	ν(C–N–C) (succinimide) **17**–**20**
1145	ν(C–N–C) (maleimide) **21**
840	δ(C=C) (maleimide) **21**
820–800	δ(C–C) (succinimide) **17**–**20**
690	δ(=C–H) (maleimide) **21**

temperature, in agreement with results obtained with the imide models. Finally, as in the case of succinimide-based models, *ortho*-substituted compounds had lower melting points.

The results obtained with these two series of compounds are very instructive and show that there are two well defined zones of reactivity for the two reactions occurring in these systems, with crosslinking occurring at higher temperature.

The results obtained with the succinimide- and maleimide-based compounds enabled us to construct a specific cartography (solid and liquid states) of physicochemical data (n.m.r. and *FT*i.r.), leading to the unambiguous identification of the transitory species or those created in the reaction mixture.

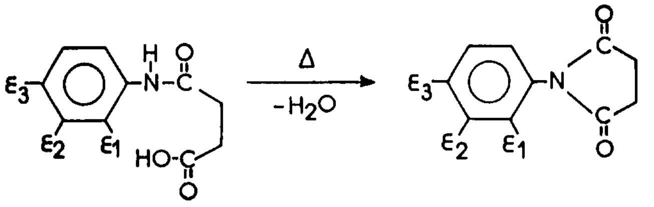


Figure 3 Pathway of the ring dehydration reaction

Table 7 Melting points and reaction temperatures of compounds 1–4

Compound	$T_{f,A}$ (°C)	$T_{f,I}$ (°C)	T_{dehyd} (°C)	$T_{dehyd,max}$ (°C)
1	152	158	^{a}	171
2	154	103	^{a}	167
3	138	114	^{a}	153
4	182	158	^{a}	196

[a] In the pic of $T_{f,A}$

These results were thus applied to the study of the polymerization of bismaleimide prepolymers in the presence of chain extenders.

RESULTS OF THE STUDY OF BMI–DDM SYSTEMS IN THE MOLTEN STATE: SIMULATING INDUSTRIAL SYSTEMS

Bismaleimide prepolymers[1] have the characteristic of yielding two types of polymerization in the presence of

Table 8 Melting points and reaction temperatures of compounds **9**–**12**

Compound	$T_{f,A}$ (°C)	$T_{dehyd,max}$ (°C)	T_{ret} (°C)	$T_{ret,max}$ (°C)
9	200	214	226	292
10	123	135	210	295
11	173	184	220	290
12	194	209	223	270

Table 9 Melting points and reaction temperatures of compounds **13**–**16**

Compound	T_f (°C)	T_{ret} (°C)	$T_{ret,max}$ (°C)
13	152	158	275
14	154	103	300
15	138	114	280
16	182	158	290

Table 10 D.s.c. results with the different systems studied

Systems	BMI/DDM	T_f (°C)	T_1 (°C)	T_{exo} (°C)	T_2 (°C)
A	1/0	150	176	207	227
B	1/1	75–110	125	178	275
C	2/1	120	139	200	262

an amine, depending on reaction conditions. The double bond of the maleimide ring is electron-poor as a result of the presence of α carbonyl groups, which favour nucleophilic addition. In the presence of mobile protons (amine type) a condensation reaction occurs with a linear extension of the chain (Michael reaction). At higher temperatures and if the ratio of reactive functions is not unity, a crosslinking reaction gives rise to a crosslinked insoluble product. This is why we were able to study a system simulating industrial resins[1] by applying the preceding physicochemical results obtained with compounds **1** through **22**.

Study of polymerization mechanisms

Mixtures of products were prepared at low temperature (cryogenic grinding in liquid nitrogen). Initial tests of mixing in solvent ($CHCl_3$) had shown that the reaction started and complexes (products–solvents) formed that were difficult to eliminate and subsequently introduced spectral artifacts, and above all erroneous mechanistic and kinetic results as a result of catalysis.

The cryo-ground powders were examined by *FT*i.r.: no change in the position and intensity of bands was observed, indicating that no chemical and/or complex reaction had occurred while the mixtures were being prepared.

Three different stoichiometric ratios were studied (*Table 10*). The three mixtures should normally simulate the different reactions expected for:

(i) crosslinking by homopolymerization (A);
(ii) chain elongation (B);
(iii) crosslinking by homopolymerization and chain elongation (C).

Study by dynamic d.s.c. The d.s.c. diagrams of systems A–C (*Figure 4*) show an initial dynamic d.s.c. endothermic transition due to melting of the systems, around 150°C (A), 75–110°C (B) and 120°C (C). Melting temperatures decreased in mixtures B and C. An exothermic transition occurred above the melting temperature and the following thermal transitions were characterized as being determinant (*Table 10*):

(i) T_1, the onset of polymerization;
(ii) T_{exo}, the temperature of the endothermic peak;
(iii) T_2, the temperature at the end of the reaction.

These values are not rigorous because the plots of tangents were difficult to determine as a result of poor baseline definition. The observed tendency nevertheless showed that, in the presence of mixtures, T_{exo} decreased considerably, in the resulting sequence:

$$T_{exo}(A) > T_{exo}(C) > T_{exo}(B)$$

With system A (BMI alone) there was a single exothermic transition, and in mixtures B and C the exotherms were binodal. These results confirm the occurrence of the reactions described in *Figure 1*.

During chain elongation reactions, a secondary amine group is created. In the presence of excess bismaleimide functions (system C), the secondary amine group can participate in a nucleophilic addition with the maleimide bond, creating a crosslinked product. According to

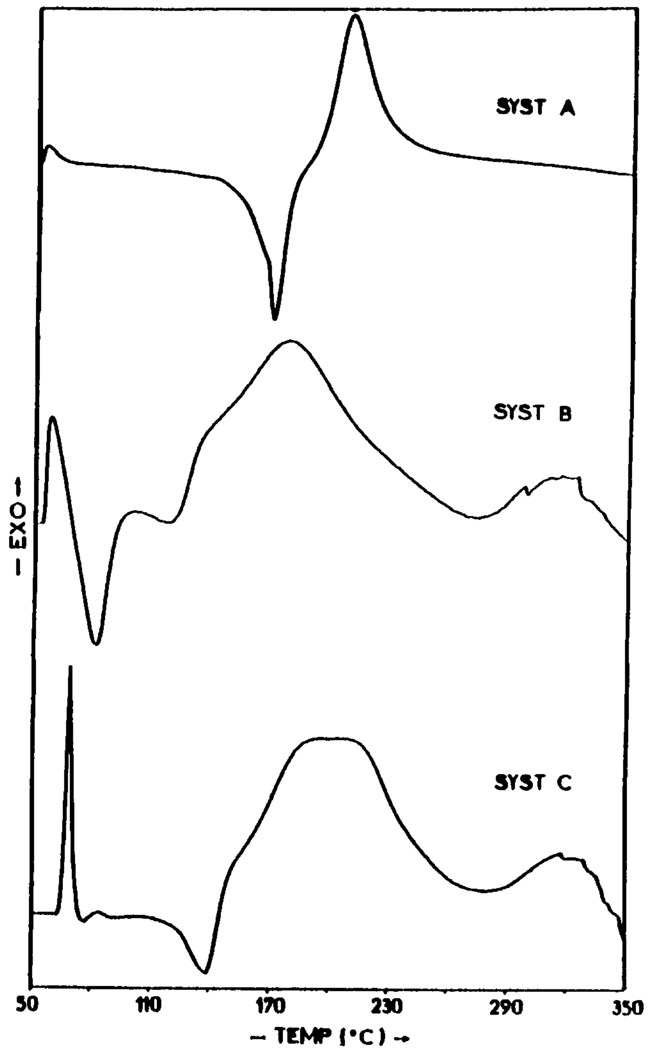


Figure 4 D.s.c. diagrams of the model systems

Varma *et al.*[8], the Michael reaction on a secondary amine occurs in the same zone of reactivity as the homopolymerization reaction of bismaleimides. We were unable to decide on the basis of only the d.s.c. diagrams. In addition, it did not seem reasonable to utilize total reaction ΔH since only ΔH of system A could be used. Furthermore, the result found for the system ($\Delta H = 107\,\mathrm{kJ\,mol^{-1}}$) differed from the published value ($90\,\mathrm{kJ\,mol^{-1}}$)[9,10], showing that the origin of products and their purity has a non-negligible influence on the thermal data of these systems.

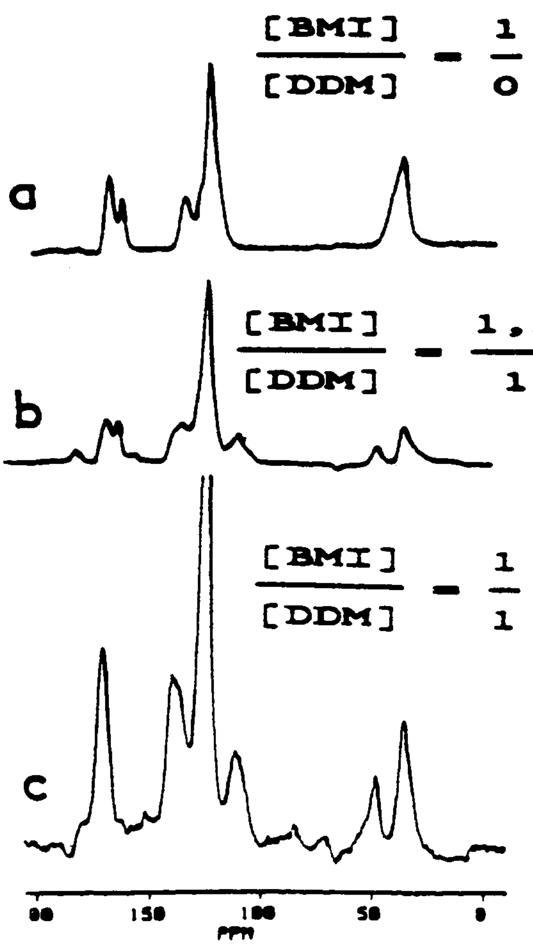


Figure 5 CP/MAS solid-state ^{13}C n.m.r. spectra of the systems: (a) pure BMI (4 h at 200°C); (b) BMI/DDM = 1.5 (1 h at 145°C); (c) BMI/DDM = 1 (1 h at 145°C)

Our conclusions from the d.s.c. study of the three systems are that the method cannot be used to follow the different reactions involved. The fact of mixing these products decreased the melting point and the temperature at which polymerization began. The study of the different mixing stoichiometries showed the presence of binodal polymerization exotherms, indicating that several reactions occurred in these systems in the temperature range of 100–350°C.

Solid-state CP/MAS ^{13}C n.m.r. study. The solid-state CP/MAS ^{13}C n.m.r. study of the different samples in the temperature range defined by the d.s.c. results confirmed certain mechanisms and furnished spectroscopic data for kinetically following these systems. *Figure 5a* is the solid-state ^{13}C n.m.r. spectrum of system A after a 4 h heat cycle at 200°C, *Figure 5b* is that for a BMI/DDM ratio of 1.5 and *Figure 5c* is the ^{13}C n.m.r. spectrum of system B.

Based on the reaction mechanisms presented above and on the spectra of the model compounds characteristic of each fragment, solid-state ^{13}C n.m.r. showed that certain regions are specific for chain polymerization and for crosslinking, simultaneously and/or in parallel. This was verified by carbonyl resonances at 169 and 175 ppm, resulting from carbonyls on residual bismaleimides and aspartimide carbonyls (after reaction), respectively. Similarly, the broad band at 115–118 ppm decreased with increasing amine concentration (*Figures 5b* and *5c*), becoming null in system A (*Figure 5a*). Finally, in the region of aliphatic carbons, resonance intensity around 40 ppm increased in low field when the homopolymerization reaction predominated, and increased in high field in the case of the Michael reaction. The peak at 52 ppm (*Figures 5b* and *5c*) resulted from carbon resonance of the methine group produced by the chain elongation reaction. *Figure 6* presents the significant results from the ^{13}C n.m.r. study of these compounds, enabling the different reactions to be followed in BMI resins in different heat cycles.

The spectra of systems A, B and C in the region of 160–175 ppm led us to attempt a quantification of the

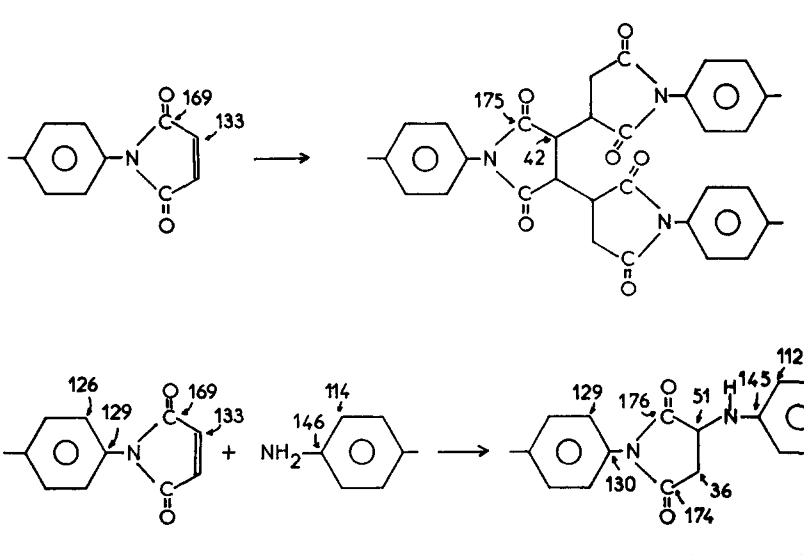


Figure 6 Significant chemical shifts used to follow the different reactions occurring in BMI/aromatic amine systems

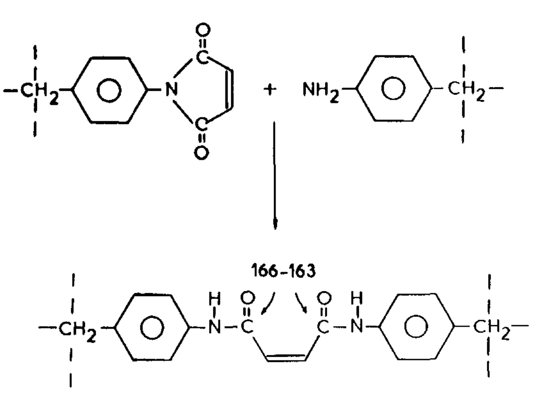


Figure 7 Reaction mechanism of aminolysis

different reactions, as a result of the presence of residual bismaleimide functions not having reacted in systems B and C. This region contained a broad peak apparently composed of two bands, around 172 and 166 ppm. Since the widths at half-height of the lines were different, we deconvoluted the spectra into basic lines. The results showed that there were three main lines, around 166 ppm (36%), 170 ppm (15%) and 174 ppm (47%). This would indicate that three carbonyls in different chemical environments were present in the polymerized product. The bands around 170 and 174 ppm corresponded to residual maleimide functions and to newly created aspartimide functions, respectively. This confirms the results obtained with line width. The line at 170 ppm was finer and corresponded to maleimides at chain extremities, which were more mobile than aspartimide or succinimide groups at the interior of the chain. The line at 166 ppm, on the other hand, was observed in none of our model compounds, suggesting the occurrence of a side reaction. When bismaleimide prepolymers were prepared in solvent, there were indications of an aminolysis reaction taking place (*Figure 7*). In this case, the carbonyl group is expected between 163 and 166 ppm and could correspond to this fragment. It is to be noted that this resonance, absent from the spectra of system A (BMI/DDM = 1/0), supports this hypothesis.

Kinetic studies

System A (BMI homopolymerization). The kinetics of this system were followed at 200°C for 25 h with CP/MAS ^{13}C n.m.r. and *FT*i.r. With the latter technique, BMI homopolymerization was characterized primarily by the opening of the double bond of the maleimide group. Once polymerized, the product presented the infra-red properties of the succinimide group. The increase and decrease of the ν(C–N–C) band at 1180 cm^{-1} (succinimide) and at 1145 cm^{-1} (maleimide) were followed. Since the broad band was complex, each spectrum was deconvoluted into basic lines in the region of 1250–1050 cm^{-1}. The surfaces of the deconvoluted bands enabled the percentages of the maleimide form to be calculated on the basis of the succinimide form.

The same samples were studied by solid-state ^{13}C n.m.r. in the form of a cryogenically ground powder. Considering the different spectral regions that could have been studied, a single region was chosen, that characteristic of carbonyls (160–190 ppm). Each spectrum was deconvoluted into basic lines, revealing three main lines that were attributed to the disappearance of maleimide and the appearance of succinimide by following the resonance surface changes of the signals from their carbonyls, at 169 and 176 ppm, respectively. The most important result, however, was the presence of a third resonance, weaker and centred on 172 ppm.

The *FT*i.r. and solid-state ^{13}C n.m.r. results (*Figure 8*) showed the 24 h changes in the percentages of maleimide and succinimide given by *FT*i.r. (changes in the bands at 1145 and 1180 cm^{-1}, respectively) and by the deconvolutions of the solid-state ^{13}C n.m.r. spectra. For the succinimide form, quantitative analysis by *FT*i.r. (band at 1180 cm^{-1}) and by solid-state ^{13}C n.m.r. (chemical shift of the carbonyl at 176 ppm) furnished similar results. Thus, the reaction had progressed by about 65% in succinimide groups after 24 h. When solid-state ^{13}C n.m.r. was used to follow the band at 172 ppm detected by deconvolution, on the other hand, the following result was obtained: its representative curve went through a maximum (12% of the total signal after 1 h at 200°C), then decreased and stabilized at 7% until the end of the reaction. This type of curve is characteristic of the formation and subsequent disappearance of a reaction intermediate. It could correspond to a low-mass molecule whose structure would be intermediate between the succinimide and maleimide forms, at least in terms of the carbonyl detected and its immediate environment. In light of this result, quantification of the maleimide form by solid-state ^{13}C n.m.r. (carbonyl at 169 ppm) and by *FT*i.r. (1145 cm^{-1}) differed by 10%. The general shape of the two curves was identical.

In an attempt to identify this reaction intermediate, we examined the soluble and insoluble fractions of each sample taken during kinetics. In each sample, the soluble and insoluble fractions were separated by extraction in boiling dimethylsulfoxide (DMSO). Spectra recorded were ^{1}H n.m.r. of the soluble fraction and solid-state ^{13}C n.m.r. of the insoluble fraction.

The ^{1}H n.m.r. spectra of the soluble fractions all contained the characteristic lines of initial, unreacted BMI (compound **21**). This would tend to indicate that the reaction intermediate detected in the kinetic study was insoluble in DMSO.

The solid-state ^{13}C n.m.r. study of the insoluble fraction was done in the same way as in the kinetic study (*Figure 9*). Similarly, after deconvolution of the 160–190 ppm region, three resonances were detected: 176 ppm corresponded to the carbonyl of the succinimide

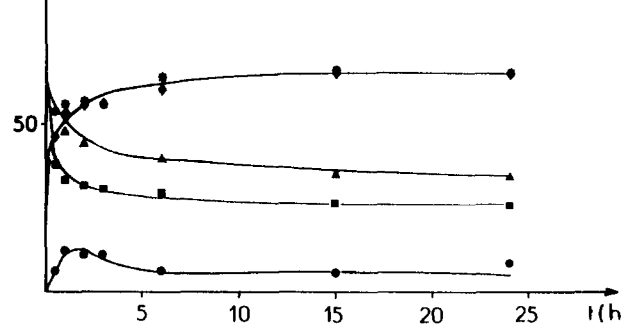


Figure 8 Following kinetics by solid-state n.m.r. and *FT*i.r. at 200°C: (◆) 176 ppm, (●) 172 ppm, (■) 169 ppm, (*) 1180 cm^{-1}, (▲) 1145 cm^{-1}

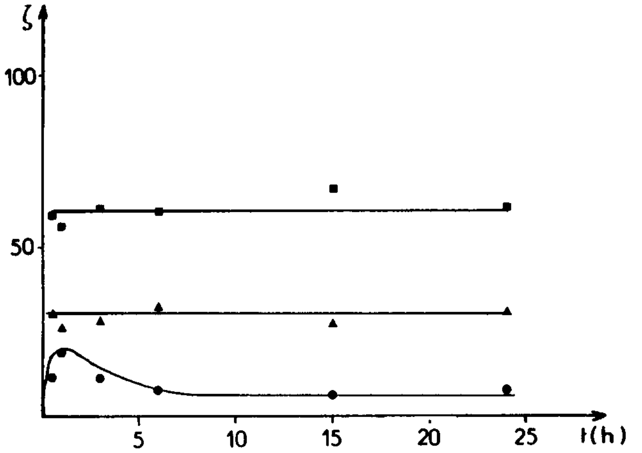


Figure 9 Following kinetics of the insoluble fraction by solid-state n.m.r.: (■) 176 ppm, (●) 172 ppm, (▲) 169 ppm

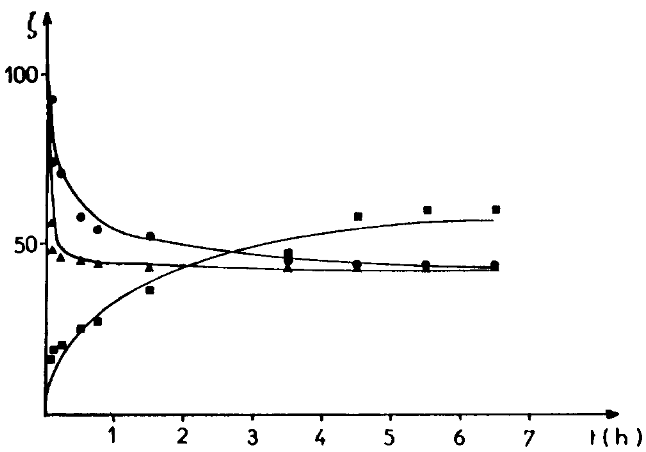


Figure 10 Following kinetics of system C by solid *FT*i.r.: (■) 1180 cm^{-1}, (●) 1145 cm^{-1}, (▲) 3338 cm^{-1}

form, 169 ppm was attributed to the carbonyl of the maleimide function and a third was centred on 172 ppm. Quantitative results of deconvolutions as a function of time (*Figure 9*) showed that the percentages of succinimide and maleimide carbonyls in the crosslinked product remained stable. There was a residual mean of 65% succinimide groups and 30% maleimide groups, results consistent with prior findings (*Figure 8*). This is equivalent to about two succinimides per maleimide.

The second result involves the curve characterizing the intermediate detected in the kinetic study. The shape of the curve, depicting changes at 172 ppm characterizing one type of carbonyl in a specific environment, was the same as that found in *Figure 8*. Its maximum was at around 1 h and we believe it to be a low-mass but crosslinked product. Comparison of the curves shows that maximum advancement of the reaction at the temperature adopted for this work was reached after 5 h. This indicates that the mobility of the system after 5 h was low, as was the probability of encounter among reactive species. In order to obtain a greater degree of advancement, it will be necessary to define a more appropriate thermal cycle for these systems.

Study of system C (BMI/DDM = 2/1). This system was followed for 7 h at 150°C. At this temperature, the addition reaction of the diamine on maleimide groups was preferentially followed. Kinetics were followed by *FT*i.r., measuring the bands characteristic of succinimide (1180 cm^{-1}) and maleimide functions (1145 cm^{-1}) in comparison to a reference band at 1512 cm^{-1}. Only the last sample at 6.5 h was analysed by solid-state ^{13}C n.m.r. As before, the broad band of carbonyl groups was deconvoluted into basic lines (*Figure 10*).

Using infra-red absorption spectroscopy, we could follow the disappearance of maleimide and primary amine groups and the appearance of succinimide groups. The initial analysis of these curves showed that the amine disappeared more rapidly than bismaleimide. Since bismaleimide was present in excess, this result is consistent with predicted kinetics, with the equilibrium shifted towards the addition product. The curves stabilized after 4 h of an isothermal heat cycle, however, and appeared to be terminated beyond that time, since there were no further changes in the intensity of infra-red bands.

Solid-state ^{13}C n.m.r. had previously shown that in the sample polymerized for 6.5 h at 150°C, there were three resonances in the region of carbonyls:

(i) 175 ppm, attributable to succinimide fragments;
(ii) 169 ppm, attributable to residual maleimide fragments;
(iii) 166 ppm, attributable to maleimide fragments from ring opening by aminolysis.

There is some apparent divergence between the results obtained with *FT*i.r. and those with ^{13}C n.m.r., except if we add for the maleimide fraction the intensities of bands at 166 and 169 ppm, characteristic of a cyclized and/or open maleimide function, which would agree with the advancement of amine reactivity.

CONCLUSIONS

Using model compounds characteristic of the different reactions expected in the polymerization of bismaleimide telechelic prepolymers in the presence of an aromatic amine, we have shown that an addition mechanism (Michael reaction) between 130 and 150°C leads to chain extension by either addition or opening of the maleimide ring (aminolysis). At higher temperatures, on the other hand, maleimide–maleimide crosslinking reactions may occur, depending on stoichiometries.

These results were obtained using *FT*i.r. and solid-state ^{13}C n.m.r. Although concordance between the techniques was not always consistent, they could be used to furnish a shape to the isothermal kinetic curves.

Solid-state ^{13}C n.m.r. results are in our opinion the most interesting, since the spectra of crosslinked products contain several regions in which the different reactions occurring in the system can be followed. Quantifying the residual chemical species or those created can be accomplished as a result of the high quality of the spectra. We have shown that caution is required when utilizing d.s.c. or *FT*i.r. analyses. The latter should be corrected on the basis of n.m.r. results, where it is perfectly possible to determine reaction advancement, e.g. by using the region of carbonyls.

REFERENCES

1 Bargain, M. Br. Pat. Spec. 338094, 1964 (Rhône-Poulenc)
2 King, J. J., Chaudhari, M. A. and Bahir, S. A. Proc. 29th Natl. SAMPE Congr. 1984, p. 392
3 Chaudhari, M. A., Galvin, C. J. and King, J. J. Proc. 30th Natl. SAMPE Congr. 1985, p. 735
4 Denny, L. A., Goldfab, J. J. and Farr, M. P. *Am. Chem. Soc., Div. Polym. Mater., Sci. Eng. Prepr.* 1987, 56565
5 Carduner, R. K. and Chattha, M. S. *Am. Chem. Soc., Div. Polym. Mater., Sci. Eng. Prepr.* 1987, 56660
6 Shaw, S. J. in 'Recent Advances in Polyimides Science and Technology' (Eds. W. D. Weber and M. R. Gupta), Society of Plastics Engineers, Roughkeepsie, NY, 1987, p. 290
7 Giglio, C. D., Gautier, M. and Jasse, B. *J. Polym. Sci.* 1984, **29**, 1771 and references therein
8 Varma, I. K. and Timari, R. *J. Thermal Anal.* 1987, **32**, 1023 and references therein
9 Whiti, J. C., Scara, M. D. and Snider, A. *J. Appl. Polym. Sci.* 1984, **29**, 1819
10 Stenzenberger, H. in 'Polyimides' (Ed. D. Wilson), Chapman and Hall, New York, 1990, p. 78 and references therein