Synthesis and properties of octafluorobenzidine bis-maleimide and of its reaction products with fluorinated diamines

Alok C. Misra and Giuliana Tesoro*
Polytechnic University, 333 Jay Street, Brooklyn, NY 11201, USA
(Received 31 January 1991; revised 3 March 1991; accepted 9 May 1991)

Octafluorobenzidine bis-maleimide (OFB/BM) and its Michael adducts with fluorine-containing diamines have been prepared and characterized. The physical, thermal and electrical properties of the polymers have been determined before and after thermal polymerization (curing). Products from different diamines and OFB/BM exhibited similar properties in spite of the different fluorine content and bis-maleimide/diamine ratios.

(Keywords: polyaspartimides; fluorine-containing diamines; bis-maleimide; octafluorobenzidine: Michael reaction; thermal properties; electrical properties)

INTRODUCTION

Fluorine-containing aromatic polyimides have been of interest in the microelectronics industry as insulating layers between levels of thin film wiring in high density electronic packaging because of their thermal and chemical resistance, low dielectric constant and retention of mechanical properties over the processing temperature range. Several investigators[1–3] have focused on polyimides prepared by condensation reactions of fluorinated diamines with dianhydrides. Polymers prepared from 2,2′-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF) and various dianhydrides have been of particular interest[4]. However, in spite of extensive work on the synthesis and polymerization of bis-maleimides of varying structure[5], addition polyimides of high fluorine content have not been reported.

In conjunction with our work on fluorine-containing condensation polyimides[6], it was of interest to study some polyimides prepared from the bis-maleimide of octafluorobenzidine (OFB). Hougham *et al.*[7] have reported that the synthesis of a condensation polyimide from OFB and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride at 150°C yielded a film-forming polymer. Its low molecular weight was attributed to the low reactivity of the diamine.

In addition, since homopolymers of aromatic bismaleimides are inherently brittle due to extensive crosslinking, products of the Michael addition reaction of several fluorine-containing aromatic diamines with the bis-maleimide prepared from OFB (polyaspartimides) were explored in this study.

EXPERIMENTAL

Materials

4,4′-Diaminooctafluorobiphenyl (octafluorobenzidine, OFB, Aldrich) was recrystallized from methylene chloride three times after charcoal treatment so as to obtain a colourless crystalline product. Maleic anhydride (MA) (Aldrich) was recrystallized from acetic anhydride. BDAF was obtained from Du Pont and was recrystallized from absolute alcohol. Diamines *p*-bis (*p*-aminophenoxy) octafluorobiphenyl (F_8) and *p*-bis (*p*-aminophenoxy) tetrafluorobenzene (F_4), were synthesized by a reported procedure[8,9]. The structures of the monomers used are given in *Figure 1*. Solvents were of highest purity grade available from Aldrich and used as received. The reactions described below were carried out on a scale of 1–5 g.

Synthesis of OFB-bis-maleimide (OFB-BM)

The bis-maleimide was prepared by a two-step and a one-step method (*Figure 1*).

In the two-step method, the well known Searle procedure[10] was modified to give an improved yield. OFB and MA (1:5 molar ratio) were dissolved separately in dry chloroform and then mixed under nitrogen to give a yellow solution. The solvent was removed and the residue was kept at 80°C for 5 h. The crude pale yellow product was washed several times with boiling chloroform to remove unreacted material. Recrystallization from ethanol–water (70/30) afforded a white crystalline compound, the desired bis-maleamic acid (yield 58–60%), m.p. 202–203°C. The structure was confirmed by i.r., n.m.r. and elemental analysis. The bis-maleamic acid was chemically cyclized to bis-maleimide with fused sodium acetate and acetic anhydride in dimethylformamide (DMF) as reported by Mellissaris and Mikroyannidis[11]. An off white product was obtained after charcoal treatment and repeated crystallizations from acetone (yield 25–30%).

In the one-step method, the procedure of Vygodski *et al.*[12] was followed, wherein OFB and MA (1:5 molar ratio) were reacted by refluxing in glacial acetic acid for 15 h under nitrogen. The reaction product was separated by precipitating in ice–water, filtered and washed

---

* To whom correspondence should be addressed

0032–3861/92/051083–07

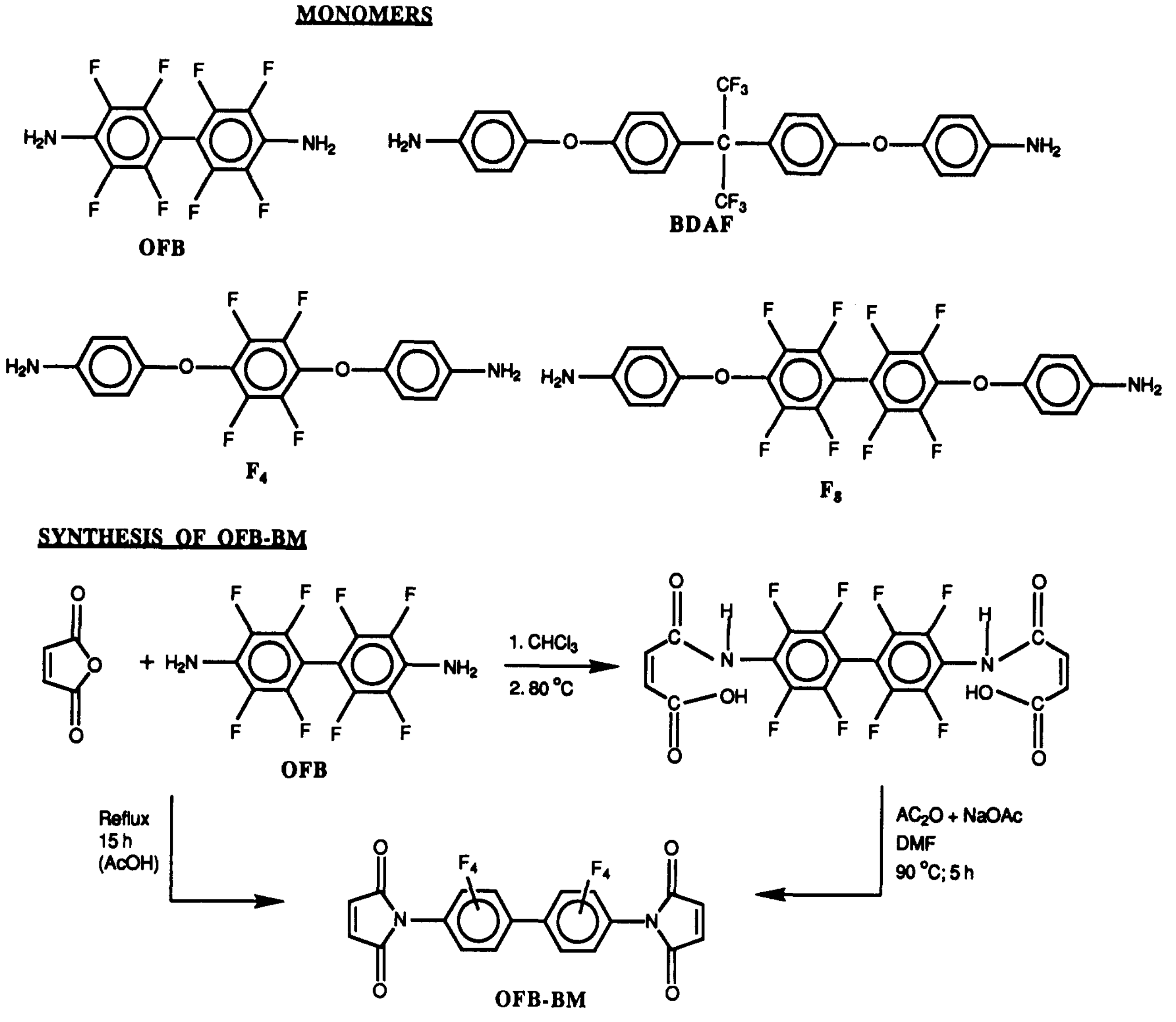

Figure 1 Monomers used and synthesis of OFB-BM

repeatedly with dilute sodium bicarbonate solution and with water. Recrystallization from acetone afforded a white crystalline product (yield 53–55%), m.p. 281–83°C. Elemental analysis: C calc., 49.1%, found, 48.54%; H calc., 0.82%, found, 0.87%; F calc., 31.14%, found, 31.25%.

Reaction of OFB-BM with aromatic diamines

The Michael addition reaction of amine to the double bonds of the bis-maleimide was carried out using the procedure of Crivello[13] at molar ratios of OFB-BM to diamine of 2 : 1 and 1 : 1 (*Figure 2*).

The required amount of diamine was dissolved in *m*-cresol in a three-necked flask with stirring under nitrogen and the solution was heated in an oil bath to 100–110°C. The required amount of OFB-BM and a catalytic amount of glacial acetic acid were added, and the amount of solvent was adjusted so as to give a 18–19% w/v concentration of the reactants. After 5 days at 100–110°C, the solution became viscous and dark brown in colour. The product was separated by pouring into methanol and washing with methanol until free from cresol. The product was purified first by precipitating from tetrahydrofuran (THF)/hexane, then by treatment with absolute ethanol at 60–70°C for 15 min and finally by washing with hot absolute ethanol (yield, 53–55%; brown in colour).

Characterization

The Fourier transform infra-red (*FT*i.r.) spectra of the samples (6–8% concentration in KBr) were recorded in a diffuse reflectance mode using a Biorad FTS-60 *FT*i.r. spectrometer. The diffuse reflectance attachment was supplied by Harrick Corp. (model DRA-3CD). The spectra were taken at 4 cm^{-1} resolution and 128 scans. Peak intensities are reported in Kubelka–Munk (K–M) units.

The molecular weight was measured at 25 ± 0.01°C on a Waters Associated model 244 GPC equipped with a refractive index detector using THF as a mobile phase at a flow rate of 1 ml min^{-1}. The molecular weights are relative to polystyrene standard and the Styragel columns connected in series were 10000, 500 and 100 Å.

The curing behaviour was studied by d.s.c. (Du Pont 9900) at a heating rate of 20°C min^{-1} in nitrogen. The thermal decomposition studies in nitrogen were carried out on a Stanton Redcroft thermobalance 706 at a heating rate of 10°C min^{-1} and a gas flow rate of 50 ml min^{-1}.

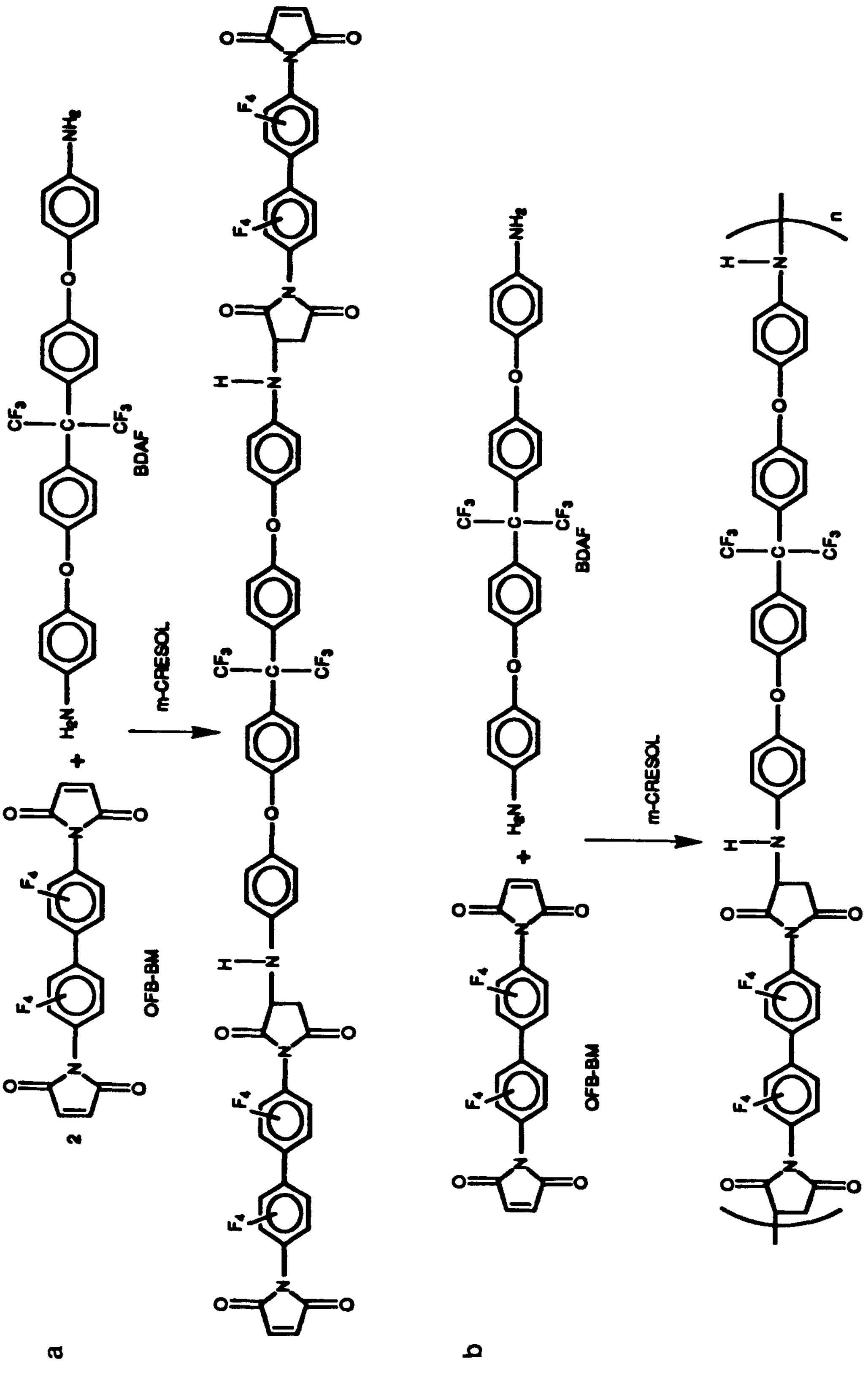

Figure 2 Michael reaction of OFB-BM with BBDAF at (a) 2/1 and (b) 1/1 molar ratio

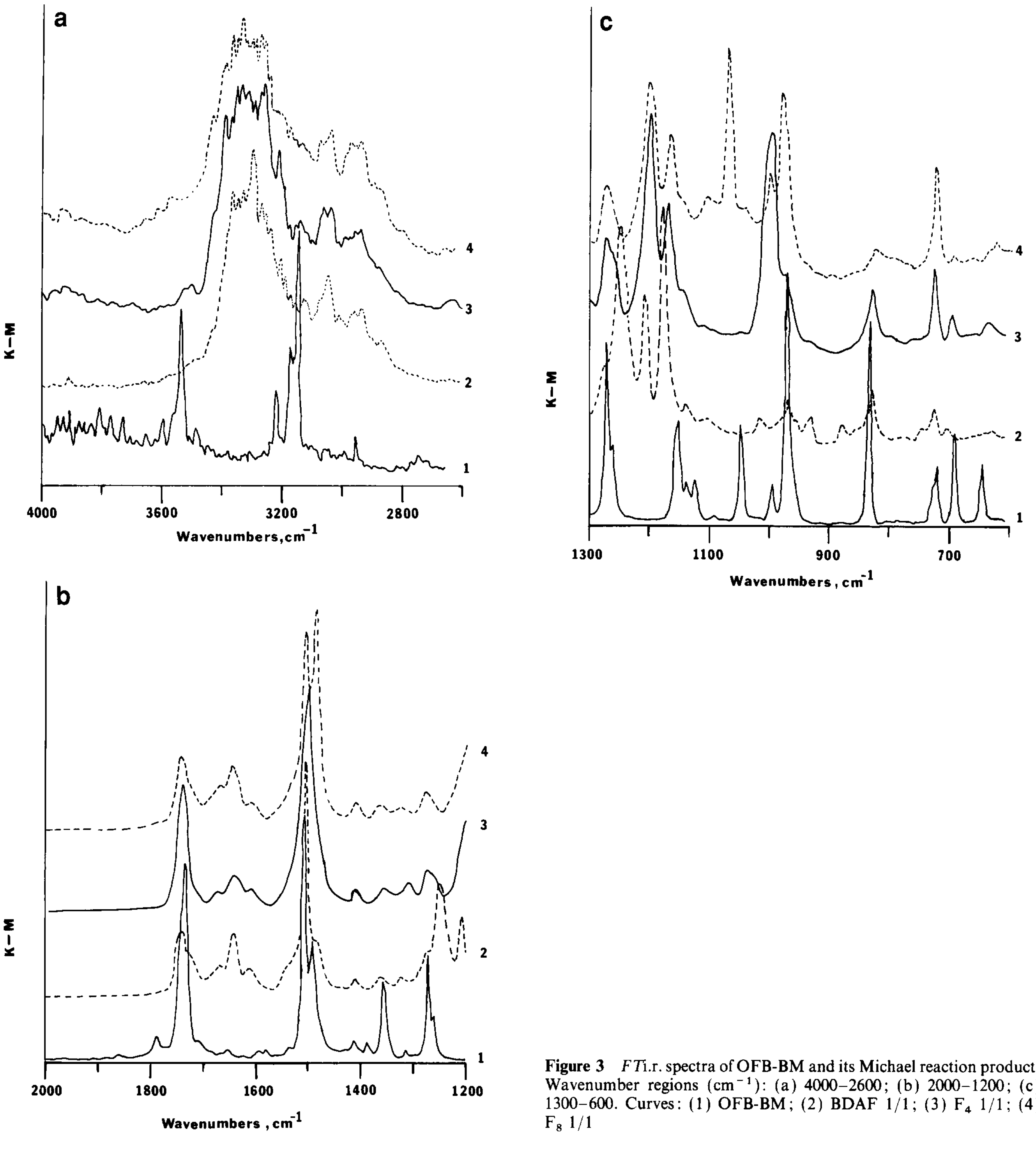

Figure 3 *FT*i.r. spectra of OFB-BM and its Michael reaction product. Wavenumber regions (cm^{-1}): (a) 4000–2600; (b) 2000–1200; (c) 1300–600. Curves: (1) OFB-BM; (2) BDAF 1/1; (3) F_4 1/1; (4) F_8 1/1

The dielectric measurements on films of cured products were carried out by Matech Associates at 100 kHz, at room temperature, and at 100, 250 and 300°C, using a set of Rutherford Research micrometer electrodes (model 1592-2T). Samples were preconditioned at 22°C and 50% relative humidity.

RESULTS AND DISCUSSION

Synthesis of OFB-BM

OFB-BM was synthesized by two methods as detailed in the Experimental section (*Figure 1*). The one-step method, i.e. refluxing in glacial acetic acid, gave a cleaner product and higher yield compared to the two-step procedure. The lower product yield in the conventional two-step method may have resulted from the low reactivity of the amino groups of the OFB, in the presence of *ortho* substitution by fluorine. In fact, the bis-maleamic acid was only formed in the MA melt. The product obtained from the one-step method was used throughout this study.

The *FT*i.r. spectrum of OFB-BM shows all the characteristic bands of bis-maleimide, namely: in the region 4000–2400 cm^{-1} (*Figure 3a*) a strong intensity band at ~3090 cm^{-1} due to ν(H–C=) of the maleimide ring and at ~3500 cm^{-1} (medium) due to harmonic ν(C=O); in the 2000–600 cm^{-1} region (*Figures 3b* and *c*) a very strong band at ~1730 cm^{-1} associated with ν(C=O) of the imide ring and at ~1155 cm^{-1} (strong)

Table 1 Chemical properties of Michael reaction products from OFB-BM

Michael reaction product		Elemental anslysis[a]			Molecular weight		
Diamine	Ratio of OFB-BM to diamine	%C	%H	%F	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
BDAF	1/1	56.26	2.65	22.53	17898	8482	2.11
		(55.86)	(2.34)	(26.57)			
	2/1	53.76	2.21	22.99	9315	3763	2.47
		(53.6)	(1.83)	(28.09)			
F_4	1/1	53.52	2.17	24.98	14309	7571	1.89
		(54.26)	(2.05)	(26.0)			
	2/1	52.35	1.87	24.79	8918	4437	2.01
		(52.56)	(1.64)	(27.7)			
F_8	1/1	52.54	1.92	25.26	15613	7572	2.06
		(52.71)	(1.58)	(30.4)			
	2/1	51.90	1.52	26.36	8399	3981	2.11
		(51.5)	(1.33)	(30.6)			

[a] Calculated values are in parentheses. Although experimental values for C and H are acceptable, the value for fluorine is consistently 3–5% lower than calculated. We have no explanation for this discrepancy

due to ν(C–N–C) of the maleimide ring. Other bands of maleimide ring unsaturation were also identified: at $\sim 830\ \mathrm{cm}^{-1}$ (strong) due to the out-of-plane hydrogen deformation of a *cis*-disubstituted double bond of a maleimide group[14] and at $\sim 690\ \mathrm{cm}^{-1}$ (strong) characteristic of the maleimide double bond[15]. The bands associated with the aromatic ring and aromatic C–F were also present.

The ^{1}H n.m.r. of OFB-BM (200 mHz; solvent acetone-d6 and TMS internal reference) showed a sharp singlet at δ 7.32 ppm due to the olefinic proton of the bis-maleimide ring.

Copolymers of OFB-BM with aromatic diamines

Copolymerization of OFB-BM with fluorinated aromatic diamines in a 1/1 and 2/1 molar ratio in *m*-cresol proceeded as illustrated schematically in *Figure 2* for the reaction of BDAF, yielding brown products.

The *FT*i.r. spectra of Michael adducts in a 1/1 molar ratio are shown in *Figures 3a–c*. The spectra of the products in a 2/1 molar ratio were essentially the same as those of products in a 1/1 molar ratio. Some of the characteristic differences observed in the spectra of the Michael reaction products compared to the spectrum of OFB-BM are as follows: there is a broad band of medium to strong intensity at $\sim 1640\ \mathrm{cm}^{-1}$ which might be due to –NH deformation, suggesting the formation of a succinimide group; a strong intensity band at $\sim 1200\ \mathrm{cm}^{-1}$ associated with the ν(C–N–C) of succinimide, whereas the band due to ν(C–N–C) of maleimide shifted to $\sim 1170\ \mathrm{cm}^{-1}$ (in OFB-BM at $\sim 1155\ \mathrm{cm}^{-1}$).

Weak intensity bands at ~ 830 and $690\ \mathrm{cm}^{-1}$ (bis-maleimide unsaturation) were also present, presumably due to unreacted bis-maleimide. A strong intensity band at $\sim 1245\ \mathrm{cm}^{-1}$ in the BDAF reaction products may be assigned to the ν(C–F) band of the hexafluoroisopropylidene group.

In the higher region (2500–4000 cm^{-1}) ν(NH) was present at $\sim 3300\ \mathrm{cm}^{-1}$. However, other bands could not be assigned with certainty (due to the presence of absorbed moisture).

The molecular weights of the Michael reaction addition products (*Table 1*) are within reasonable limits for products made with a 1/1 molar ratio. However, with the 2/1 molar ratio molecular weights are unexpectedly high. Leung *et al.*[16] have also reported higher molecular weights in the reaction of 1,1′-(methylene-4,1-phenylene) bis-maleimide with methylene dianiline using a 2/1 molar ratio. It appears that the double bonds of bis-maleimide not only react with diamine, but undergo homopolymerization as has been observed by Nagai *et al.*[15].

Curing behaviour

The curing behaviour of OFB-BM and of the products of Michael reactions was investigated by d.s.c. (*Table 2*). In all instances, there was no endothermic transition except in the case of OFB-BM, where there was a sharp endotherm at ~282°C, presumably due to melting. The OFB-BM and Michael reaction products exhibited exotherms between 285°C and 390°C. These were absent in the cured materials, and therefore seem to be associated with a curing reaction of residual double bonds in the bis-maleimide. The onset temperature of the curing exotherm in OFB-BM is 284.5°C and this shifts to higher temperature for the Michael reaction products (*Table 2*).

In general, the higher curing onset temperature in Michael reaction products can be attributed to the presence of an increased amount of fluorine substitution between the maleimide moieties, which by virtue of its electron-withdrawing character decreases the reactivity of maleimide double bonds. Further, an increase in the molecular weight of the structure between two terminating imide groups may also contribute to an increase in the onset temperature[14].

The peak temperature of the curing exotherm is marginally higher for some of the Michael reaction products as compared to OFB-BM.

Based on these results, the following curing profile was selected for films of these polymers from *N*-methyl pyrrolidone (NMP) solution (at a concentration of 20% w/v) on silicon wafers: 100°C, overnight, then 150, 200 and 250°C for 6 h each, followed by 300°C for 15 min.

Table 2 Thermal behaviour of OFB-BM and its Michael reaction adducts

Michael reaction product		Curing exotherm (d.s.c.)		Thermal decomposition (nitrogen)			
				T_b (°C)[a]		Residue at 600°C (%)	
Diamine	Ratio of OFB-BM to diamine	T_{onset}	T_{peak}	Uncured	Cured	Uncured	Cured
–	–	284.5	337.1	295	470	29	60
BDAF	1/1	298.2	343.7	315	522	49	78
	2/1	300.9	344.9	341	350	55	60
F_4	1/1	301.7	340.1	315	450	50	63
	2/1	285.8	335.4	330	335	50	60
F_8	1/1	312.3	349.7	318	490	52	69
	2/1	298.9	338.8	340	340	50	62

[a] T_b, temperature of extrapolated beginning of weight loss

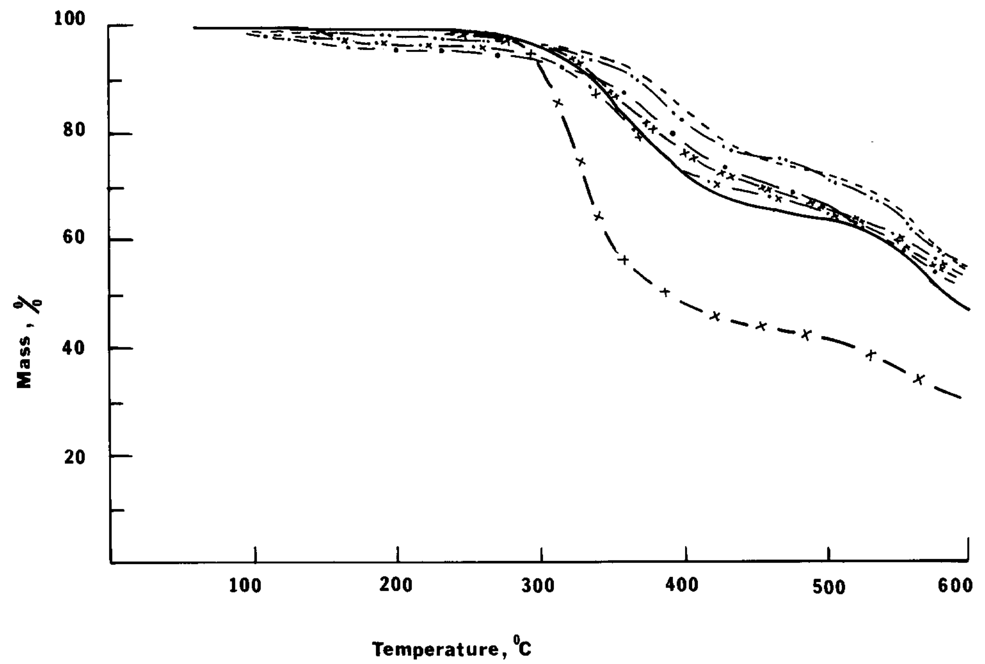

Figure 4 Thermogravimetric curves of uncured OFB-BM and Michael reaction products in nitrogen: (— ×) OFB-BM; (—) BDAF 1/1; (— —) BDAF 2/1; (– × ×) F_4 1/1; (— ·) F_4 2/1; (— · ×) F_8 1/1; (– · ·) F_8 2/1

The d.s.c. scans of cured polymers did not show any thermal transitions (endo, exo or glass transition) up to 350°C.

All films were brown in colour and were self-supporting.

Thermal behaviour

The uncured OFB-BM and Michael reaction products degrade in nitrogen by a two-step process, the first step occurring between 300°C and 450°C with a 20–30% weight loss (except OFB-BM where a 50% weight loss was observed after the first step) (*Table 2*, *Figure 4*). The second step begins at ~500°C and 50–55% residue remains at 600°C (except for OFB-BM). The degradation starts at higher temperature in the Michael reaction products as compared to OFB-BM and it is greater for 2/1 molar ratio products as compared to 1/1 molar ratio products. However, the amount of residue left in all Michael reaction products is almost the same, thereby suggesting that the major decomposition path is the same for uncured Michael reaction products generally.

The decomposition pathway changed after curing of OFB-BM and of its diamine adducts prepared at 1/1 molar ratio to a one-step process with an increase in onset temperature of degradation (an increase of 100–200°C) as compared to uncured material (*Table 2*, *Figure 5*). Higher amounts of residue remained in the cured 1/1 reaction products, reflecting higher thermal stability. Unexpectedly, the cured products from Michael reaction at 2/1 molar ratio exhibited behaviour similar to that of uncured material during decomposition. However, thermal stability was increased in the 2/1 reaction products after curing, since a higher amount of residue remained as compared to residue for uncured materials in this case also (*Table 2*).

The dielectric constant and dissipation factor of the films from Michael reaction products vary from 2.84 to 3.20 and 0.0026 to 0.0045, respectively, over the temperature range studied at 100 kHz (*Table 3*). In all products, the dielectric constant increases with temperature, except in the products from BDAF where it is unaffected up to 100°C. For all the products investigated

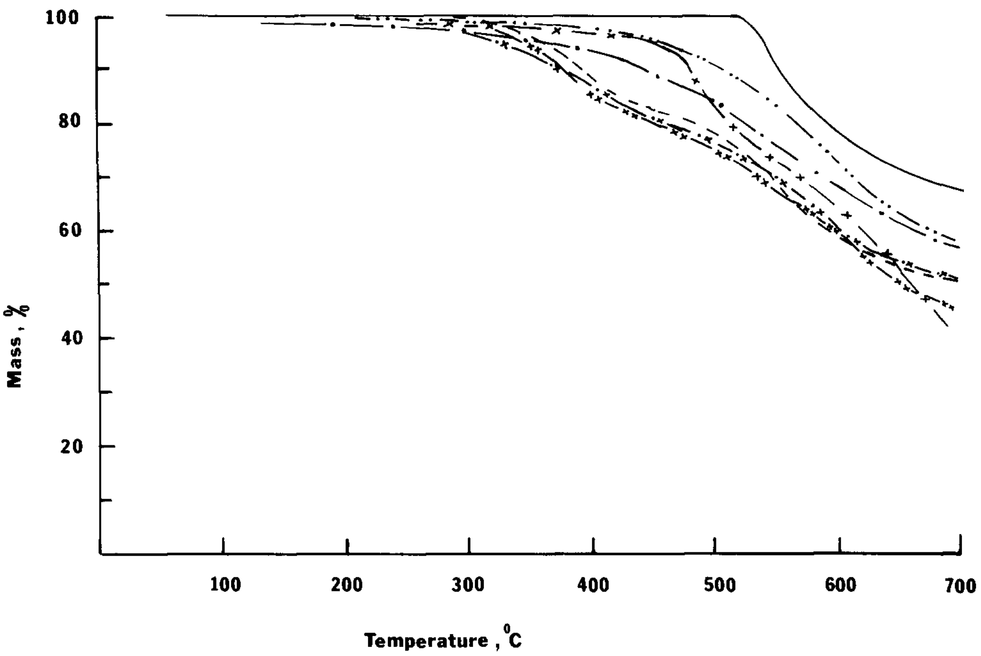

Figure 5 Thermogravimetric curves of uncured OFB-BM and Michael reaction products in nitrogen: (— ×) OFB-BM; (—) BDAF 1/1; (— —) BDAF 2/1; (— ·) F_4 1/1; (— × ×) F_4 2/1; (— · ·) F_8 1/1; (– · ×) F_8 2/1

Table 3 Dielectric behaviour of film from Michael reaction products

Diamine	Ratio of OFB-BM to diamine	Dielectric constant (dissipation factor) at RT	100°C	250°C	300°C
BDAF	1/1	2.90	2.89	3.09	3.14
		(0.0028)	(0.0027)	(0.0035)	(0.0045)
	2/1	2.93	2.93	3.16	3.17
		(0.0027)	(0.0026)	(010035)	(0.0043)
F_4	1/1	2.91	2.96	3.08	3.17
		(0.0026)	(0.0029)	(0.0036)	(0.0042)
	2/1	2.92	3.00	3.13	3.18
		(0.0026)	(0.0026)	(0.0032)	(0.0045)
F_8	1/1	2.84	2.91	3.10	3.19
		(0.0028)	(0.0028)	(0.0034)	(0.0044)
	2/1	2.88	2.97	3.08	3.20
		(0.0028)	(0.0032)	(0.0034)	(0.0045)

here, only small differences in dielectric behaviour were observed. This may be due to the fact that essentially all the fluorine is present as substituents in aromatic rings and it may have an effect on dielectric behaviour up to certain fluorine concentration and then level off. Work is in progress to study the mechanism by which the incorporation of fluorine lowers the dielectric constant in polyimides[17].

ACKNOWLEDGEMENT

Financial support for this work from the IBM Corporation (Fishkill Facility) is gratefully acknowledged.

REFERENCES

1 Mittal, K. L. (Ed.) 'Polyimides—Synthesis, Characterization and Applications', Vols 1 and 2, Plenum Press, New York, 1984
2 Weber, W. D. and Gupta, M. R. (Eds) 'Recent Advances in Polyimide Science and Technology', Society of Plastics Engineers, Brookfield, 1987
3 Feger, C., Khojasteh, M. and McGrath, J. E. (Eds) 'Polyimides—Materials, Chemistry and Characterization', Elsevier, Amsterdam, 1989
4 Jones, R. J. and Silverman, E. M. *SAMPE J.* 1989, **25**, 41
5 Stenzenberger, H. *Br. Polym. J.* 1988, **20**, 383
6 Misra, A. C., Tesoro, G. C., Hougham, G. and Pendharkar, S. *Polymer* 1992, **33**, 1078
7 Hougham, G., Tesoro, G. and Shaw, J. in 'Polyimides—Materials, Chemistry and Characterization', (Eds C. Feger, M. Khojasteh, and J. E. McGrath), Elsevier, Amsterdam, 1989, pp. 465–477
8 Borodin, A. E. and Malichenko, B. F. *Dopov. Akad. Nauk UKZ RSR Ser. Geol. Khim. Biol.* 1978, **8**, 710; **9**, 819
9 Kolchina, E. F., Ogneva, L. N., Sheremet, O. P. and Gerasimova, N. *IZV Sib. Otb Akad. Nauk USSR Ser. Khim Nauk* 1981, **2**, 122
10 Searle, N. E. *US Pat 2444536*, 1948; *US Pat 2467835*, 1949
11 Mellissaris, A. P. and Mikroyannidis, J. A. *J. Polym. Sci., Polym. Chem. Edn.* 1989, **27**, 245
12 Vygodskii, Ya. S., Adigezalov, V. A. *et al. Polym. Sci. USSR* 1980, **21**, 2951
13 Crivello, J. V. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 1185
14 Rao, B. S. *J. Polym. Sci., Polym. Chem. Edn.* 1989, **27**, 2509
15 Nagai, A., Takahashi, A., Wayima, M. and Tsukanishi, K. *Polym. J.* 1988, **25**, 125
16 Leung, C. L., Liao, T. T. and Tung, C. M. *Am. Chem. Soc. Polym. Mater. Sci. Eng. Div.* 1985, **52**, 134
17 Hougham, G. and Tesoro, G. unpublished results