Preparation and Characterization of Bismaleimides Chain-Extended by Ureylene Linkages

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SYNOPSIS

The bismaleimides chain-extended by ureylene linkages were obtained by the reaction of a diamine with maleic anhydride (1 : 1 molar ratio) first and then by the reaction of the resulting solution with a diisocyanate, followed by the cyclodehydration of the diamic acid. The bismaleimides were characterized by elemental analysis, IR, ^{1}H-NMR, and ^{13}C-NMR. The results of thermal analysis show that the solidification reaction takes place above 200°C for most bismaleimides and the crosslinking products decompose at higher temperatures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Bismaleimide monomers and oligomers are thermally polymerized into thermosetting resins as heat-resistance adhesives and matrix resins for composite materials.[1,2] These resins are characteristic of good tractability, high thermal stability, high durability, good water resistance, grind resistance, fire resistance, radiation resistance, and relatively low cost. The polymeric materials with high mechanical and electrical properties and capacity can perform long-term service at elevated temperature and, hence, have been widely used.[3] However, the major disadvantage of these polymers is their brittleness due to high crosslinking density that occurs during polymerization, which, therefore, restricted their applications considerably.[4]

To overcome this problem, various attempts have been made to improve the impact and fracture toughness of bismaleimide materials. These efforts include the blending of bismaleimides with liquid rubbers[5] and/or thermoplastic resins[6] and the copolymerization of bismaleimides with epoxy resins[7] and/or other oligomers.[8] The more effective method is to synthesize novel chain-extended bismaleimides by various groups to increase the flexibility of the cured resins. Much work has been done by Mikro-yannidis et al.[9] in this field, and many achievements have been obtained.

In the present investigation, a series of chain-extended bismaleimides by ureylene linkages were synthesised and characterized, and their thermal properties were also investigated.

EXPERIMENTAL

Materials and Instrumentation

All reagents were of analytical grade and used without further purification. IR spectra were recorded with a 7400 instrument of Shanghai Analytical Instrument Factory with KBr pellets, ^{1}H-NMR spectra were measured using the Vavian FT-80A spectrometer in DMSO-d_6, ^{13}C-NMR spectra were obtained with the Vavian XL-200 spectrometer in DMSO-d_6, TG–DTA were carried out with a PCT-1 balance of Beijing Optical Instrument Factory at a heating rate of 10°C/min in air, and DSC were investigated with the Perkin-Elmer DSC-2 analyzer at the heating rate of 20°C/min in N_2. For elemental analysis, C, H, and N contents were determined using the Perkin-Elmer 240C elemental analysis instrument.
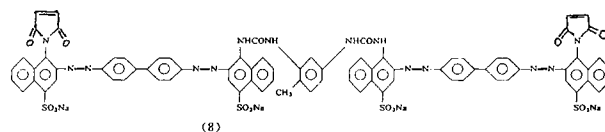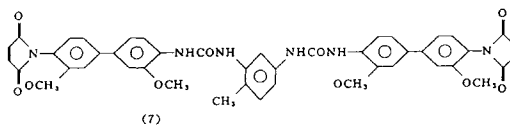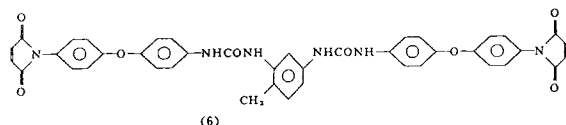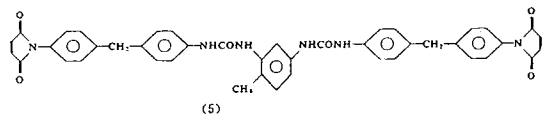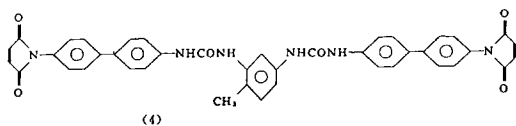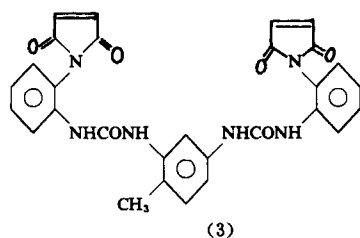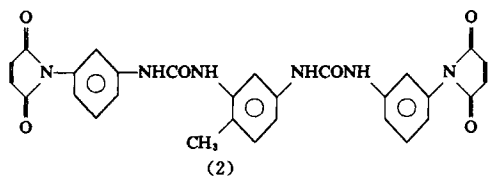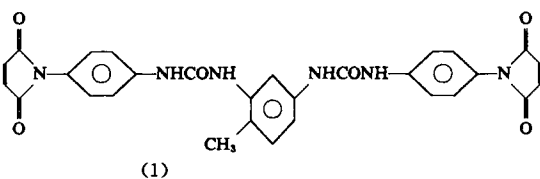
Synthesis of Bismaleimides

A series of chain-extended bismaleimides by ureylene linkages were synthesized according to the following reaction:

$$H_2N-Ar-NH_2 + \xrightarrow[\text{mol 1:1}]{} $$

(BMA)

$$\xrightarrow[\text{mol 2:1}]{OCN-Ar'-NCO}$$

(BMA)

$$\xrightarrow{-2H_2O}$$

(BMI)
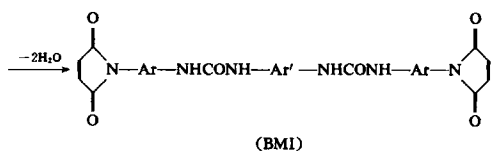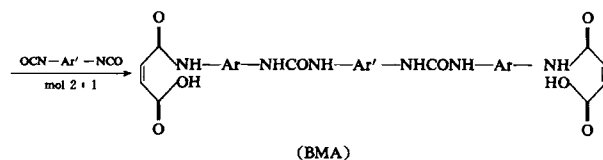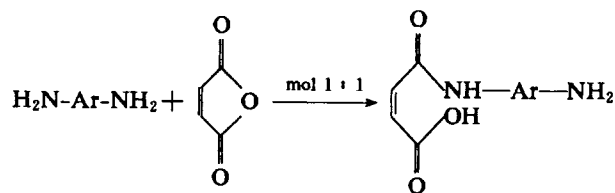
These bismaleimides (BMI) are numbered as follows:

(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

Their corresponding bismaleamic acids (BMA) are numbered 1'–8', respectively.

A flask equipped with a mechanical stirrer, thermometer, and addition funnel was partially filled with a solution of diamine in DMF. To the vigorously stirred solution, an equimolar amount of maleic anhydride dissolved in DMF was added dropwise. Stirring of the mixture lasted for 4 h at ambient temperature. A half-molar amount of diisocyanate dissolved in DMF was added portionwise to the stirred solution. The mixture was reacted at 60°C for 3 h more. An aliquot of the reaction solution was poured into water and a yellow deposit appeared. The solid was filtered, washed with water, and dried to yield the bismaleamic acid.

Acetic anhydride and sodium acetate were added to the remaining solution. The mixture was boiled under reflux at 90°C for 3 h and was subsequently poured into a large amount of water. The brown solid obtained was filtered, washed with a dilute solution of sodium bicarbonate, then with water, and dried. The yields of bismaleimides thus synthesized were over 80%.

RESULTS AND DISCUSSION

Characterization of Bismaleimides

The bismaleimides (BMIs) as well as their diamic acids (BMAs) were characterized by IR and NMR.

Table I Elemental Analysis Data of BMI (Calcd) (%)

Sample	C	H	N
1	63.52(63.21)	3.98(4.00)	15.14(15.25)
2	63.61(63.21)	3.87(4.00)	15.20(15.25)
3	63.72(63.21)	3.92(4.00)	15.33(15.25)
4	69.87(70.01)	4.15(4.27)	11.82(11.95)
5	71.81(70.61)	4.73(4.65)	11.65(11.49)
6	65.91(66.96)	3.95(4.08)	11.40(11.43)
7	66.14(65.63)	4.48(4.62)	10.03(10.21)
8	56.09(56.26)	3.07(2.89)	11.46(11.35)

Table II   Wavenumbers of IR of BMA (cm⁻¹)

Sample	Amide and Ureas Structure			Carboxyl		Aromatic Ring		C=C	C—CH₃	
1'	3320–3240	1545	1635	1725	2850–2640	1600	1500	1610	2880	1445
2'	3320–3240	1545	1630	1710	2840–2640	1595	1490	1610	2880	1455
3'	3325–3250	1540	1630	1710	2860–2640	1595	1515	1600	2880	1445
4'	3320–3240	1545	1635	1715	2840–2640	1595	1495	1620	2880	1455
5'	3320–3245	1545	1630	1715	2810–2640	1600	1510	1610	2885	1455
6'	3400–3270	1550	1640	1715	2880–2680	1600	1500	1610	2900	1455
7'	3400–3280	1545	1650	1710	2840–2600	1595	1510	1615	2920	1455
8'	3440–3240	1545	1650	1700	2880–2600	1595	1500	1615	2885	1465

The elemental analyses of BMI are shown in Table I. The found values of the elemental analyses agreed well with the calculated values.

The characteristic absorptions and their assignments of BMA and BMI are listed in Tables II and III.

As can be seen in Figure 1, the typical IR spectra of the BMI 5 and the corresponding BMA 5′ give different features. In the spectra of BMA 5′, the carboxyl groups give the absorption bands at 2840–2640 cm⁻¹ (OH) and 1715 cm⁻¹ (C=O); the amide structure (—NHCOCH=) and the ureylene linkages (—NHCONH—) exhibited absorption bands at 3320–3240 cm⁻¹ (ν_{VH}), 1630 cm⁻¹ ($\nu_{C=O}$), and 1545 cm⁻¹ (ν_{C-N} and δ_{C-N}); the C=C structure of BMA gives absorption bands at 1610 cm⁻¹; and the phenyl ring shows the absorption bands at 1600 and 1500 cm⁻¹.

The IR spectra of BMI 5 have no absorption bands at 2840–2640 cm⁻¹ associated with the carboxylic —OH stretching vibration. In addition, a strong absorption at 1720 cm⁻¹ and weak absorptions at 1780, 1110, and 720 cm⁻¹ appeared, which are the characteristic absorptions of imide ring; the absorption bands at 3440–3240, 1650, and 1530 cm⁻¹ are associated with the —NHCONH— groups; and

the bands at 1610 and 830 cm⁻¹ are due to the C=C structure of BMI.

The ¹H-NMR spectra of BMA and BMI were recorded in DMSO-d_6 solution and the results are listed in Tables IV and V. Figure 2 presents typical ¹H-NMR spectra of BMA 5′ and BMI 5. In the spectrum of BMA 5′, the peaks can be assigned as follows: The protons of —OH of carboxylic acids give a singlet at a chemical shift of δ = 10.42 ppm and the protons in

—NHCONH— and ⟩CHCONH—
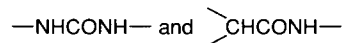
show four peaks at δ = 8.98, 8.88, 8.56, and 8.46 ppm. All the above peaks can be exchanged by D₂O. The peaks at 7.91 ppm and part of 7.61 ppm are associated with the protons of the phenyl ring
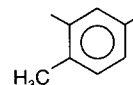
the multiplet at δ = 7.61–7.09 ppm is associated with the protons of the phenyl ring
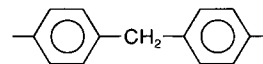
the doublet of a double at δ = 6.57–6.19 ppm is the characteristic spectra of the protons in —CH=CH— of BMA; the peak at δ = 3.85 ppm

Table III   Wavenumbers of IR of BMI (cm⁻¹)

Samples	—NHCONH—				Imide Structure				Aromatic Ring		C=C		C—CH₃	
1	3440–3280	1550	1640	1775	1715	1385	1110	715	1595	1510	1610	830	2900	1460
2	3440–3240	1535	1665	1770	1715	1385	1115	715	1590	1490	1610	825	2885	1450
3	3440–3340	1550	1650	1770	1720	1385	1110	720	1595	1500	1615	825	2890	1450
4	3440–3280	1530	1650	1770	1720	1380	1110	720	1595	1500	1610	825	2900	1455
5	3440–3240	1530	1650	1780	1720	1380	1110	720	1600	1510	1610	830	2900	1455
6	3400–3200	1540	1650	1780	1725	1380	1110	725	1590	1495	1610	830	2880	1470
7	3440–3240	1545	1650	1775	1720	1385	1110	720	1595	1510	1610	835	2900	1450
8	3440–3240	1540	1645	1770	1715	1380	1110	725	1590	1500	1600	825	2885	1465

Table IV ^{1}H-NMR Spectral Data of BMA

| Sample	Chemical Shifts (δ, ppm) and Assignments
1'	10.50(S,2H,—COOH); 8.99—8.59(f, 6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 7.93–7.13(m,11H,aromatic); 6.42(dd,4H,—CH=CH—); 2.18(S,3H,—CH$_3$)
2'	10.55(S,2H,—COOH); 9.14–8.43(f, 6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 8.00–7.23(m,11H,aromatic); 6.44(bs,4H,—CH=CH—); 2.21(S,3H,—CH$_3$)
3'	10.53(S,2H,—COOH); 8.95–8.43(f,6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 8.00–7.19(m,11H,aromatic); 6.74–6.24(dd,4H,—CH=CH—); 2.20(S,3H,—CH$_3$)
4'	10.51(S,2H,—COOH); 9.11–8.62(f,6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 8.00–7.10(m,11H,aromatic); 6.72(bs,4H,—CH=CH—); 2.20(S,3H,—CH$_3$)
5'	10.42(S,2H,—COOH); 8.96–8.56(f,6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 7.91–7.09(m,19H,aromatic); 6.57–6.19(dd,4H,—CH=CH—); 2.17(S,3H,—CH$_3$); 3.85(S,2H,—CH$_2$—)
6'	10.51(S,2H,—COOH); 9.02–8.60(f,6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 7.94–6.91(m,19H,aromatic); 6.60–6.19(dd,4H,—CH=CH—); 2.20(S,3H,—CH$_3$)
7'	10.17(S,2H,—COOH); 8.53–8.31(f,6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 8.18–7.11(m,15H,aromatic); 6.63–6.40(dd,4H,—CH=CH—); 2.24(S,3H,—CH$_3$); 3.90,3.80(d,6H,—OCH$_3$)
8'	10.25(S,2H,—COOH); 8.90–8.61(f,6H, $\overset{\diagdown}{\underset{\diagup}{}}$CHCO<u>NH</u>— and —NHCONH—); 8.43–7.50(m,39H,aromatic); 6.52(dd,4H,—CH=CH—); 2.12(S,3H,—CH$_3$)

s, singlet; bs, broad singlet; d, double; dd, doublet of a double; f, four peaks; m, multiplet.

is due to the protons of —CH$_2$— overlapping with that of H$_2$O; and the peak at δ = 2.17 ppm responds to the protons of —CH$_3$.

Unlike that of BMA 5', in the spectrum of BMI 5, there are no peaks at δ = 10.42 and 6.57–6.19 ppm. The other peaks may be assigned as follows: The four peaks at δ = 8.96, 8.85, 8.58, and 8.45 ppm are associated with the protons of —NHCONH— (exchangeable to D$_2$O); the bands at δ = 7.94 and 7.84 ppm are associated with the protons of the phenyl ring
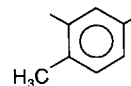
the multiplet at δ = 7.55–7.09 ppm responds to the protons of the phenyl ring
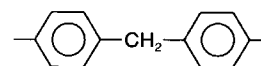
the peaks of protons in —CH=CH— of BMI are shifted to downfield and give a singlet at δ = 7.15 ppm; and the bands at δ = 4.04 and 2.18 ppm are
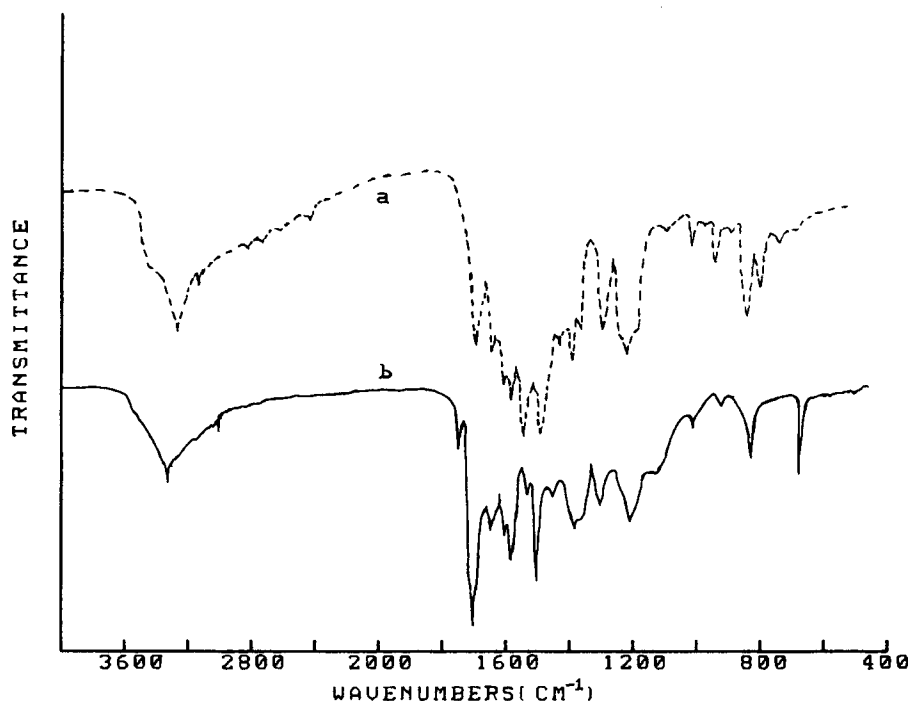
Figure 1 IR Spectra of (a) BMA 5' and (b) BMI 5.

relative to the protons of $-CH_2-$ and $-CH_3$, respectively.

In the ^{1}H-NMR spectra, besides having no peak of $-OH$ in BMI, the characteristic difference between BMA and BMI is the bands of protons in $-CH=CH-$. In BMA, they give double doublets with the chemical shift at $\delta = 6.70-6.00$ ppm; but in BMI, they show a singlet due to the equality of the protons in $-CH=CH-$ as well as a downfield shift to $\delta = 7.10-7.20$ ppm. Meanwhile, the bands of protons in the aromatic ring also vary to some extent.

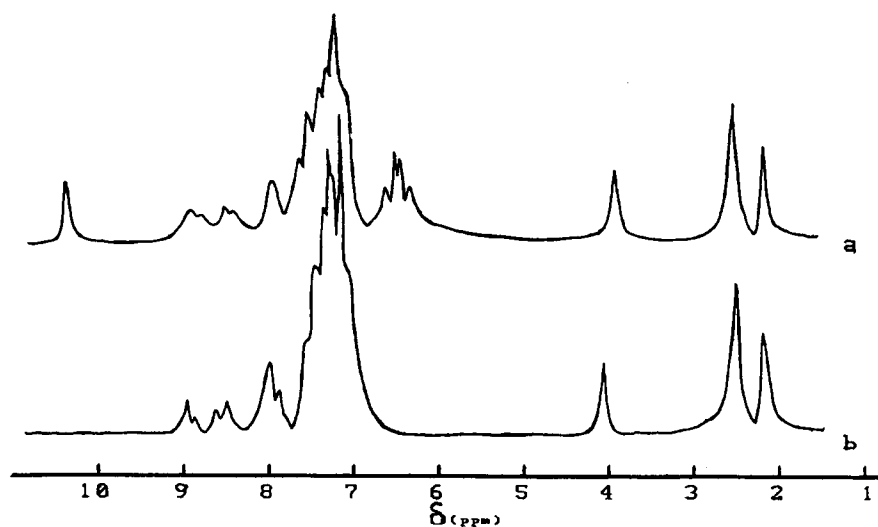The ^{13}C-NMR spectra of BMA 5' and BMI 5 were also determined in DMSO-d_6 solution as shown in

Figure 2 ^{1}H-NMR spectra of (a) BMA 5' and (b) BMI 5.

Table V ¹H-NMR Spectral Data of BMI

| Sample	Chemical Shifts (δ, ppm) and Assignments
1	8.99–8.51(f,4H,—NHCONH—); 7.95–7.12(m,11H,aromatic); 7.12(S,4H,—CH=CH—); 2.1(S,3H,—CH₃)
2	9.20–8.65(f,4H,—NHCONH—); 7.96–7.11(m,11H,aromatic); 7.11(S,4H,—CH=CH—); 2.0(S,3H,—CH₃)
3	9.43–8.91(f,4H,—NHCONH—); 7.99–7.16(m,11H,aromatic); 7.16(S,4H,—CH=CH—); 1.9(S,3H,—CH₃)
4	9.21–8.80(f,4H,—NHCONH—); 7.95–7.11(m,19H,aromatic); 7.11(S,4H,—CH=CH—); 2.1(S,3H,—CH₃)
5	8.96–8.58(f,4H,—NHCONH—); 7.94–7.09(m,19H,aromatic); 7.15(S,4H,—CH=CH—); 2.18(S,3H,—CH₃); 4.04(S,2H,—CH₂—)
6	9.40–8.98(f,4H,—NHCONH—); 7.64–6.82(m,19H,aromatic); 7.13(S,4H,—CH=CH—); 2.2(S,3H,—CH₃)
7	9.31–8.88(f,4H,—NHCONH—); 7.89–7.29(m,15H,aromatic); 7.11(S,4H,—CH=CH—); 2.3(S,3H,—CH₃); 3.91,3.83(d,6H,—CH₃)
8	9.31–8.75(f,4H,—NHCONH—); 8.33–7.56(m,39H,aromatic); 7.18(S,4H,—CH=CH—); 2.1(S,3H,—CH₃)

s, singlet; d, double; f, four peaks; m, multiplet.

Figures 3 and 4, and the chemical shifts may be assigned as follows:
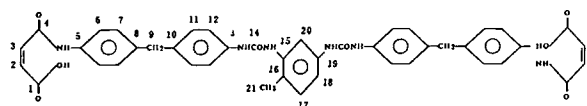
(1) 167.0; (2) 131.6; (3) 131.0; (4) 163.1; (5) 136.5; (6) 119.8; (7) 129.1; (8) 137.1; (9) 40.0; (10) 137.9; (11) 129.1; (12) 118.3; (13) 137.9; (14) 152.6; (15) 135.0; (16) 130.3; (17) 120.0; (18) 112.3; (19) 134.7; (20) 110.5; (21) 17.3 ppm, respectively
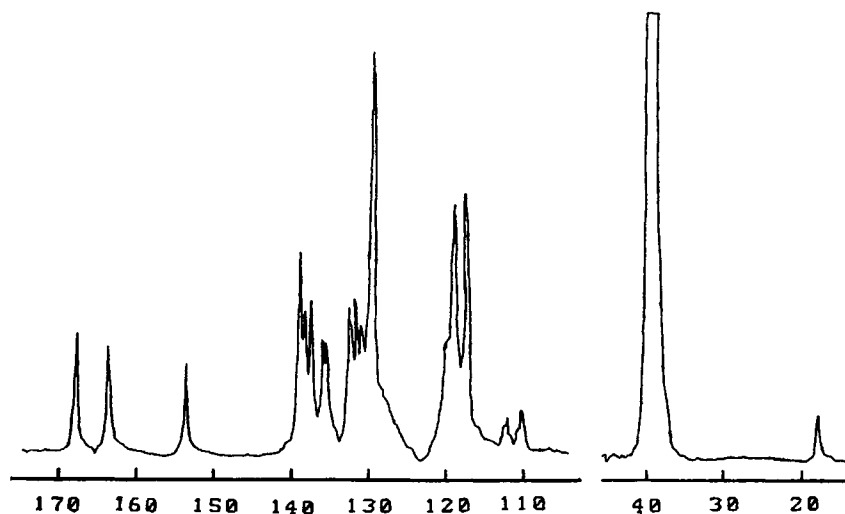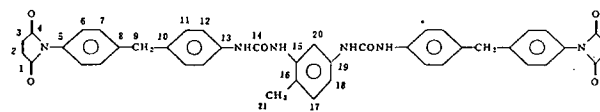
Figure 3 ¹³C-NMR spectrum of BMA 5′.

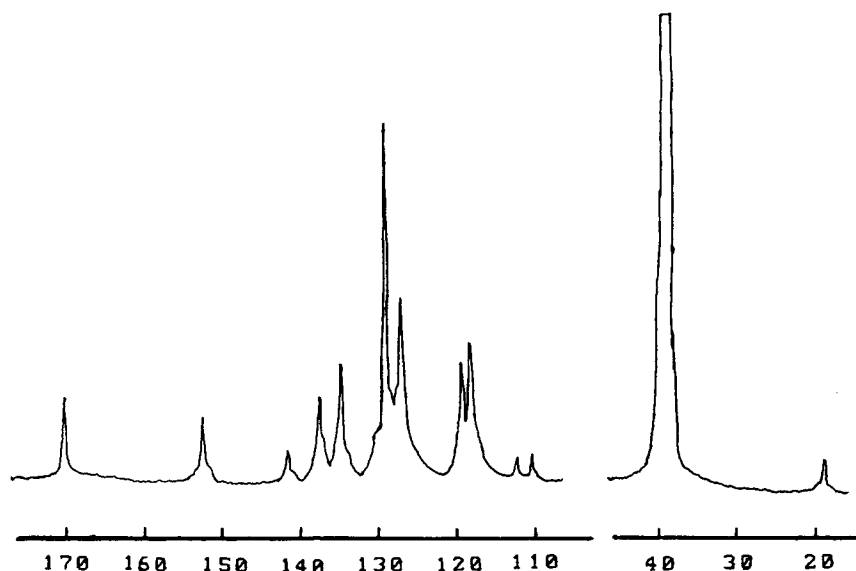**Figure 4** ^{13}C-NMR spectrum of BMI 5.

(1) 169.9; (2) 134.6; (3) 134.6; (4) 169.9; (5) 141.2; (6) 126.9; (7) 128.9; (8) 137.4; (9) 40.0; (10) 137.4; (11) 128.9; (12) 118.1; (13) 137.4; (14) 152.4; (15) 134.6 (16) 130.1; (17) 120.0; (18) 112.1; (19) 134.6; (20) 110.0; (21) 17.2 ppm, respectively

Thermal Analyses

Thermal properties of BMI and their polymers were determined by TG–DTA in air and DSC in N_2. Figure 5 presents typical TG–DTA curves of BMI 5. It

is seen that the monomer gave no weight loss up to 274.8°C, while at 411.8°C, the second plateau appeared and exhibited a small exotherm at 196–270.8°C with the peak temperature at 232.0°C. Consequently, this exotherm was attributed to the thermal polymerization reaction through its olefinic bond linkage to yield a crosslinked structure. The exothermic peaks at 319.0, 461.5, and 543.5°C are due to the thermooxidative decomposition of the polymer. The DSC curve showed a small exotherm at 215–261°C, with the peak temperature at 241°C. The small endotherm at 297°C and the big endo-
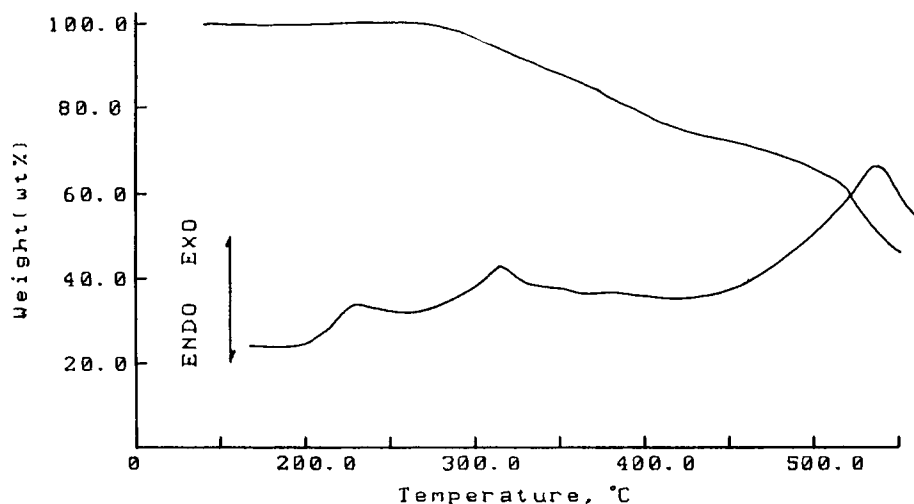

Figure 5 TG–DTA curves of BMI 5.

Table VI   TG–DTA Data of BMI (°C)

Sample	TG		DTA			
	T_1	T_2	T_3	T_4	T_P	
1	335.0	366.8	209.2–318.3	264.2	358.5	473.0
2	294.8	427.8	214.8–294.6	249.8	320.0	543.0
3	288.0	366.8	237.2–286.8	258.5	331.5	511.2
4	362.1	398.0	204.0–256.8	246.2	354.8	461.5
5	274.8	411.8	196.8–270.8	232.0	319.0	461.5
6	270.8	407.8	209.2–276.2	234.0	331.2	496.5
7	262.8	430.2	a	a	331.2	496.5

T_1, temperature of initial weight loss; T_2, temperature of weight loss of the second plateau; T_3, temperature range of exotherm of BMI in crosslinking; T_4, the peak temperature of T_3; T_P, temperature of the exotherm of crosslinking products in thermoxidative decomposition.

a Unseen.

therm at 365°C and 387°C are due to the thermal decomposition of the polymer. The TG–DTA and DSC traces of monomers are listed in Tables VI and VII. It is concluded that the crosslinking reaction takes place above 200°C for most BMI and the crosslinking products decompose at higher temperatures. The temperatures of crosslinking and initial weight loss were influenced by the atmosphere, the heating rate, and the chemical structures of the diamines utilized for monomer preparation.

Table VII   DSC Data of BMI (°C)

Sample	T_1	T_2	T_3		T_4	
1	232–269	249	337		361	
2	223–273	245	291	347		371
3	242–282	367	301		359	
4	a	a	357		381	
5	215–261	241	297	365		387
6	a	a	290	313		439
7	219–245	231	283	318		389
8	a	a	311	349		393

T_1, temperature range of exotherm of BMI in crosslinking; T_2, the peak temperature of T_1; T_3, the onset temperature for thermal degradation; T_4, the peak temperature of thermal degradation.

a Unseen.

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