

CHAPTER 3

PHYSICO-CHEMICAL CHARACTERIZATION

This chapter deals with the infrared spectroscopic (IR) and viscosity characterization of the formation of siliconized epoxy graft interpenetrating network (IPN) and characterization of the synthesized bismaleimides namely BMI-1, BMI-2, BMI-3 and BMI-4 by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopic methods. It also describes the homopolymerization of bismaleimides in the presence of epoxy resin.

3.1 SILICONIZED EPOXY NETWORK STRUCTURE

Silane coupling agent (γ -APS) containing amine and alkoxy groups, which can work as 'molecular bridge' to react with not only the epoxy groups of DGEBA but also with the hydroxyl groups of HTPDMS, has been used as crosslinking agent.

The formation of siliconized epoxy network structure proceeds in two steps and is evaluated by IR (Figure 3.1). The first step involves the reaction between epoxide ring of the epoxy resin and amino group of the γ -aminopropyltriethoxysilane, which is confirmed by the disappearance of epoxy band at 913 cm^{-1} and appearance of hydroxyl band at 3420 cm^{-1} (Figure 3.1b). Absorption peaks appeared at 1150 cm^{-1} and 2833 cm^{-1} confirm the presence of $-\text{Si}-(\text{CH}_2)_3-$ and $-\text{Si}-\text{OCH}_2\text{CH}_3$ respectively in epoxy resin cured

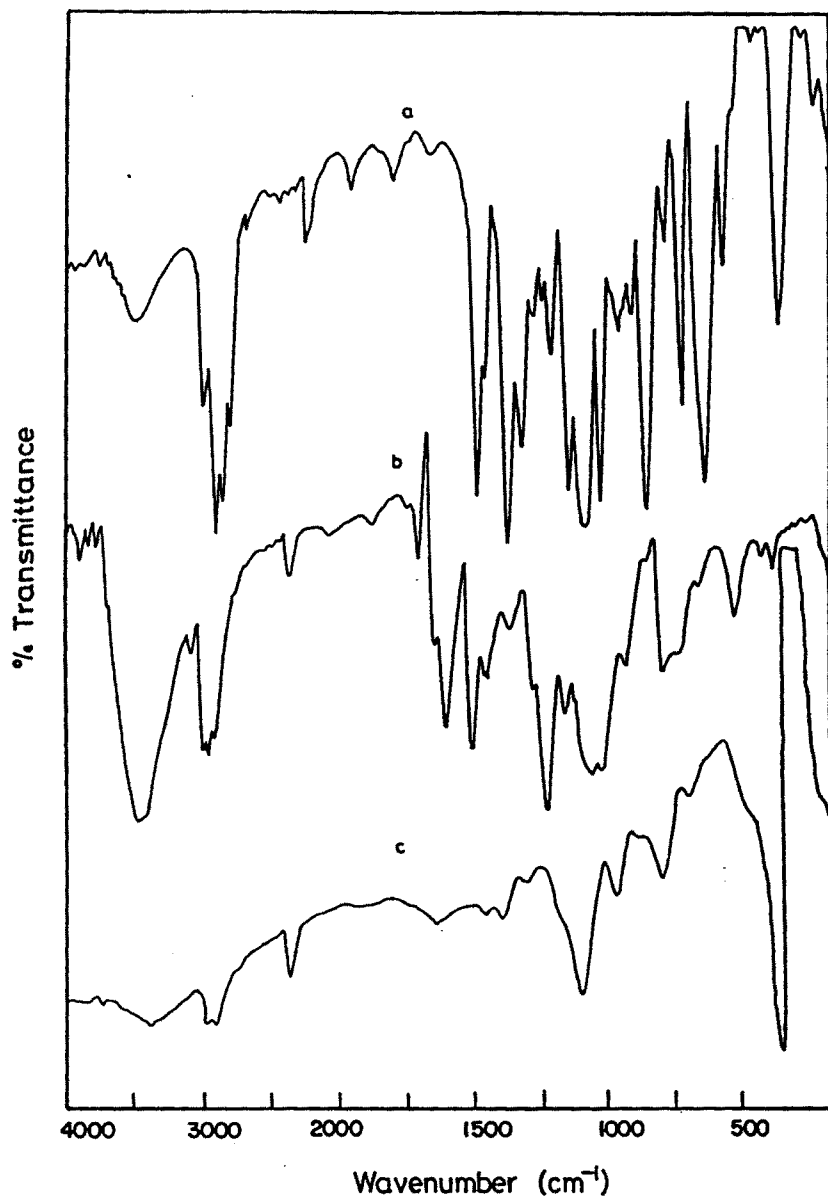


Figure 3.1 FTIR Spectra of (a) Unmodified epoxy, (b) γ -APS cured epoxy and (c) γ -APS

with γ -aminopropyltriethoxysilane (Figure 3.1b). In the second step, the alkoxy groups present in the γ -aminopropyltriethoxysilane react with hydroxyl groups of hydroxyl-terminated polydimethylsiloxane.

3.2 VISCOSITY

The effectiveness of siliconization of epoxy resin was examined by viscosity measurements. From Table 3.1, it is observed that the viscosity of epoxy resin increases when siloxane content increases, since HTPDMS is chemically bonded with epoxy resin through γ -aminopropyltriethoxysilane. This implies that the siliconization of epoxy resin is effective.

Table 3.1 Viscosity of siliconized epoxy prepolymer

Sl.No.	Epoxy/HTPDMS composition	Viscosity (cP) at 30° C
1	100/00	9200 – 10004
2	100/05	14600 – 15700
3	100/10	23400 – 24200
4	100/15	31300 – 32700

HTPDMS : Hydroxyl-terminated polydimethylsiloxane

3.3 FTIR CHARACTERIZATION OF BISMALIMIDES

FTIR spectra were recorded using Perkin Elmer 781 infrared spectrometer with KBr pellets for solid bismaleimide samples. The viscous liquid samples were directly applied by dabbing onto a KBr pellet.

BMI-1

IR (KBr) : ν (cm^{-1}) 3097 (= C - H); 3467, 1700 (C = O); 1385, 1148 (C - N - C) (Figure 3.2)

BMI-2

IR (KBr) : ν (cm^{-1}) 3105 (= C - H); 3455, 1720 (C = O); 1390, 1145 (C - N - C) (Figure 3.3)

BMI-3

IR (KBr) : ν (cm^{-1}) 3101 (= C - H); 2658 (C - H); 3468, 1709 (C = O); 1411, 1127 (C - N - C) (Figure 3.4)

BMI-4

IR (KBr) : ν (cm^{-1}) 3090 (= C - H); 2941 (C - H); 3450, 1699 (C = O); 1406, 1132 (C - N - C) (Figure 3.5)

3.4 NMR CHARACTERIZATION OF BISMALEIMIDES

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer with dimethylsulfoxide - d_6 (DMSO- d_6) or CDCl_3 as solvent.

BMI-1

^1H -NMR (d_6 -DMSO): δ = 7.36 (d, 2H, $J=8.3$ Hz, H_b), 7.26 (d, 2H, $J=8.3$ Hz, H_a), 7.15 (s, 4H, olefinic-H_c), 4.03 (s, 2H, CH₂) (Figure 3.6)

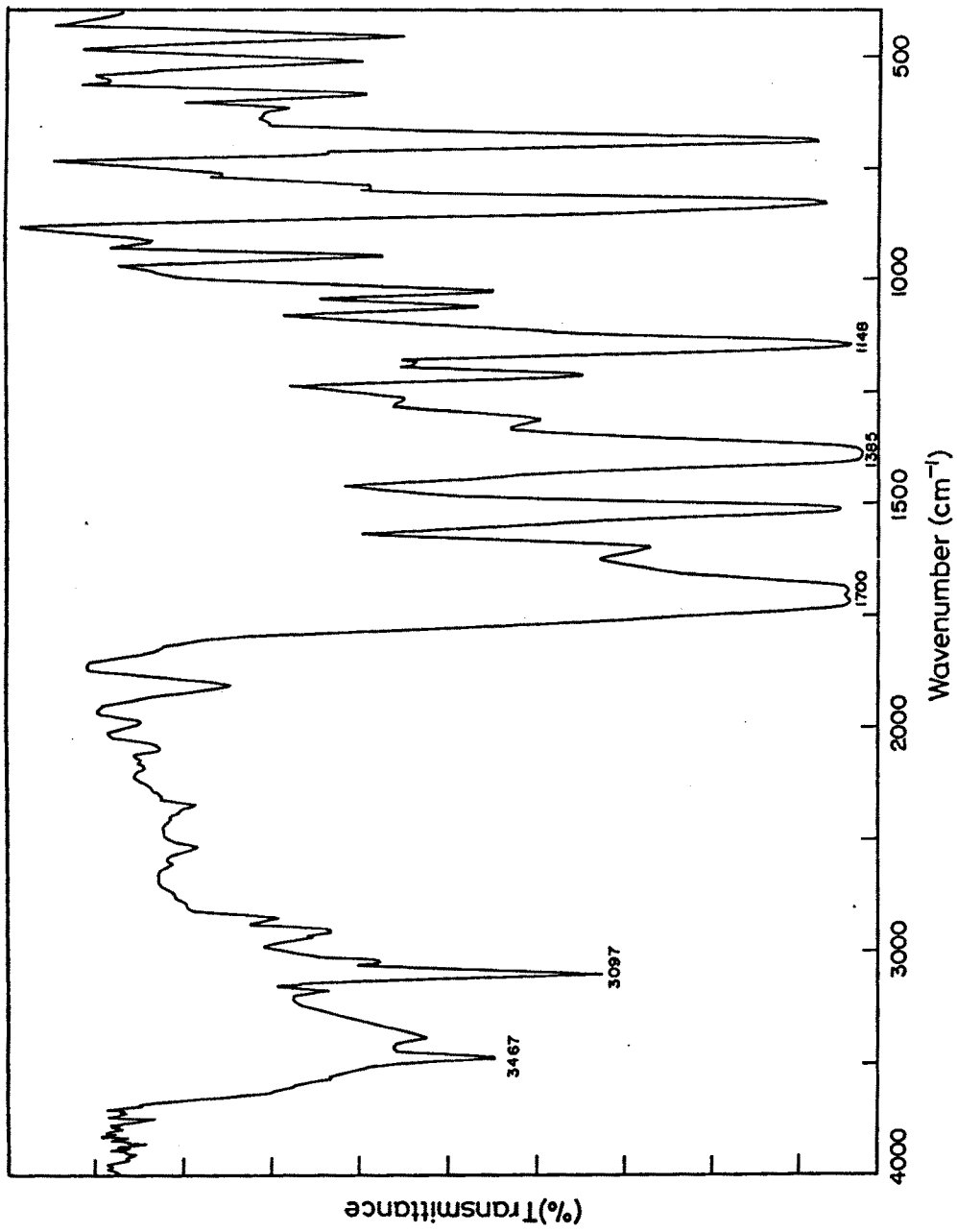


Figure 3.2 FTIR spectra of BMI-1

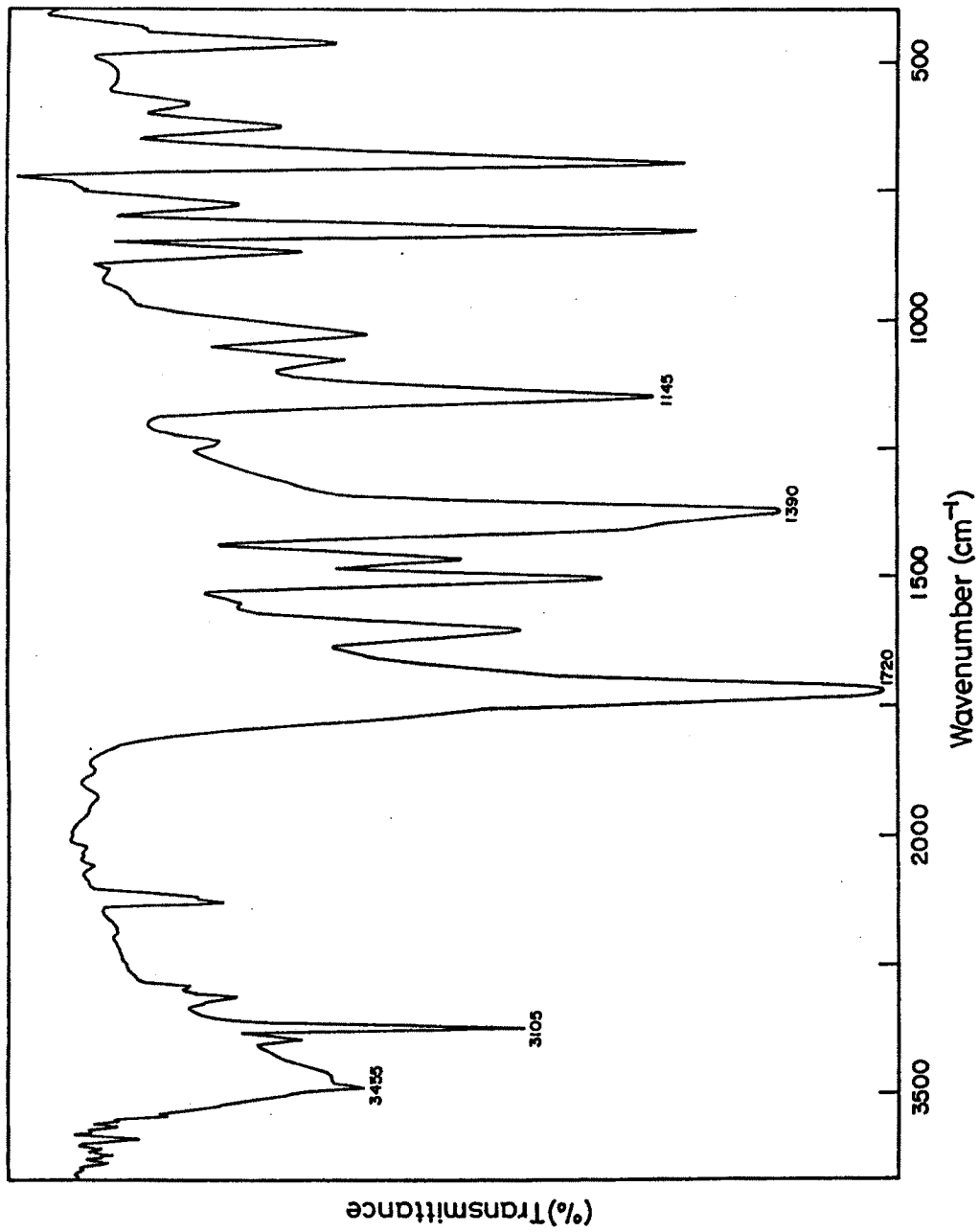


Figure 3.3 FTIR spectra of BMI-2

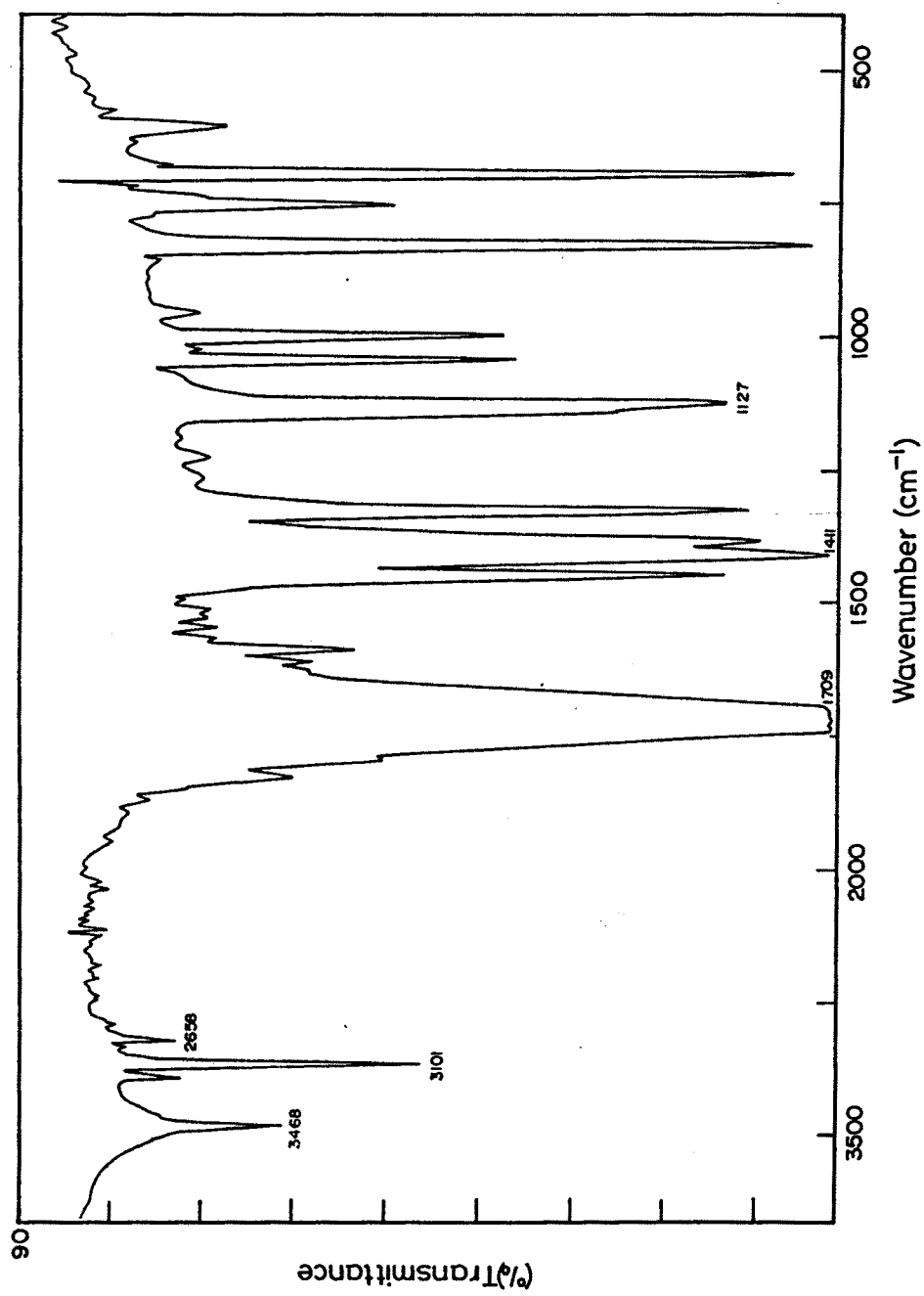


Figure 3.4 FTIR spectra of BMI-3

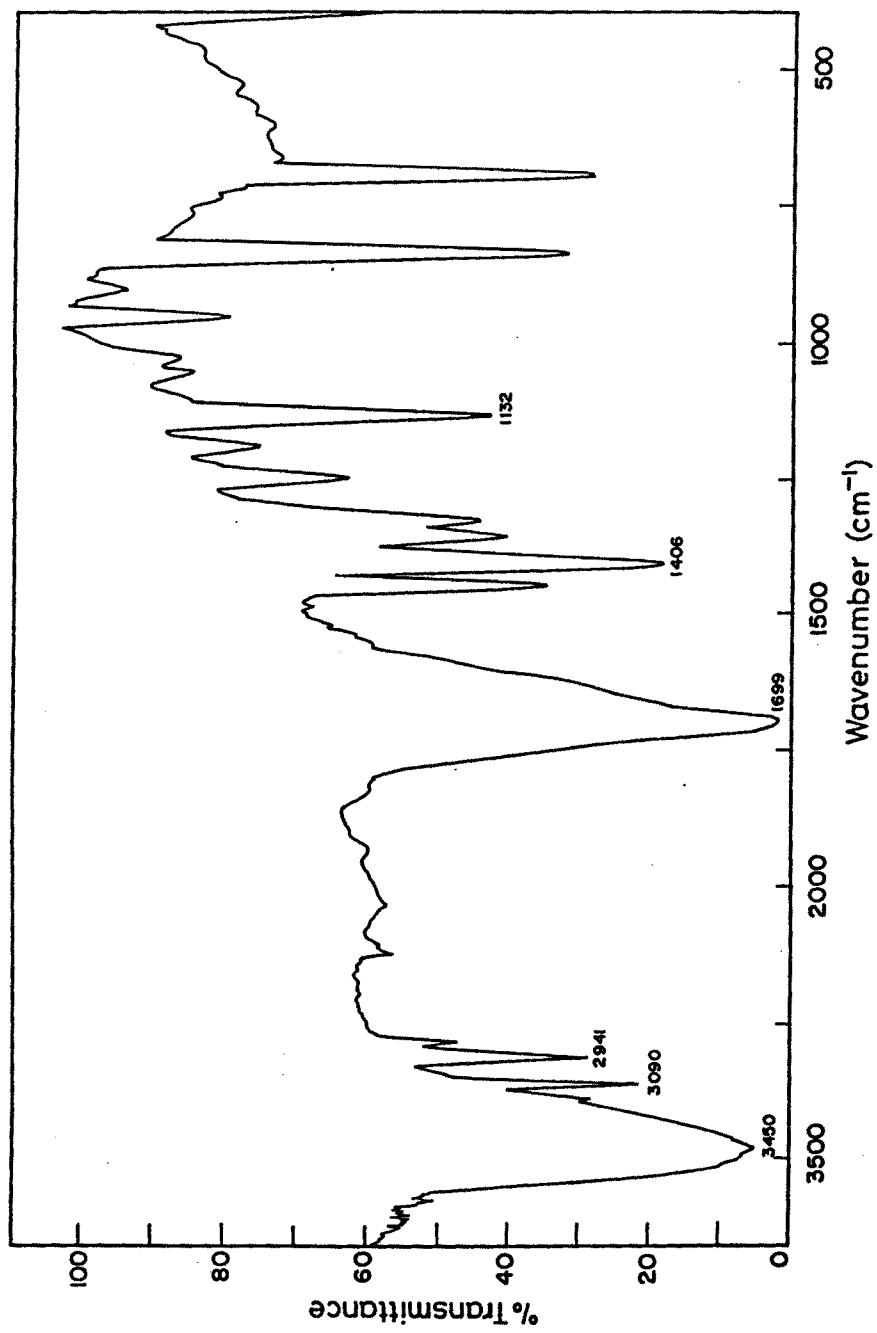


Figure 3.5 FTIR spectra of BMI-4

$^{13}\text{C-NMR}$ ($\text{d}_6\text{-DMSO}$): $\delta = 126.8, 129.1, 129.5$ ($\text{C}_{\text{aromatic}}$); 134.6 ($\text{C} = \text{C}$); 140.6 ($\text{N} - \text{C}_{\text{aromatic}}$); 169.9 ($\text{C} = \text{O}$) (Figure 3.7)

BMI-2

$^1\text{H-NMR}$ ($\text{d}_6\text{-DMSO}$): $\delta = 7.60$ (t, 1H, $J=8$ Hz, Hc), 7.39 (dd, 2H, $J=8.0$ and 2.0 Hz, Hb), 7.36 (t, 1H, $J=2$ Hz, Ha) 7.20 (s, 4H, olefinic-Hd) (Figures 3.8 and 3.9)

$^{13}\text{C-NMR}$ ($\text{d}_6\text{-DMSO}$): $\delta = 124.8, 126.1, 129.2$ ($\text{C}_{\text{aromatic}}$); 132.0 ($\text{N} - \text{C}_{\text{aromatic}}$); 134.7 ($\text{C}=\text{C}$); 169.7 ($\text{C} = \text{O}$) (Figure 3.10)

BMI-3

$^1\text{H-NMR}$ ($\text{d}_6\text{-DMSO}$): $\delta = 7.01$ (s, 4H, olefinic); 3.56 (s, 4H, ($\text{N} - \text{CH}_2$)₂); (Figures 3.11 and 3.12)

$^{13}\text{C-NMR}$ ($\text{d}_6\text{-DMSO}$): $\delta = 35.8$ (CH_2); 134.5 ($\text{C} = \text{C}$); 170.8 ($\text{C} = \text{O}$) (Figure 3.13)

BMI-4

$^1\text{H-NMR}$ (CDCl_3): $\delta = 6.68$ (s, 4H, olefinic-H), 3.51 (t, 4H, N-CH_2), 1.6 (m, 4H, $-\text{CH}_2-$), 1.3 (m, 4H, $-\text{CH}_2-$) (Figures 3.14 and 3.15)

$^{13}\text{C-NMR}$ (CDCl_3): $\delta = 26.1$ (CH_2); 28.3 (CH_2); 37.6 ($\text{N} - \text{CH}_2$); 133.9 ($\text{C} = \text{C}$); 170.8 ($\text{C} = \text{O}$) (Figure 3.16)

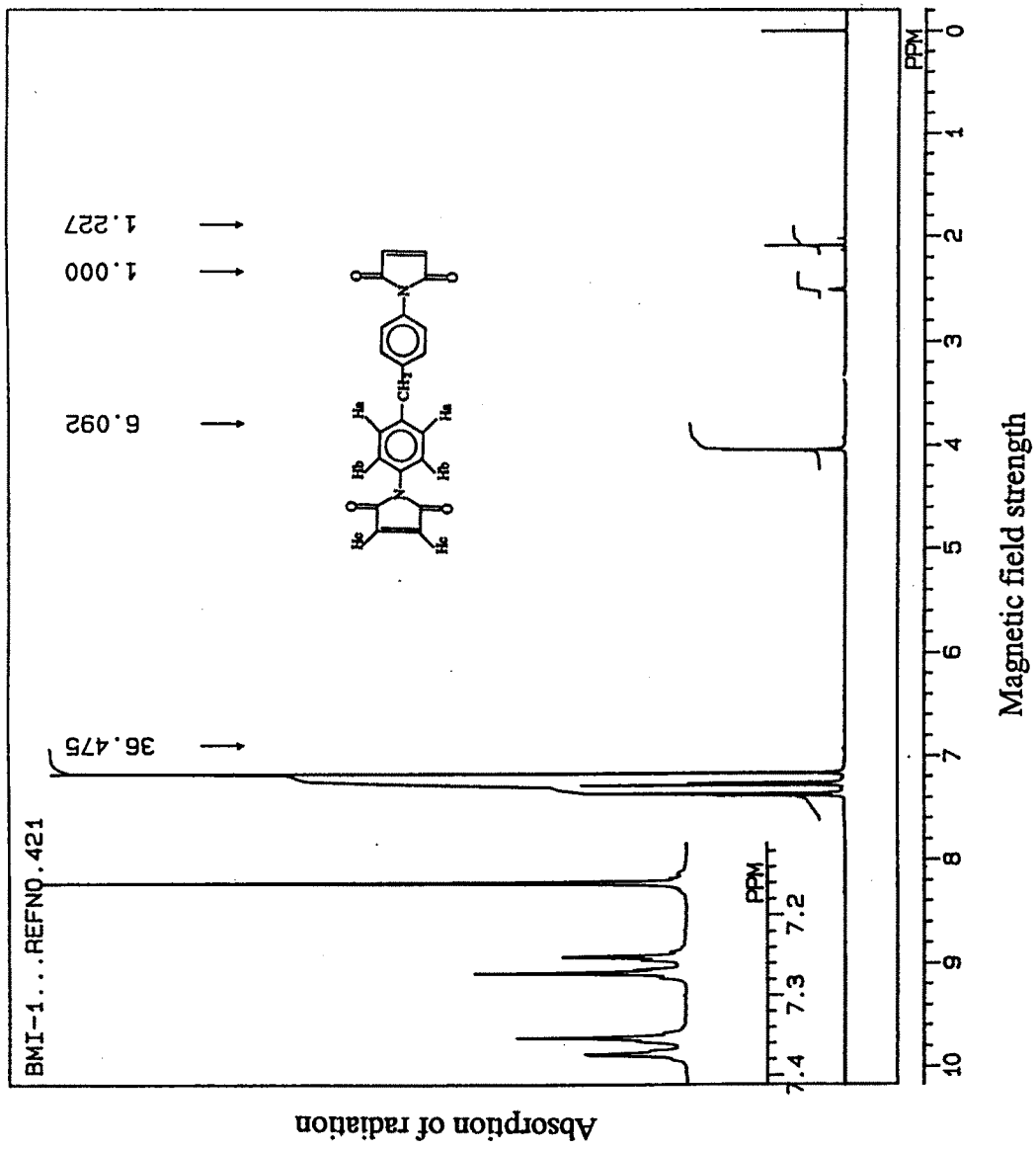


Figure 3.6 ¹H-NMR spectra of BMI-1

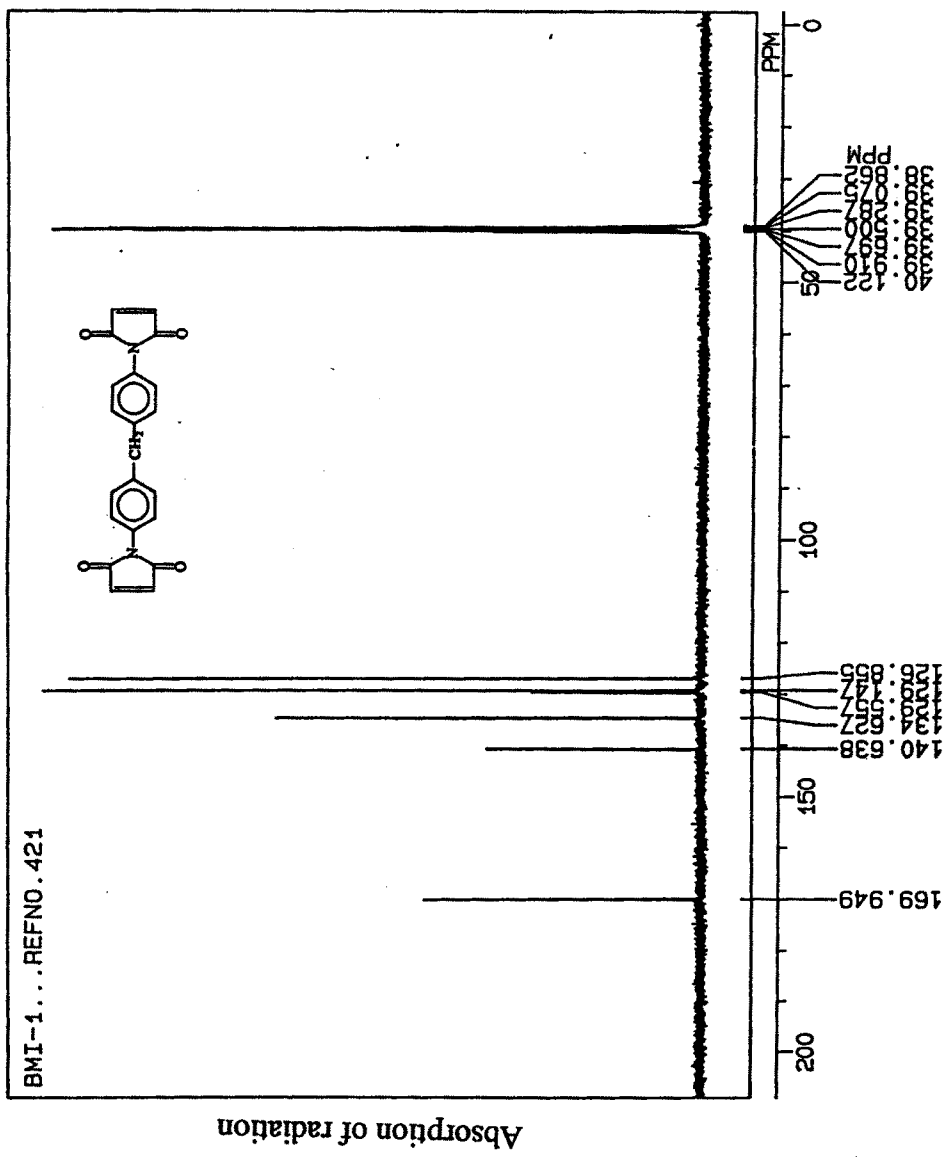


Figure 3.7 $^{13}\text{C-NMR}$ spectra of BMI-1

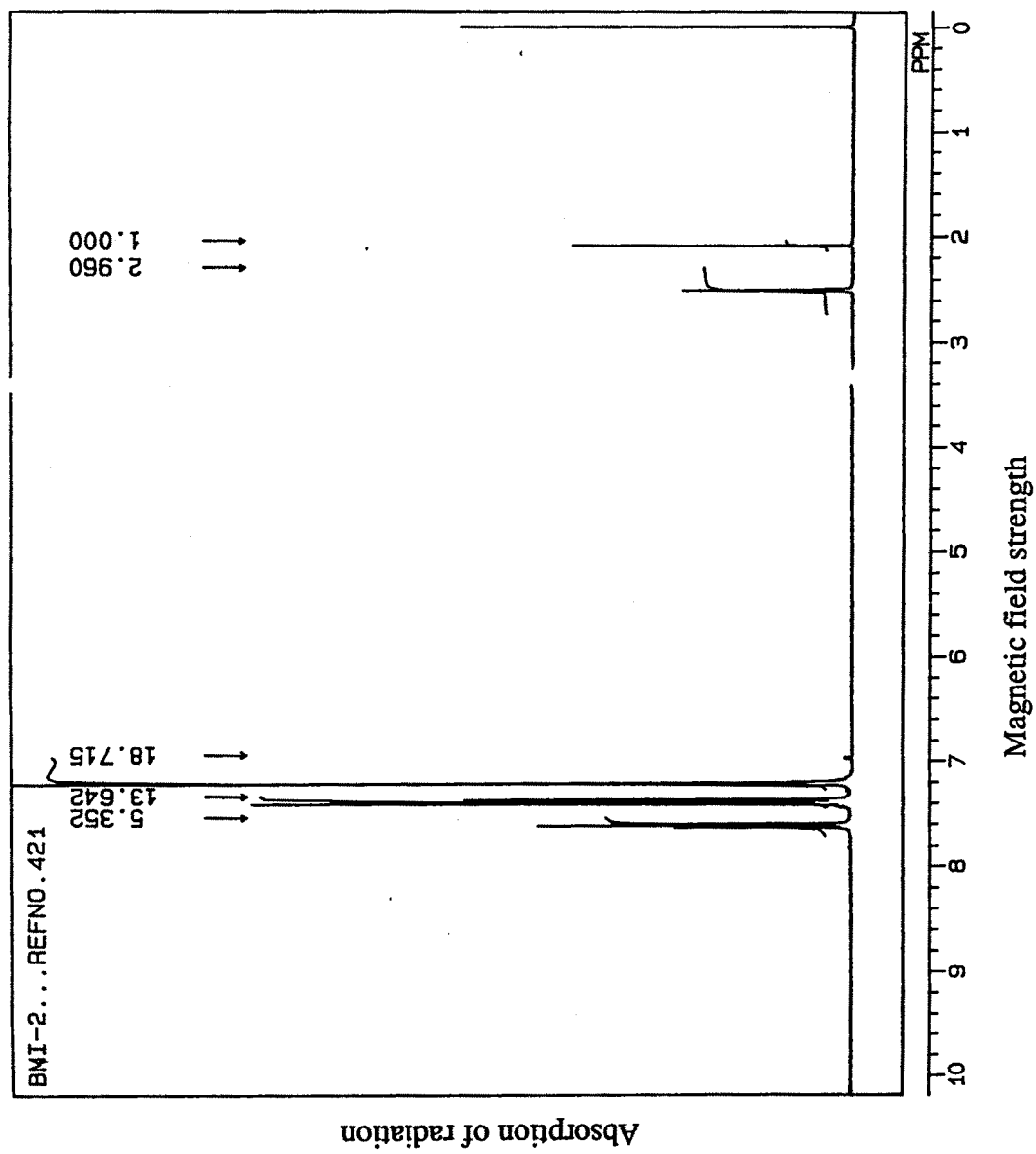


Figure 3.8 1H NMR spectra of BMI-2

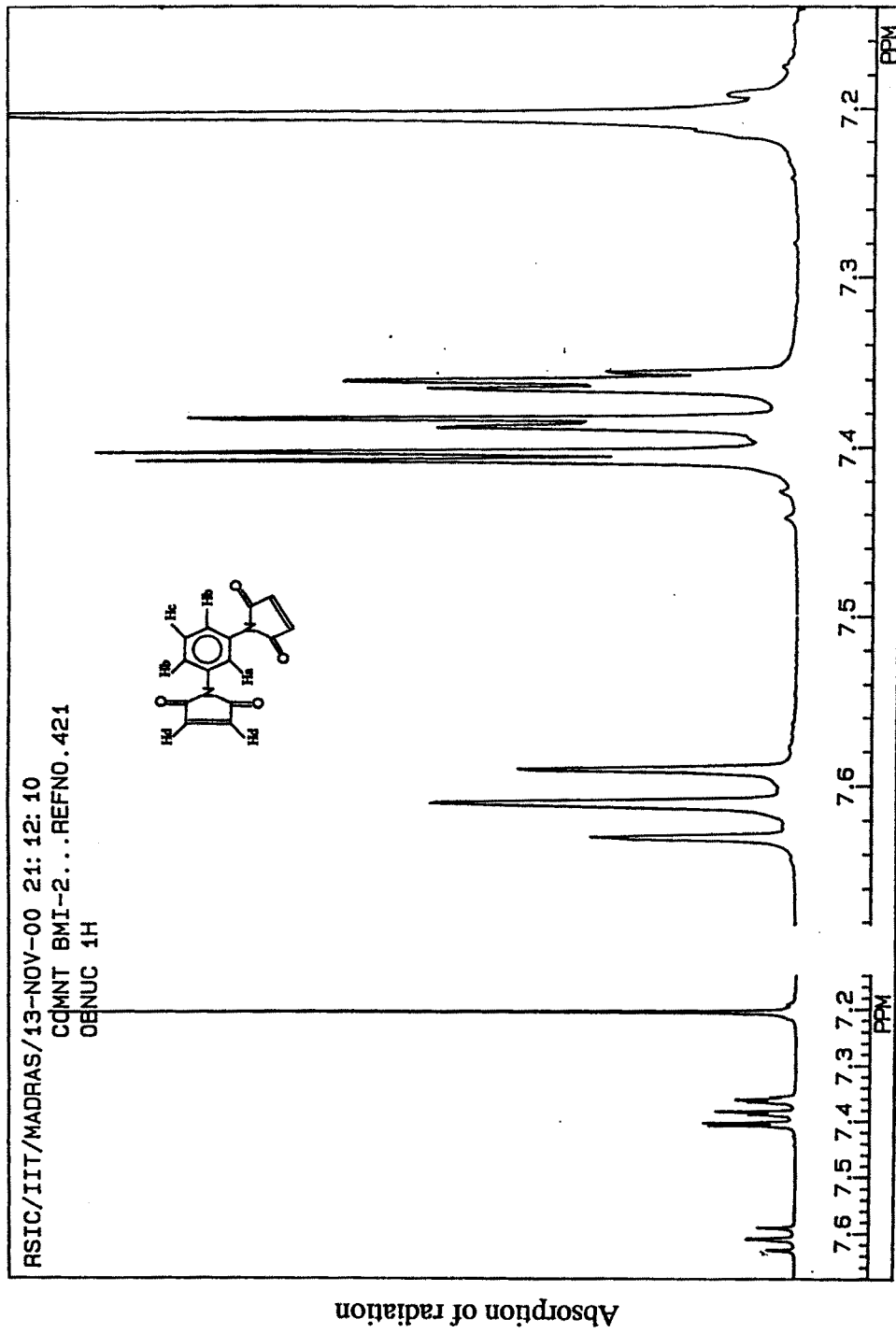


Figure 3.9 Expanded ¹H-NMR spectra of BMI-2

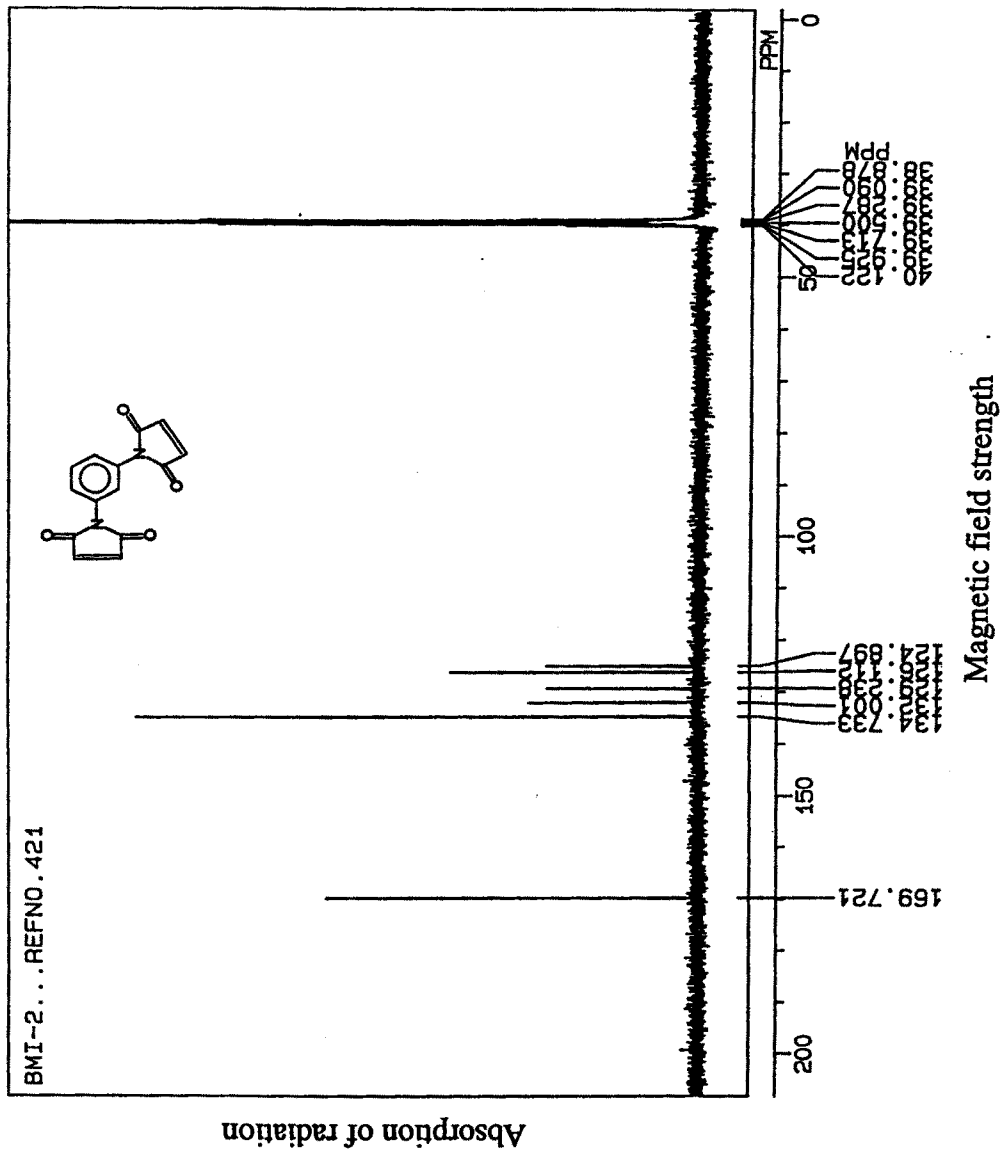


Figure 3.10 ^{13}C -NMR spectra of BMI-2

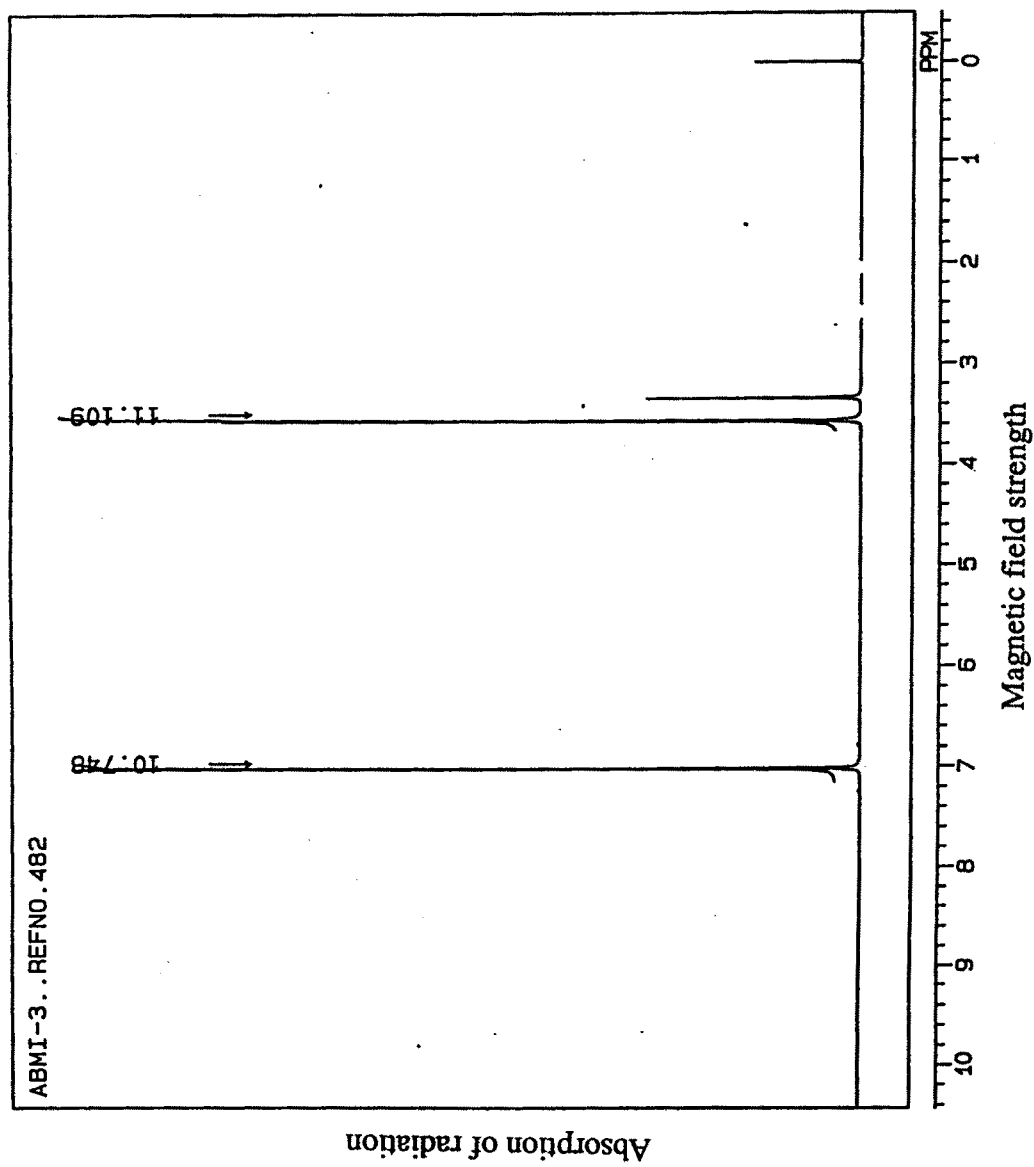


Figure 3.11 ¹H-NMR spectra of BMI-3

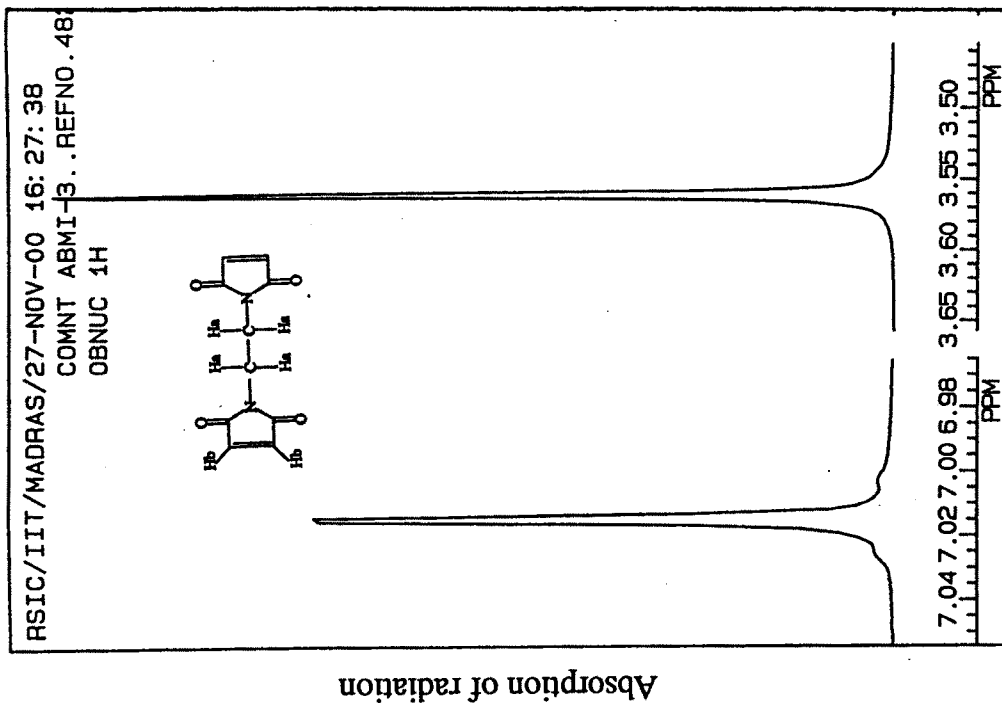


Figure 3.12 Expanded ¹H-NMR spectra of BMI-3

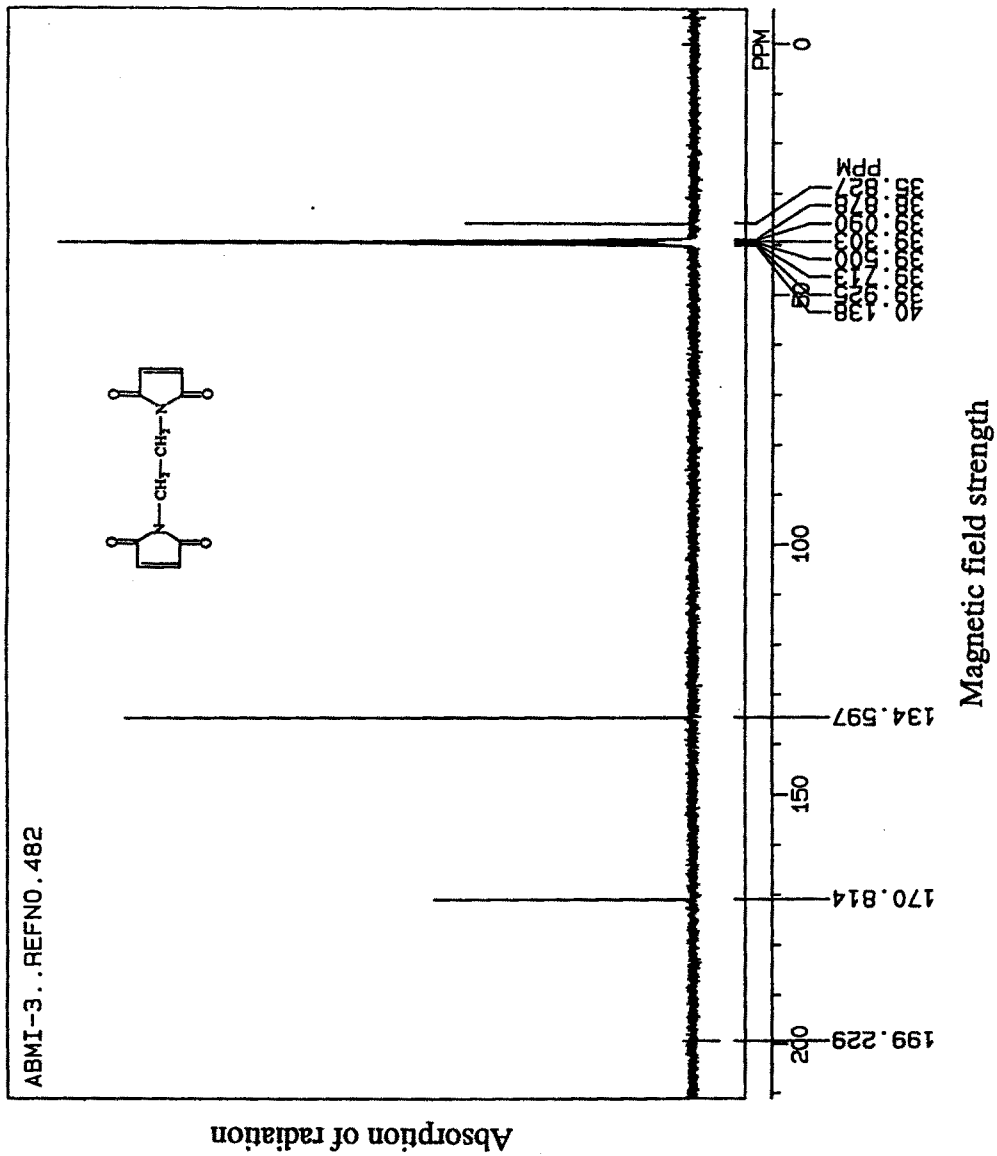


Figure 3.13 ¹³C-NMR spectra of BMI-3

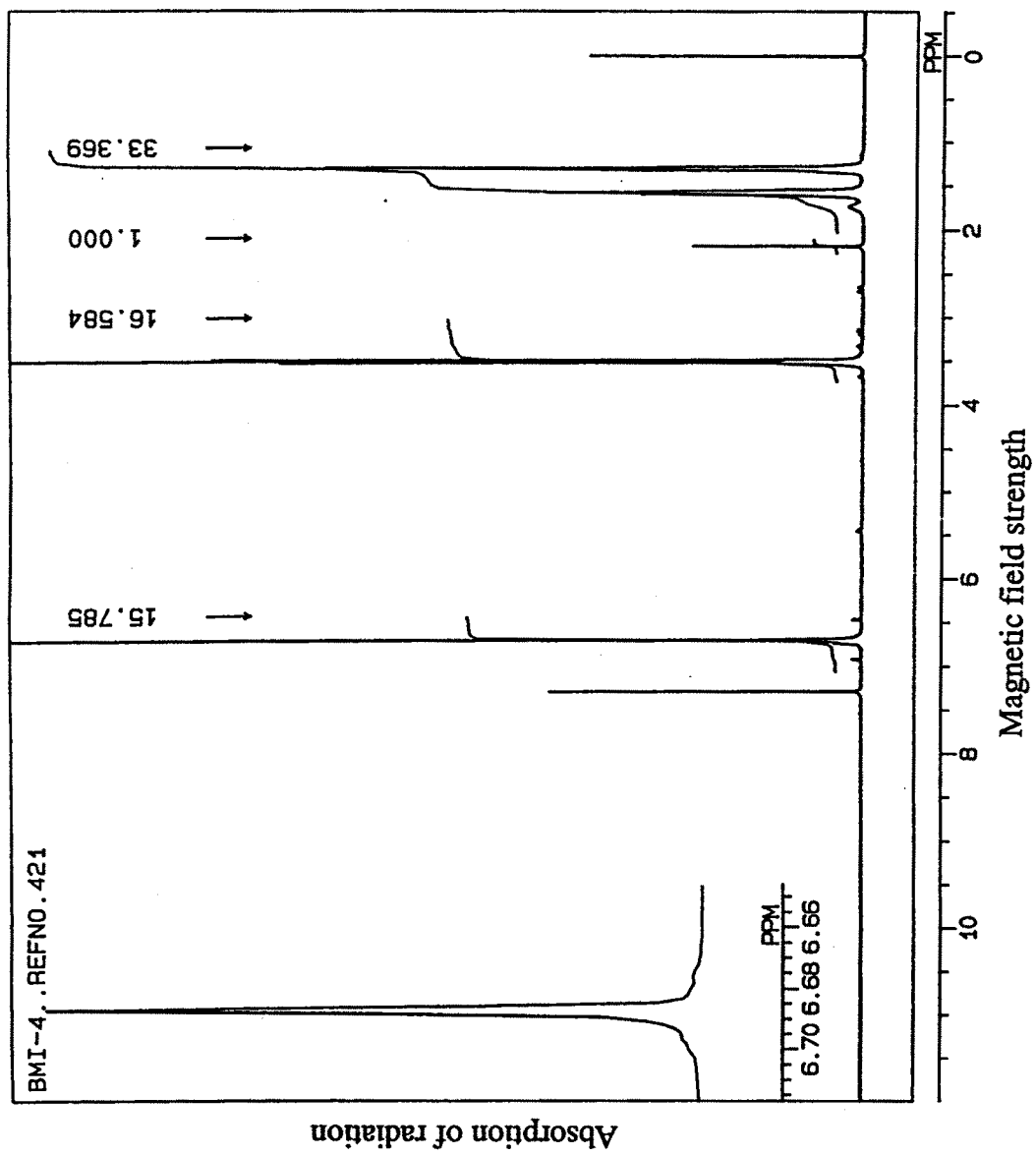


Figure 3.14 ¹H-NMR spectra of BMI-4

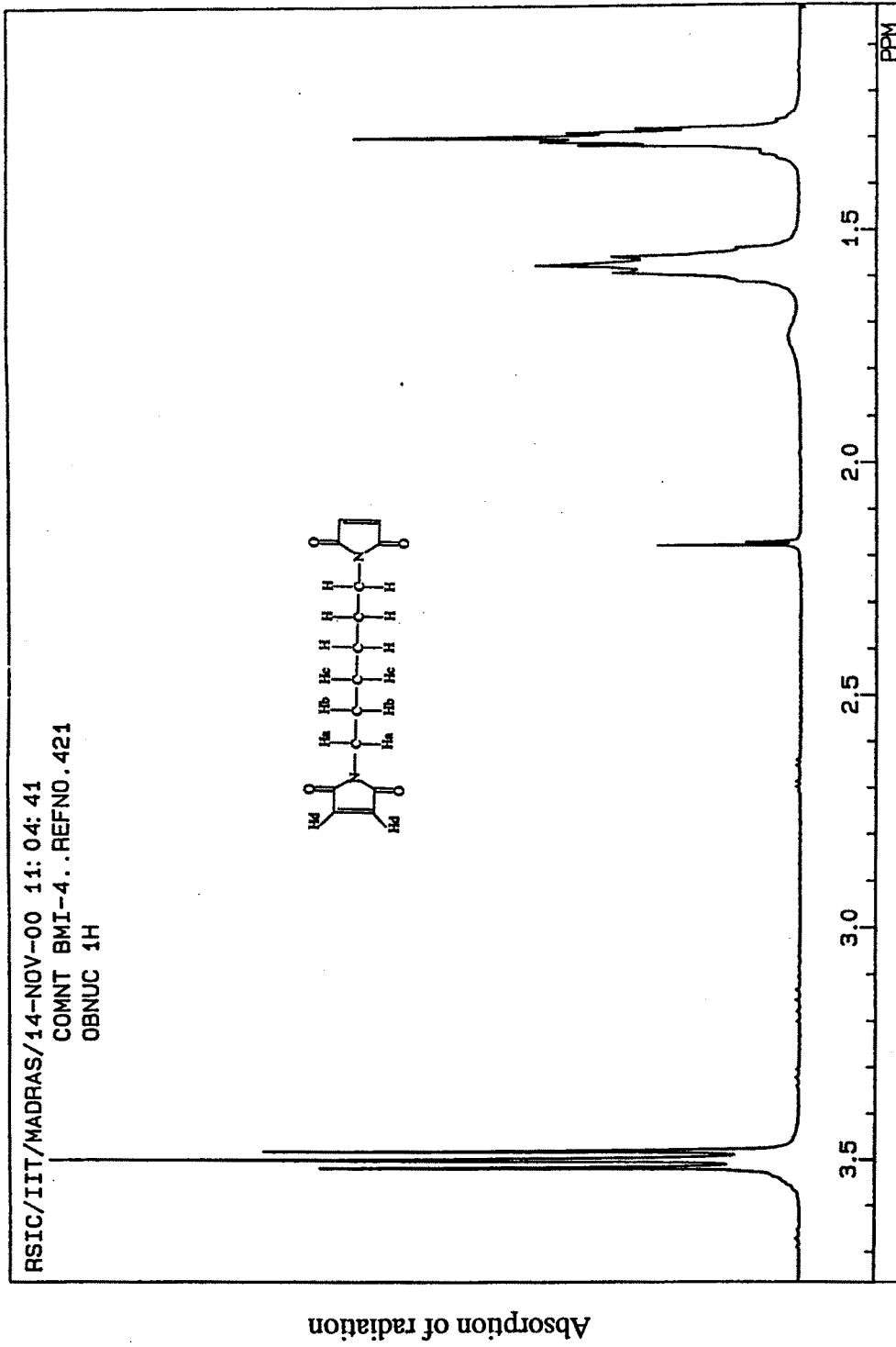


Figure 3.15 Expanded ¹H-NMR spectra of BMI-4

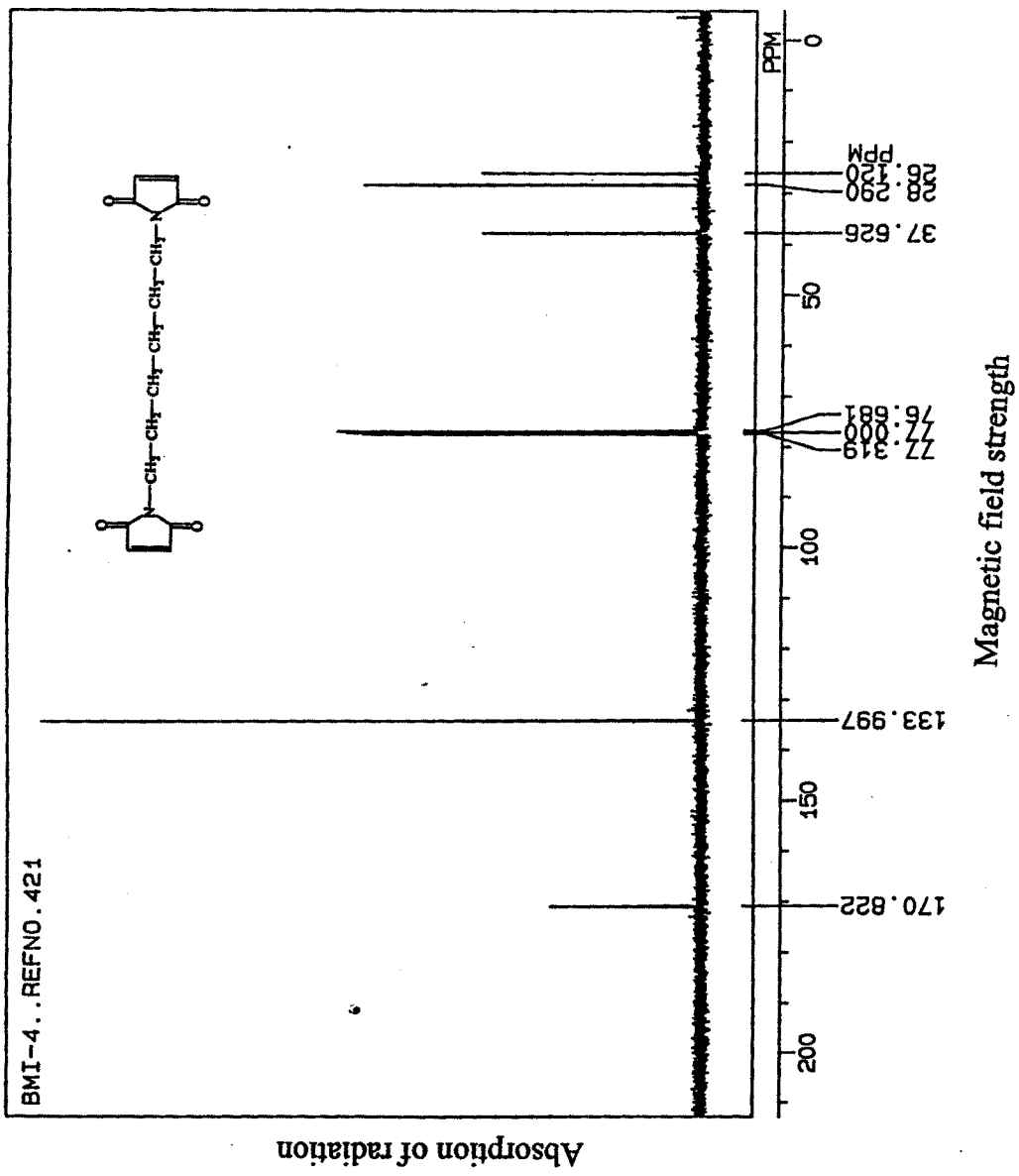


Figure 3.16 ^{13}C -NMR spectra of BMI-4

3.5 HOMOPOLYMERIZATION OF BISMALIMIDES

Figures 3.17 - 3.20 represent IR spectroscopic evidence for the homopolymerization reaction of bismaleimides BMI-1, BMI-2, BMI-3, and BMI-4 in the presence of epoxy resin.

Figures 3.17a - 3.20a represent IR spectra of pure bismaleimides BMI-1, BMI-2, BMI-3, and BMI-4 and Figures 3.17b - 3.20b represent IR spectra of unmodified epoxy resin respectively. Whereas Figures 3.17c - 3.20c and 3.17d - 3.20d represent IR spectra of the mixture of epoxy resin and bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) with a composition of 100:10 and 100:50 respectively. The IR spectra of the mixture of epoxy resin and bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) with a composition of 100:50 taken after heating at 150°C for four to five hours are given in Figures 3.17e - 3.20e.

Figures 3.17a - 3.20a show that the peaks at 3098 cm^{-1} , 3105 cm^{-1} , 3100 cm^{-1} and 3090 cm^{-1} correspond to H-C= vibration of bismaleimides BMI-1, BMI-2, BMI-3 and BMI-4 respectively and are widely accepted as reference to follow the conversion of BMI double bonds.

The peaks observed at 3098 cm^{-1} , 3105 cm^{-1} , 3100 cm^{-1} and 3090 cm^{-1} in Figures 3.17d - 3.20d respectively confirm the presence of bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) in the epoxy mixture. The corresponding peaks are poorly resolved in Figures 3.17c - 3.20c due to lower concentration of bismaleimides.

The considerable decrease in the intensity of peaks at 3098 cm^{-1} , 3105 cm^{-1} and 3101 cm^{-1} in the IR spectra of the mixture of epoxy resin and

bismaleimides (BMI-1, BMI-2 and BMI-3 respectively) with a composition of 100:50 taken after heating at 150°C for four to five hours (Figures 3.17e - 3.20e) are observed. It confirms the occurrence of bismaleimides homopolymerization reaction at lower temperature (140°C - 150°C) in the presence of epoxy resin. This may be explained due the formation of zwitter ion adduct between the oxirane ring of epoxy resin and double bonds of bismaleimides, which anionically induce homopolymerization reaction at lower temperature (Musto *et al.*, 1998) whereas, the homopolymerization reaction of pure bismaleimides BMI-1, BMI-2, and BMI-3 normally occurs at 180°C, 203°C, and 195°C respectively. In the IR spectra of epoxy and BMI-4 mixture, (Figure 3.20e) there is no significant change in the intensity of peak observed at 3090 cm⁻¹. This implies that the homopolymerization reaction of BMI-4 is not effective, since the activation energy required for BMI-4 homopolymerization reaction is very high and it occurs only at 227°C. Hence epoxy resin effectively aids the homopolymerization reaction of bismaleimides BMI-1, BMI-2 and BMI-3 at lower temperature than BMI-4. This observation is well in agreement with Musto *et al.* (1998).

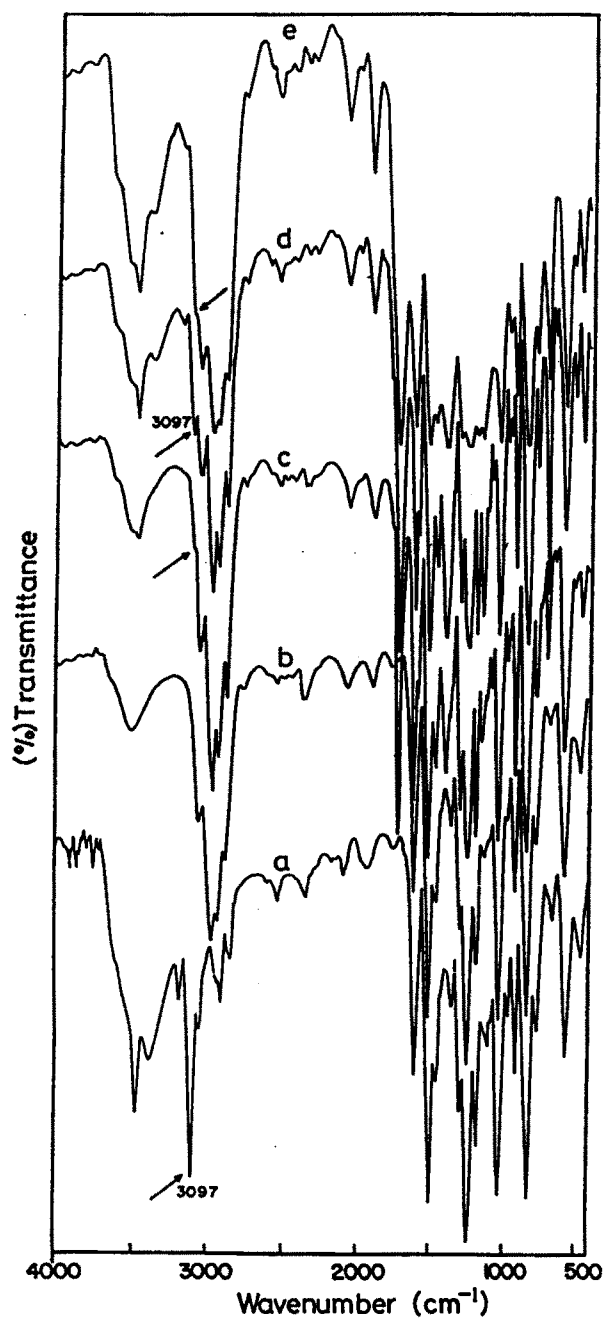


Figure 3.17 FTIR spectra of (a) pure BMI-1, (b) unmodified epoxy, (c) epoxy/BMI-1 : 100/10, (d) epoxy/BMI-1 : 100/50 and (e) epoxy/BMI-1 : 100/50 after heating at 150°C for four hours.

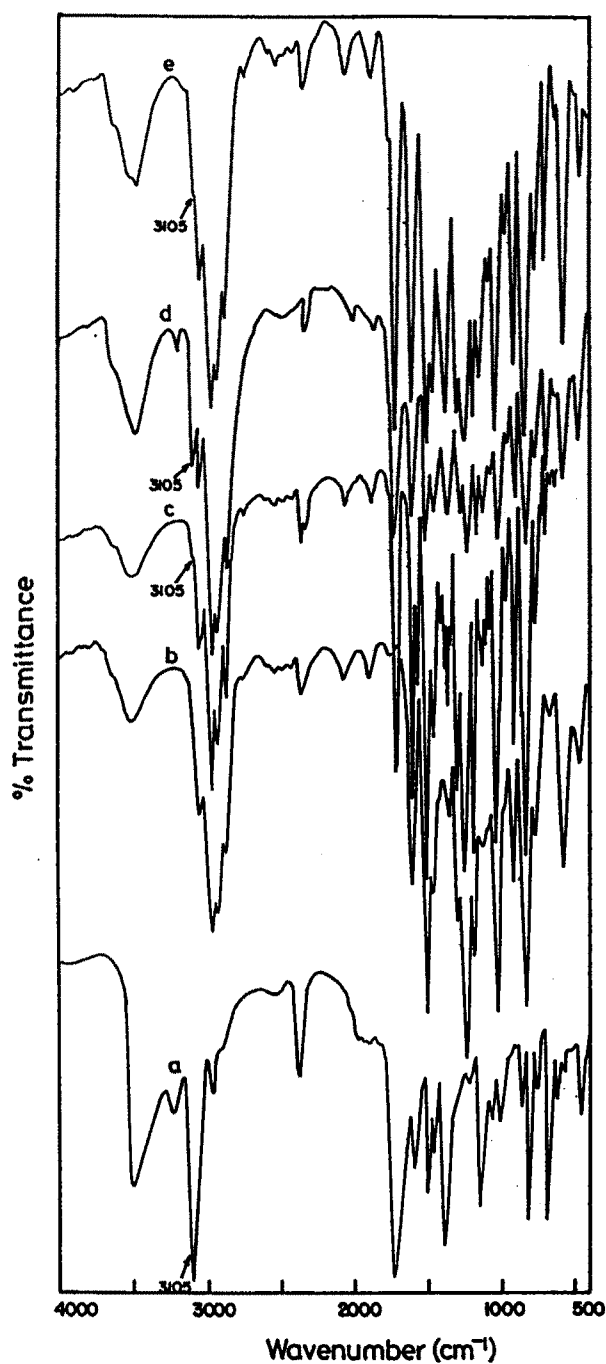


Figure 3.18 FTIR spectra of (a) pure BMI-2, (b) unmodified epoxy, (C) epoxy/BMI-2 : 100/10, (d) epoxy/BMI-2 : 100/50 and (e) epoxy/BMI-2 : 100/50 after heating at 150°C for four hours.

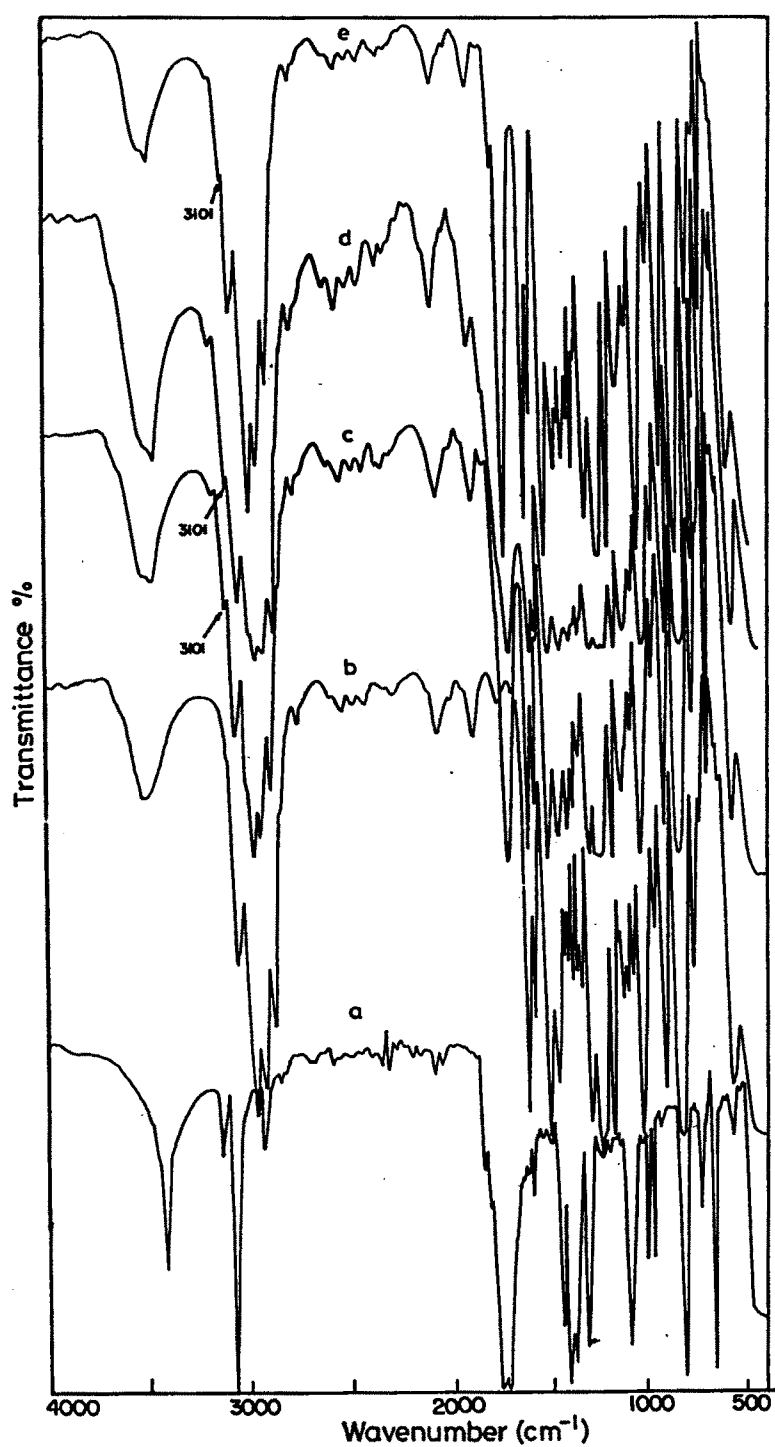


Figure 3.19 FTIR spectra of (a) pure BMI-3, (b) unmodified epoxy, (c) epoxy/BMI-3 : 100/10, (d) epoxy/BMI-3 : 100/50 and (e) epoxy/BMI-3 : 100/50 after heating at 150°C for four hours.

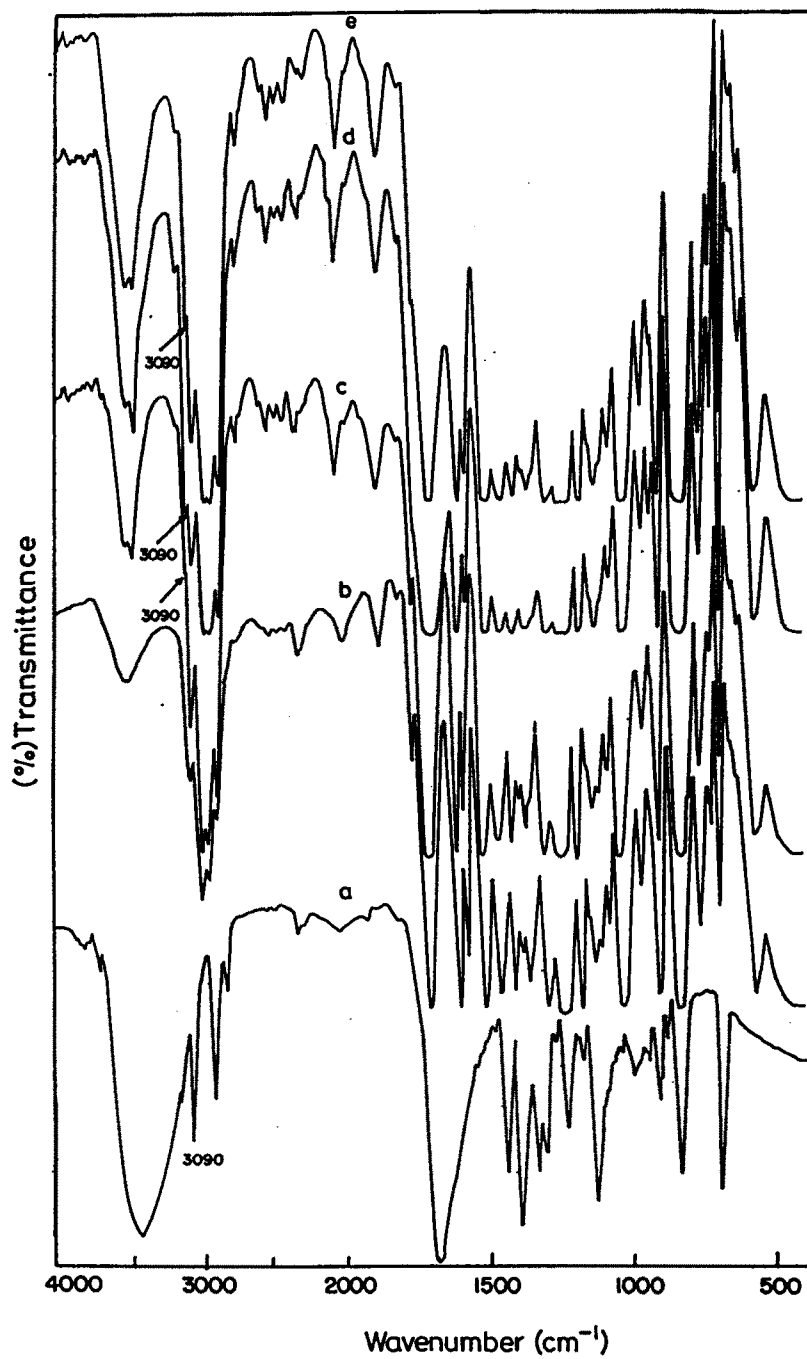


Figure 3.20 FTIR spectra of (a) pure BMI-4, (b) unmodified epoxy, (c) epoxy/BMI-4 : 100/10, (d) epoxy/BMI-4 : 100/50 and (e) epoxy/BMI-4 : 100/50 after heating at 150°C for four hours.