CHAPTER - II

CHAPTER-2

PREPARATION AND CHARACTERIZATION OF CIS-1,4 POLYBUTADIENE BASED MODIFIERS FOR PVC.

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2.1 INTRODUCTION

Chemical modification of diene elastomers, alongside blending, has emerged as an active field of research for altering and optimizing the physico-chemical and mechanical properties of these polymers. More recently, there has been growing interest in the modification of rubbers by epoxidation with peracids and other methods, as the modified products show certain outstanding properties vis-a-vis, the unmodified rubber[1,2]. Introduction of polar functional groups ~~like~~ such as epoxide units ~~epoxy~~ along the backbone is one of the most promising methods of modifying polydienes. Ref ? ×

? Natural rubber (NR) ~~was first~~ has been epoxidized[3], ~~and~~ the chemistry of epoxidation of unsaturated compounds and subsequent ring opening reactions have been reported in literature[4-6] and 6 years* 12 years recently reviewed[1]⑦. Epoxidation of polydienes with various peracids has also been studied by many authors[8-18], who have investigated the kinetics of the reactions, reactivity of the double bonds, and the effect of reaction parameters on the number of epoxy groups introduced into the polymeric chain. The reactivity of double bond in PBR towards epoxidation, showed that 1,4-unsaturation is more reactive than 1,2-unsaturation[19, 20].

1988
4
1982
are not recent

The choice of epoxidized polymers as potential plasticizers was prompted by the knowledge that the existence of an oxirane ring in low molecular weight compounds leads to exothermic mixing with chlorine containing compounds[21]. Also low molecular weight epoxidized oils form a special class of plasticizers possessing inherent advantages[22]. However, high molecular weight materials are expected to provide relatively superior permanence in physical properties than their low molecular weight counterparts, which in turn impart higher flexibility than the former[23-25].

Among the polydienes, PBR with a ~~C~~cis-1,4-structure has a lower glass transition temperature (Tg) than NR. Therefore, PBR-based modifiers would be more efficient plasticizers in terms of depressing Tg of a polymer like poly(vinyl chloride.)

In the present work, therefore, high molecular weight PBR has been used as the backbone polymer and epoxidized under optimised conditions to achieve various degrees of epoxidation in the range 5 to 25 mol%.

The degree of epoxidation has been determined by HBr titration, ^{1}H NMR, ^{13}C NMR and elemental analysis. Further, characterization has been done by IR, solution viscosity, thermal analysis and contact angle measurements.

A chlorohydrin derivative of PBR has also been prepared and characterized.

2.2 EXPERIMENTAL

2.2.1 MATERIALS

Cis-1,4 polybutadiene (PBR) was supplied by M/s Indian Petrochemicals Corporation Limited, Baroda. It was purified before use. PBR was dissolved in toluene and filtered. The polymer was reprecipitated in excess of methanol and dried under vacuum at room temperature to constant weight.

Hydrogen peroxide (9%), formic acid (85%) and hydrochloric acid were obtained from Qualigens, India. Toluene, methanol, chloroform, glacial acetic acid, HBr in glacial acetic acid (30% solution), chlorobenzene and pyridine were supplied by BDH, India. Crystal violet was obtained from Ferale, Germany. All the reagents used were LR or AR grade and used without further purification.

2.2.2 PREPARATION OF EPOXIDIZED POLYBUTADIENE

Epoxidized polybutadiene (EPBR) with various levels of epoxy content (~5 - 25 mol %) and its derivatives reported in this chapter were prepared by a solution precipitation polymerization technique[11,26,27]. Epoxidation was carried out in a 2 liter, three-necked flask equipped with a mechanical stirrer, a thermometer and an addition funnel. The reaction mixture was maintained at 25 ± 1°C with the aid of a water bath. Table 2.1 gives the details of the reactant compositions and other conditions used.

?

Table 2.1

Feed compositions for epoxidation reactions

Temp : 25°C. PBR = 550 m mol, Toluene=1000 ml, cm³

Reaction time;5 h.

Sr. No	Code No.	H_2O_2 m/mol	HCOOH m/ mol
1	E_1	74	312
2	E_2	111	489
3	E_3	148	636
4	E_4	222	978
5	E_5	296	1291

In a typical epoxidation run 30 g of purified PBR was dissolved in 1000 cm³ ~~ml~~ of toluene. To this, the desired amount of formic acid was added followed by calculated amount of hydrogen peroxide. The bath temprature was fixed at 25 ± 1 °C throughout, maintaining a low stirring speed. The reaction was continued for 5 h after which EPBR was recovered by precipation in an excess of methanol. The samples were further washed with fresh methanol and dried in vacuum at room temperature to constant weight. Epoxide equiv weight det?

Chlorohydrin derivative of PBR :

EPBR with 25 mol% epoxidation level was used to prepare the chlorohydrin derivative. Epoxy sample (20 g) was dissolved in 1000 ml of tetrahydrofuran (THF). By using a dropping funnel, HCl (1N M) was added to it dropwise with vigorous stirring. The reaction was continued for 2 h. The chlorohydrin derivative was recovered by methanol precipitation. The polymer sample was washed until the washings were free of acid and dried in vacuum at room temperature ~~till~~ to constant weight.

2.2.3 CHARACTERIZATION

How was the extent of chlorohydrin formation — heterogeneous product.

PBR, EPBR and chlorohydrin derivative were characterized by HBr titration, I.R, NMR, elemental analysis, thermal analysis, contact angle measurements and viscosity measurements.

2.2.3.1 Infra-red spectroscopy

Infra red spectra of the samples were recorded on Shimadzu IR and/or Bruker IFS-113V (FTIR). Thin solution cast films of the samples were prepared for recording the spectra.

2.2.3.2 HBr - titration

The Epoxy content ~~in~~ of the samples was estimated by the HBr titration technique reported in the literature [28, 29]. Typically the EPBR sample (0.1 gm) was dissolved in 25 ml of toluene. To this 25 ml of mixture of chloroform and chlorobenzene (1:1) were added followed by 4 - 6 drops of crystal violet solution (1%) in glacial acetic acid, and the resulting solution was titrated against a standard solution of HBr in glacial acetic acid to a blue-green end point which was stable for 30 sec. Long term stability of the end point is not to be anticipated as the HBr will slowly add to the polymer unsaturation in the absence of epoxide groups. The HBr reacts stoichiometrically with epoxy groups to form bromohydrins. The quantity of acid consumed was used to calculate the epoxy content by the procedure given elsewhere[28,29].

2.2.3.3 Nuclear Magnetic Resonance (NMR) Spectroscopy :

^{1}H NMR and ^{13}C NMR studies of all the samples were carried out by using JEOL JNM - F x 100 Fourier Transform - NMR spectrometer. A 5% solution in chloroform ($CDCl_3$) was used for ^{13}C NMR analysis and 1% solution in ($CDCl_3$) was used for ^{1}H NMR analysis using tetra methyl silane (TMS) as the internal standard.

How used quantitatively
Info needed

2.2.3.4 Elemental analysis

Elemental analysis of PBR, EPBR and chlorohydrin derivative was carried out by using Carlo-Erba Elemental Analyser Model - 1106 (R & D centre, I.P.C.L. Baroda). Before the analysis samples were dried at 50°C under high vacuum to minimize interference by trace moisture or other volatiles.

2.2.3.5 Thermal analysis

DSC thermograms of some of the samples were recorded in a nitrogen atmosphere on a Du pont 910 instrument fitted with a liquid nitrogen cooled subambient accessory (University of Leeds, U.K.) at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out by using a Shimadzu Thermo- analyser, DT 30, at the heating rate of 10°C/min in nitrogen atmosphere.

2.2.3.6 Contact angle measurements

Contact angle measurements of various solvent/polymer systems were carried out with a horizontal low power microscope equipped with a protractor eye piece and rotatable cross wire. This contact angle θ meter was fabricated at University of Leeds, U.K. A drop of the liquid about 2µl in size was placed on the horizontal surface of the sample and the contact angles at both sides of the projected silhouette of the drop were measured. Average values for five drops were taken as representative of the given solvent/surface system. All the readings were taken after 2 minute of contact allowing the drops to spread and reach steady state.

2.2.3.7 Intrinsic viscosity

The Intrinsic viscosity of all the samples were measured by using an Ubbelohde viscometer at 30.0 ± 0.1°C. Toluene was used as the solvent.

The intrinsic viscosities were obtained from the following relations ;

$$[\eta] = (\eta_{sp}/c)_{c=0}$$

where, $[\eta]$ is intrinsic viscosity, c is concentration in g/100 ml and η_{sp} is specific viscosity which is calculated ~~by~~ after. measuring the flow time of solution (t) and solvent (t_0) from following expression

Logic

$$\eta_{sp} = \frac{t - t_0}{t_0}$$

2.3 RESULTS AND DISCUSSION

Epoxidation of unsaturated polymers ~~and~~ including polybutadiene has been reported by many authors[1-7]. The methods use d ~~added~~ peroxy acids ~~or~~ and their formation involved in situ using a mixture of hydrogen peroxide with aliphatic acids. In the present study s epoxidation of PBR was carried out by using the H_2O_2/HCOOH system. Formation of EPBR can be described by the following reactions:

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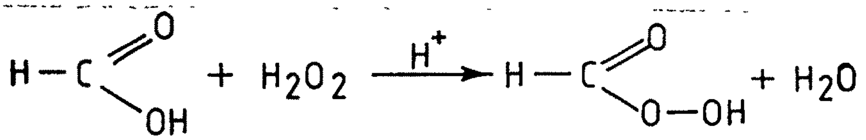
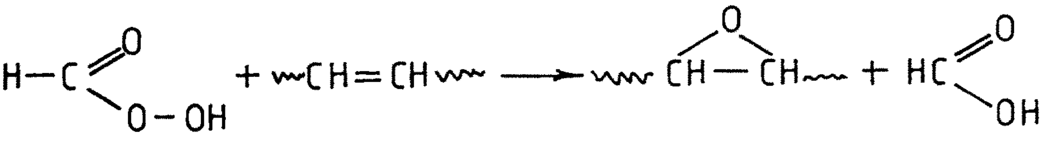
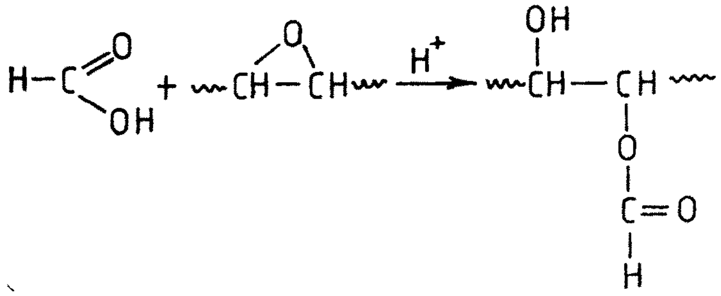


$$HCOOH + H_2O_2 \xrightarrow{H^+} HCOOOH + H_2O$$ ......(1)



$$HCOOOH + \sim CH=CH \sim \longrightarrow \sim CH(O)CH \sim + HCOOH$$ --(2)

The likely side reaction in this case is:



(3)

Reactions(1) and (3) are catalysed by strong mineral acids. By optimising the H_2O_2/HCOOH ratio, the desired level of epoxidation was achieved without the use of an acid catalyst and thereby avoiding the undesirable oxirane ring-opening side reaction (3).

? EPBR samples with degrees of epoxidation in the range 5-25 mol% were prepared. Samples with a modification level higher than 25 mol% showed crosslinking and gelation under the experimental conditions and hence were not prepared.

logic: If they were not prepared, how did they show Xlinking!

The Epoxy content of the various EPBR samples ~~were~~ was determined by HBr titration, ^{1}H NMR, ^{13}C NMR and elemental analysis (Table. 2.2). These methods have been used earlier[30] for the analysis of epoxidised diene polymers including EPBR. These are essentially primary methods of analysis. However, it is also possible to make use of parameters such as the Tg, the density and the contact angle, which are found to be related to the epoxy content, for the estimation of degree of epoxidation but with independent calibration[31].

not quantitative

Table 2.2

Analysis of Epoxidised poly(butadiene) (EPBR).

Sr. No.	Code No.	Epoxidation level (mol%)					Tg (K) from DSC
		HBr	^{1}H NMR	^{13}C NMR	*E.A		
			How done		%C	%O	
1.	R	-	-	-	-	-	170
2.	E_1	4.9	4.4	5.5	5.5	4.8	-
3.	E_2	9.8	9.5	10.2	10.5	9.5	-
4.	E_3	15.1	14.3	15.1	15.5	14.5	191 3
5.	E_4	20.3	20.8	20.5	21.5	21.0	197.5
6.	E_5	24.1	25.5	26.2	26.3	23.8	204.1

* Epoxy content was calculated from elemental analysis by % carbon and % oxygen method.

2.3.1 Infra red spectroscopy:

Due to difficulties in obtaining polymer films of uniform thickness, quantitative spectral analysis was not possible. However, IR spectra yield, qualitative information regarding the modification brought about in PBR. ?

An IR spectrum of PBR sample used in this study is shown in Fig. 2.1 which compares well with the spectrum given in the literature[31]. The spectrum exhibits a characteristic -C=C- stretching band corresponding to cis-C=C- at 1660 cm^{-1}. The Intensity of this peak decreases with the degree of epoxidation as shown in the representative spectrum of an EPBR sample (Fig. 2.2, 2.3). On the other hand, new bands appear at 885, 1240 and 1385 cm^{-1} that are characteristic of the epoxy ring[32,33], intensity of which are found to increase with the degree of epoxidation (Fig. 2.2 and 2.3). Also, even at 25 mol% epoxidation, the spectrum does not exhibit any band in the range 3200-3600 cm^{-1}. This shows that the cyclization side reactions which generate hydroxyl functionality are unimportant upto this epoxidation level.

Treatment of EPBR with HCl gave the chlorohydrin derivative by ring opening reaction. This results in the disappearance/decrease in intensities of the bands at 885, 1240, 1385 cm^{-1} that are characteristic of the epoxy ring as shown in the Fig. 2.3 and 2.4; and appearance of a broad band corresponding to hydrogen bonded hydroxyl group.

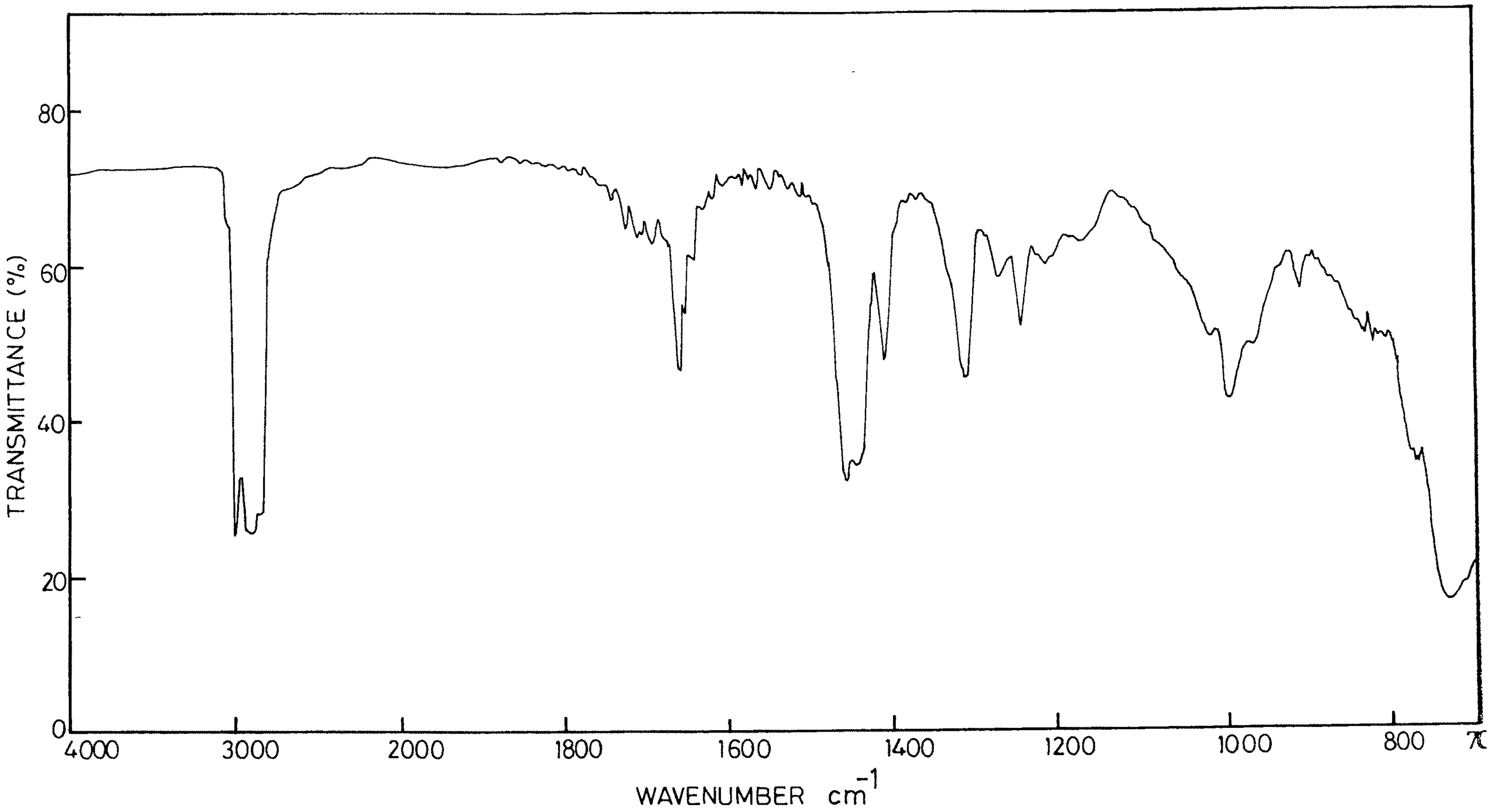


FIG 21 I R. SPECTRUM OF PBR

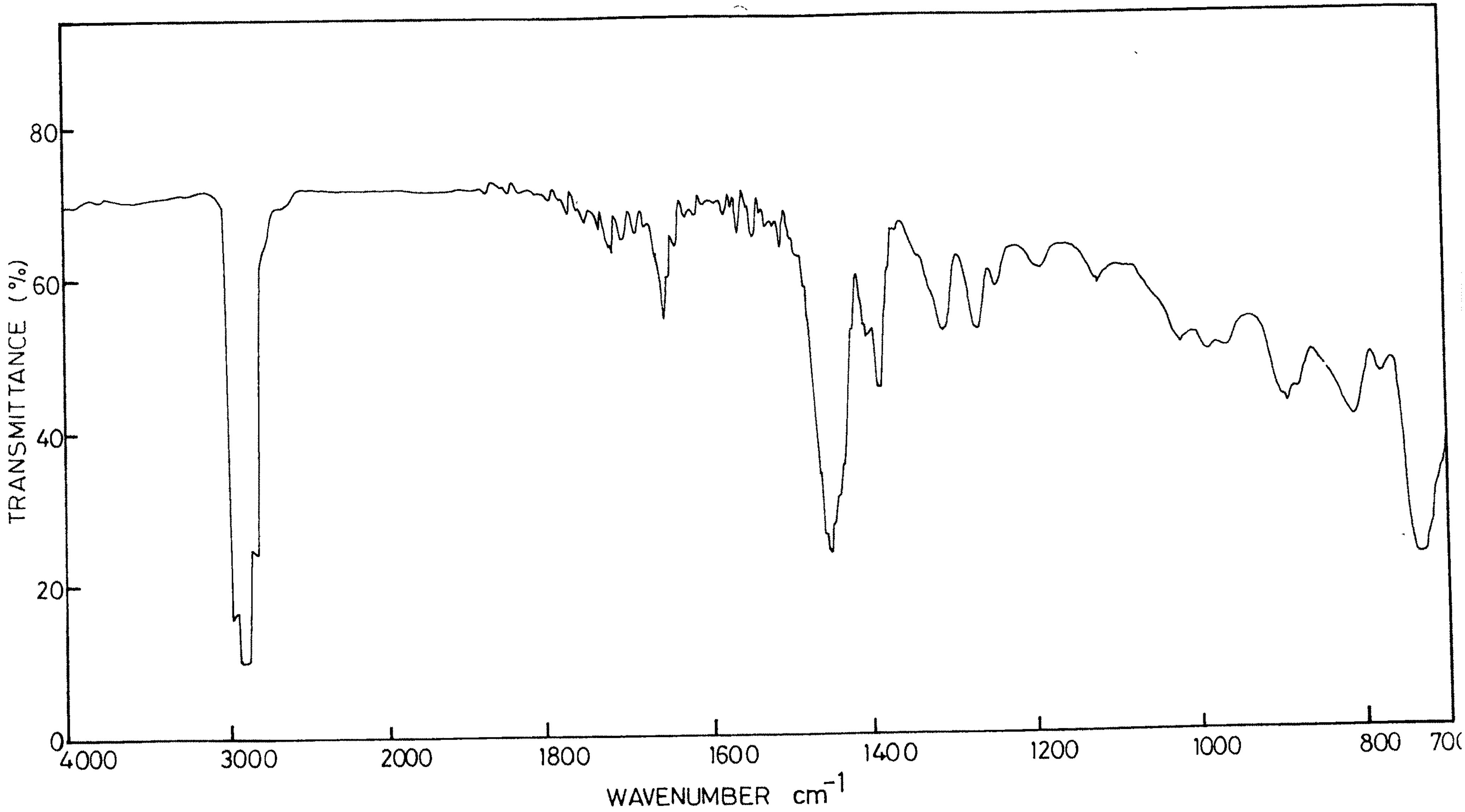


FIG 2 2 I. R SPECTRUM OF EPBR (E_5)

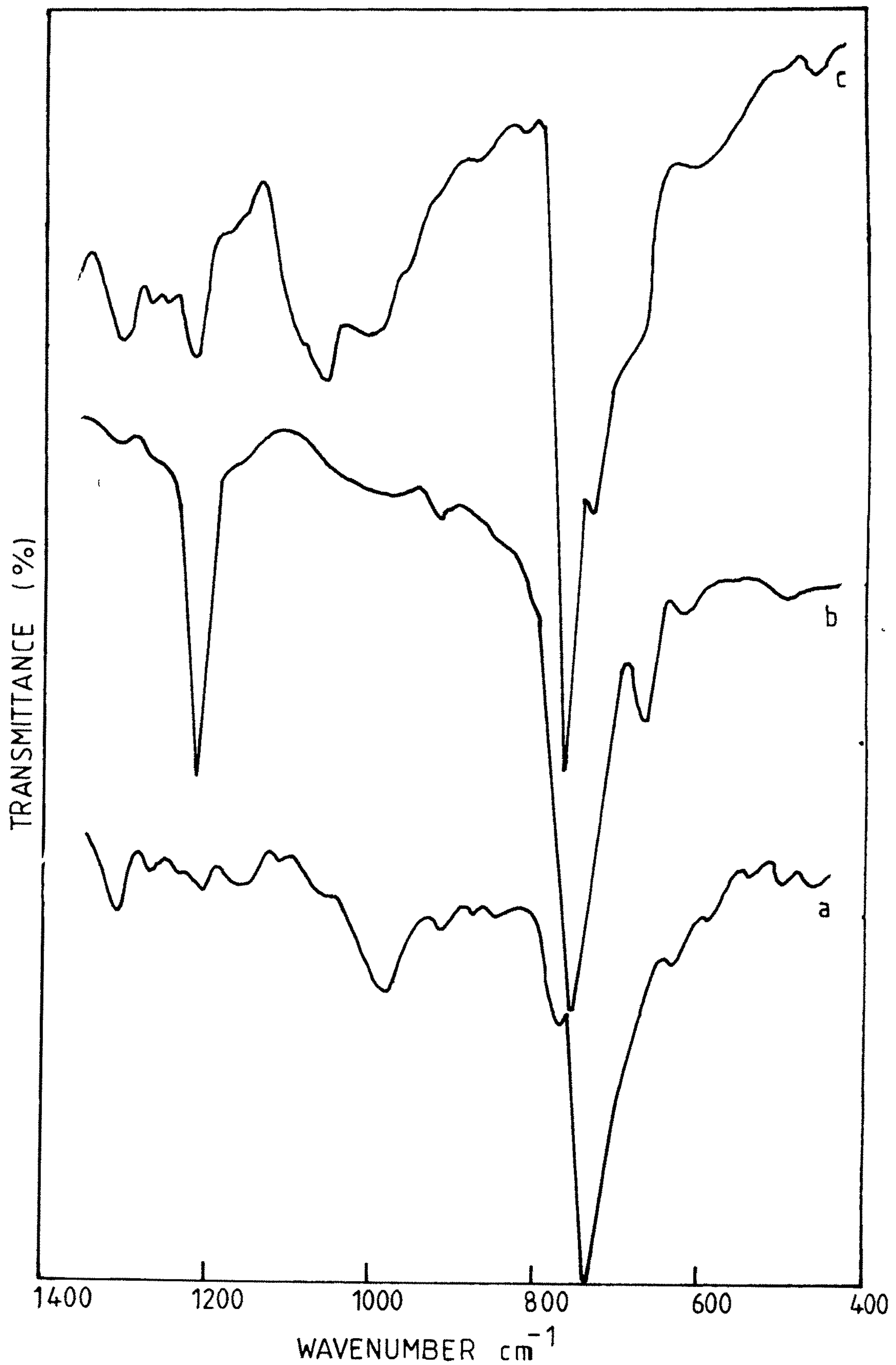


FIG 2 3. FTIR SPECTRA OF (a) PBR (b) EPBR (c) CHLOROHYDRIN DERIVATIVE OF PBR.

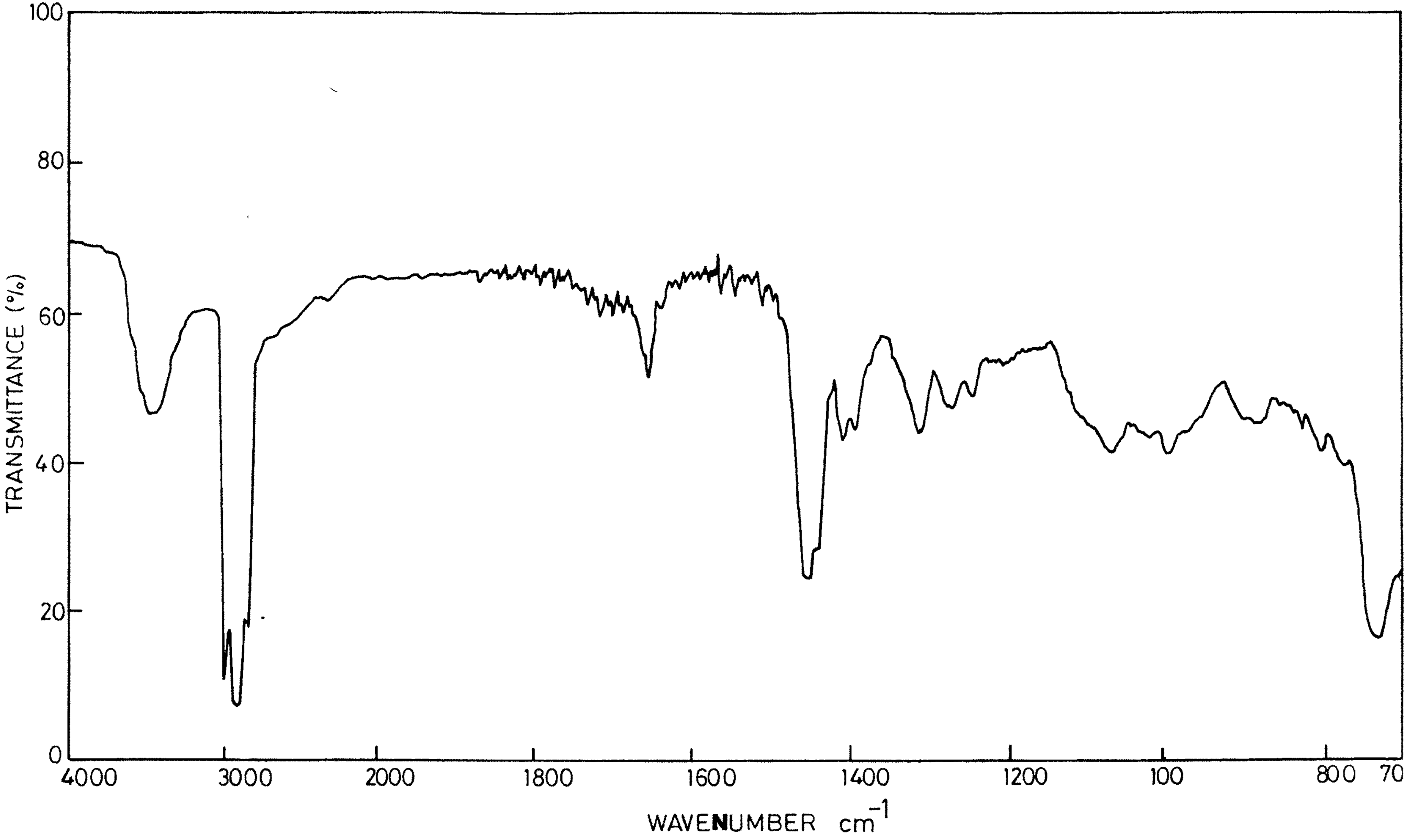


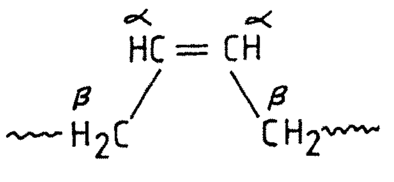
FIG 2.4 I R. SPECTRUM OF CHLOROHYDRIN DERIVATIVE OF PBR

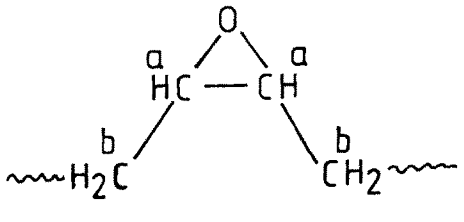
2.3.2 HBr - titration:

Direct titration of oxirane ring with HBr has earlier been shown to be essentially quantitative and with few interferences for epoxidised poly(isoprene) at low modification levels[28-30]. At higher modification levels cyclization side reactions such as those shown earlier may limit solubility resulting in lower analysis figures. In the present study, this titrimetric method gave results that are reproducible and comparable with the results obtained by other methods (Table 2.2) indicating that cyclization is unimportant in the epoxidation range studied. This may be due to lower frequency of adjacent oxirane rings.

2.3.3 Nuclear Magnetic Resonance (NMR) spectroscopy :

^{1}H NMR spectra of all the samples are characterised by rather broad but readily assignable resonances. Labelling the protons of the structural units of PBR and EPBR is as given below :





^{1}H NMR spectrum of PBR is shown in the Fig. 2.5a. In symmetrical units of Cis-1,4 polybutadiene exhibit one resonance peak for protons attached to olefinic carbons (α-peak, $\delta = 5.38$) and one peak for protons bonded to equivalent methylinic carbons (β-peak, $\delta = 2.08$). ^{1}H NMR

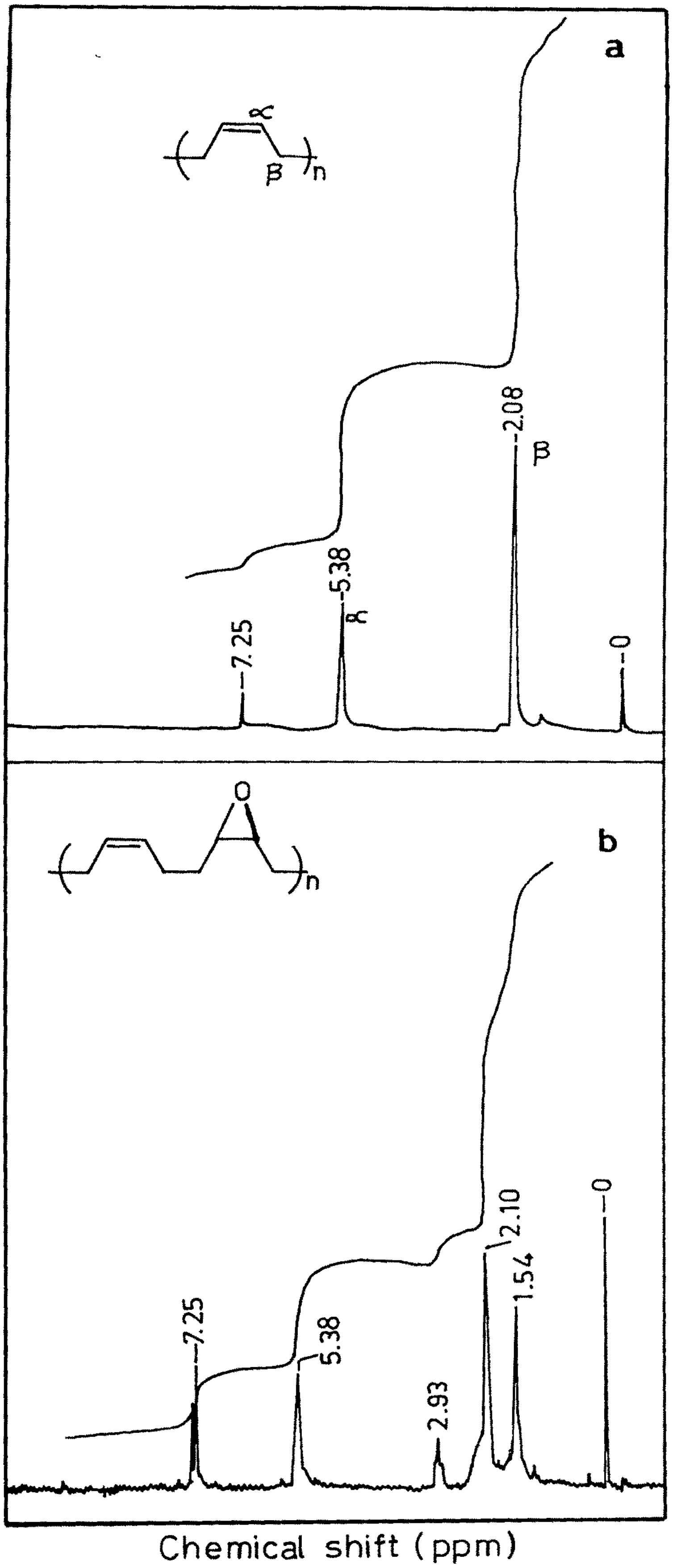


FIG 2.5. ^{1}H NMR SPECTRA OF (a) PBR (b) EPBR (20 mol %)

spectrum of EPBR (Fig. 2.5b) is characterised by two additional signals at $\delta = 1.54$ and $\delta = 2.93$ and the intensities of these small peaks are in the ratio 2:1. These can be attributed to protons H^b and H^a respectively, in the epoxidised unit. Comparison of the spectra of PBR and EPBR shows that during the course of epoxidation a decrease in intensity of the peak of olefinic protons ($\delta = 5.38$) and the corresponding increase in the intensity of the peaks at $\delta = 1.54$ and $\delta = 2.93$, are observed. From the ^{1}H NMR spectra also, it is obvious that no significant side reaction, such as ring opening reaction, occurs in this epoxidation system.

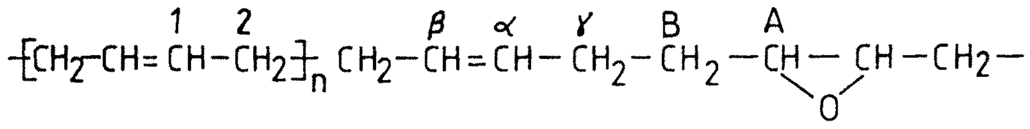
From the integrated areas of the signals of the olefinic and epoxy ring protons, it is possible to determine the epoxy content in the sample by the method described in the literature[30]. Thus, the epoxidation level is given by the relationship :

$$\text{mol \% epoxide} = 100 \left(\frac{A_{2.93}}{A_{2.93} + A_{5.38}} \right)$$

where $A_{2.93}$ and $A_{5.38}$ denote integrated areas of the signals at $\delta = 2.93$ and $\delta = 5.38$ respectively. The degree of epoxidation of various samples calculated by this method is given in Table 2.2. In the epoxidation range studied, viz 5 to 25 mol%, the reproducibility of duplicate measurements was found to be within ± 1.5 mol% except at the lowest concentration where variation was slightly higher.

The resonances at δ = 1.65 and δ = 2.93, characteristic of the epoxide group diminished in intensity and two small new peaks appeared at δ = 3.65 and δ = 3.89 attributable to protons on carbon atoms bearing OH and Cl groups (Fig. 2.6) when EPBR (25 mol%) is treated with HCl to yield the chlorohydrin derivative of PBR[32].

^{13}C NMR spectra of PBR and partially epoxidised PBR in $CDCl_3$ were recorded at 40°C on a 100 MHz spectrometer with TMS as internal standard. Labelling of carbon atoms is as follows .



^{13}C NMR spectra of PBR and EPBR are given in Fig 2.7 and the following peak assignments can be made :

1	2	A	B
C : 129.56,	C : 27.67,	C : 57.78,	C · 28 1,

α	β	γ
C : 130.19,	C : 128.78,	C : 24.61

The weak resonances marked with asterisks correspond to the solvent $CDCl_3$. These assignments are in close agreement with data

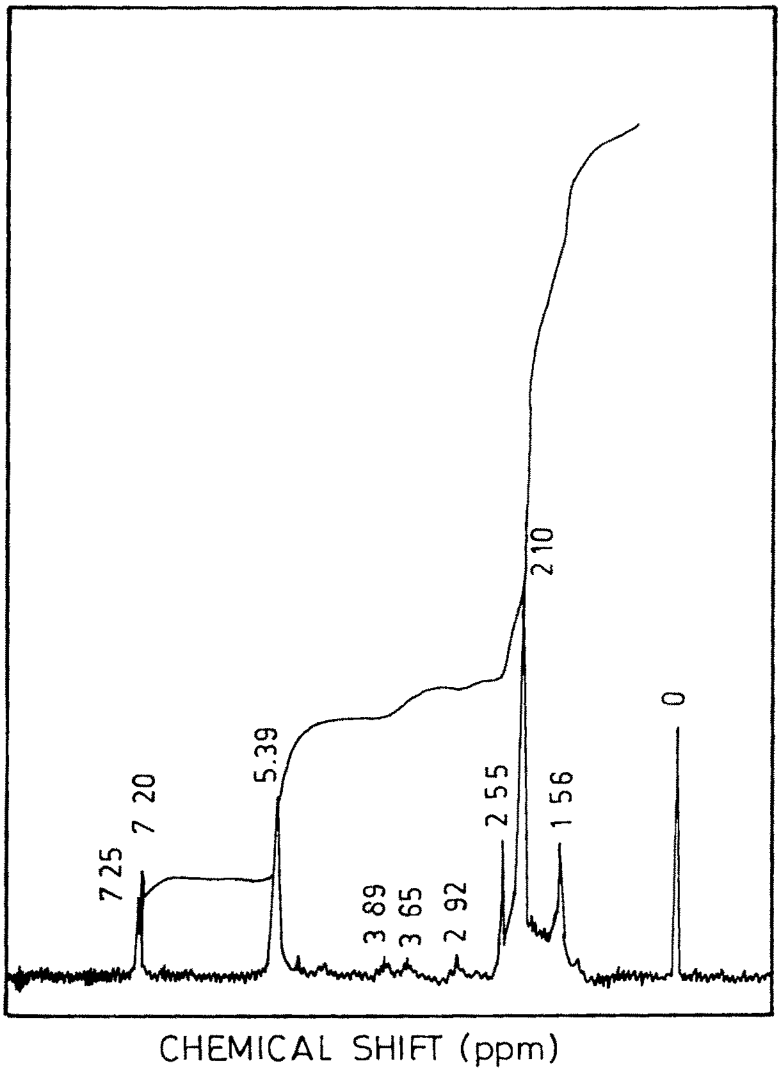
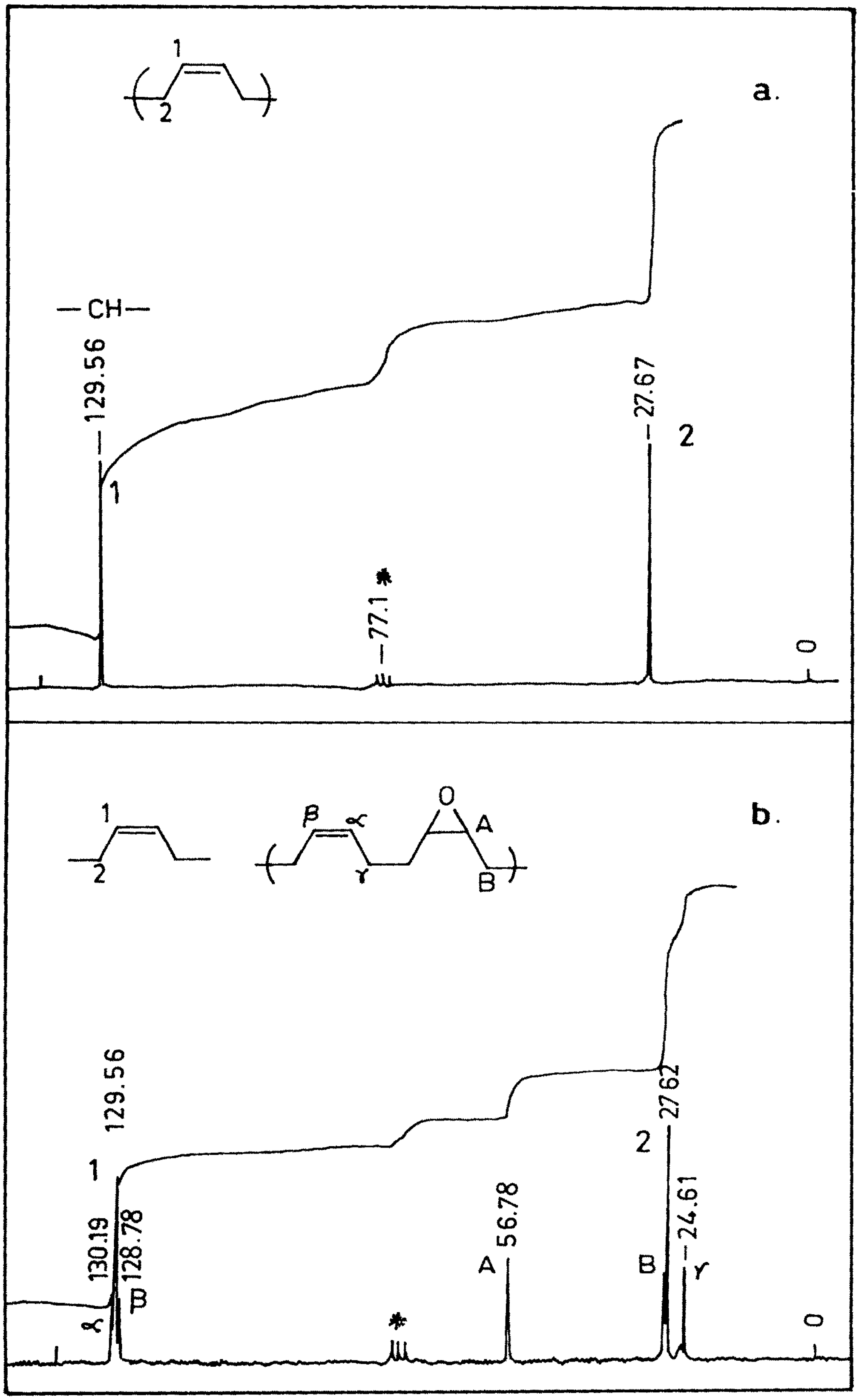


FIG 2.6. ^{1}H NMR SPECTRUM OF CHLOROHYDRIN



Chemical shift (ppm)

Fig. 2.7 ^{13}C NMR SPECTRA OF (a) PBR (b) EPBR (20 mol %)

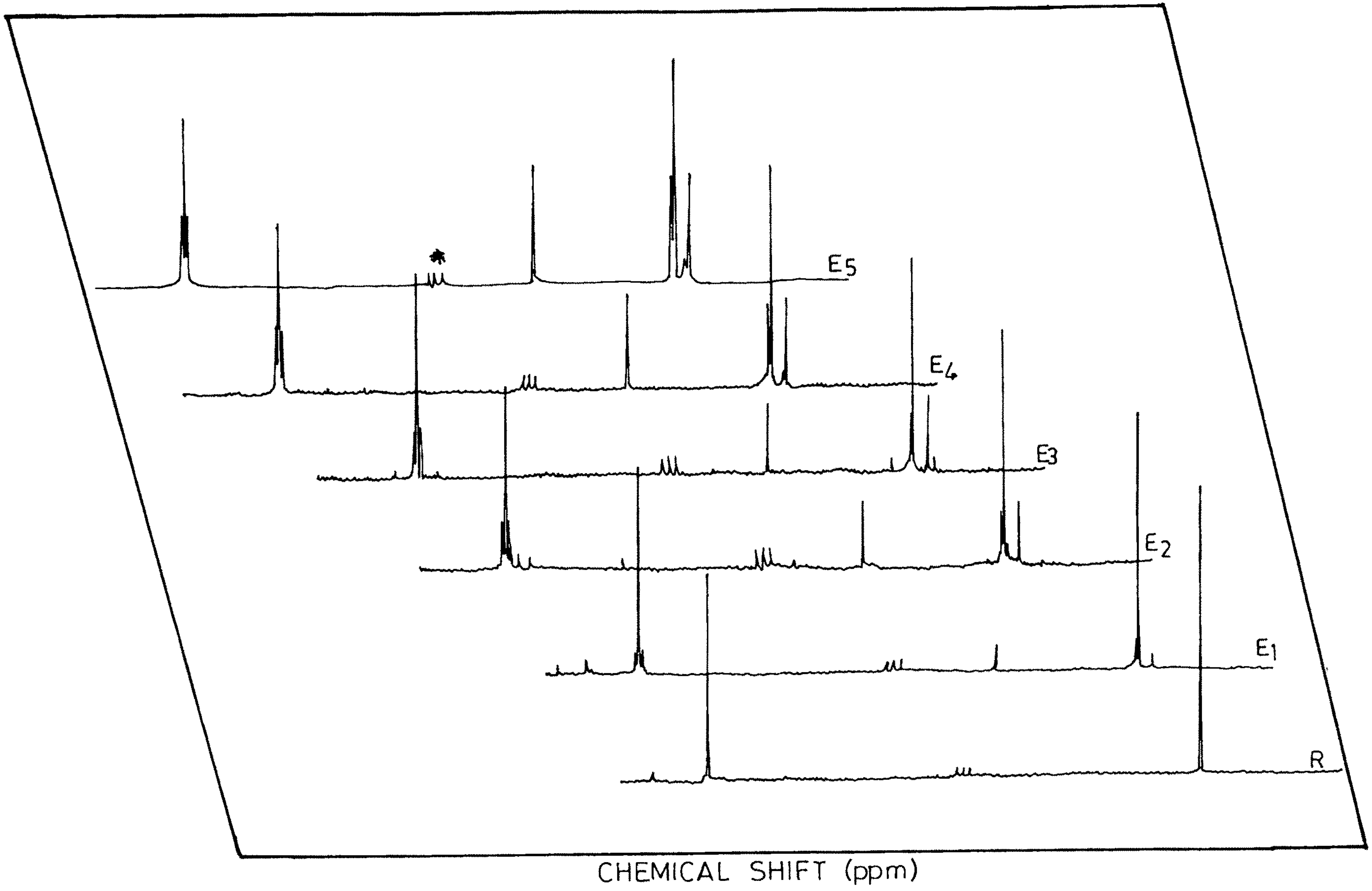


FIG 28 ^{13}C NMR SPECTRA OF EPBR WITH DIFFERENT EPOXY CONTENT

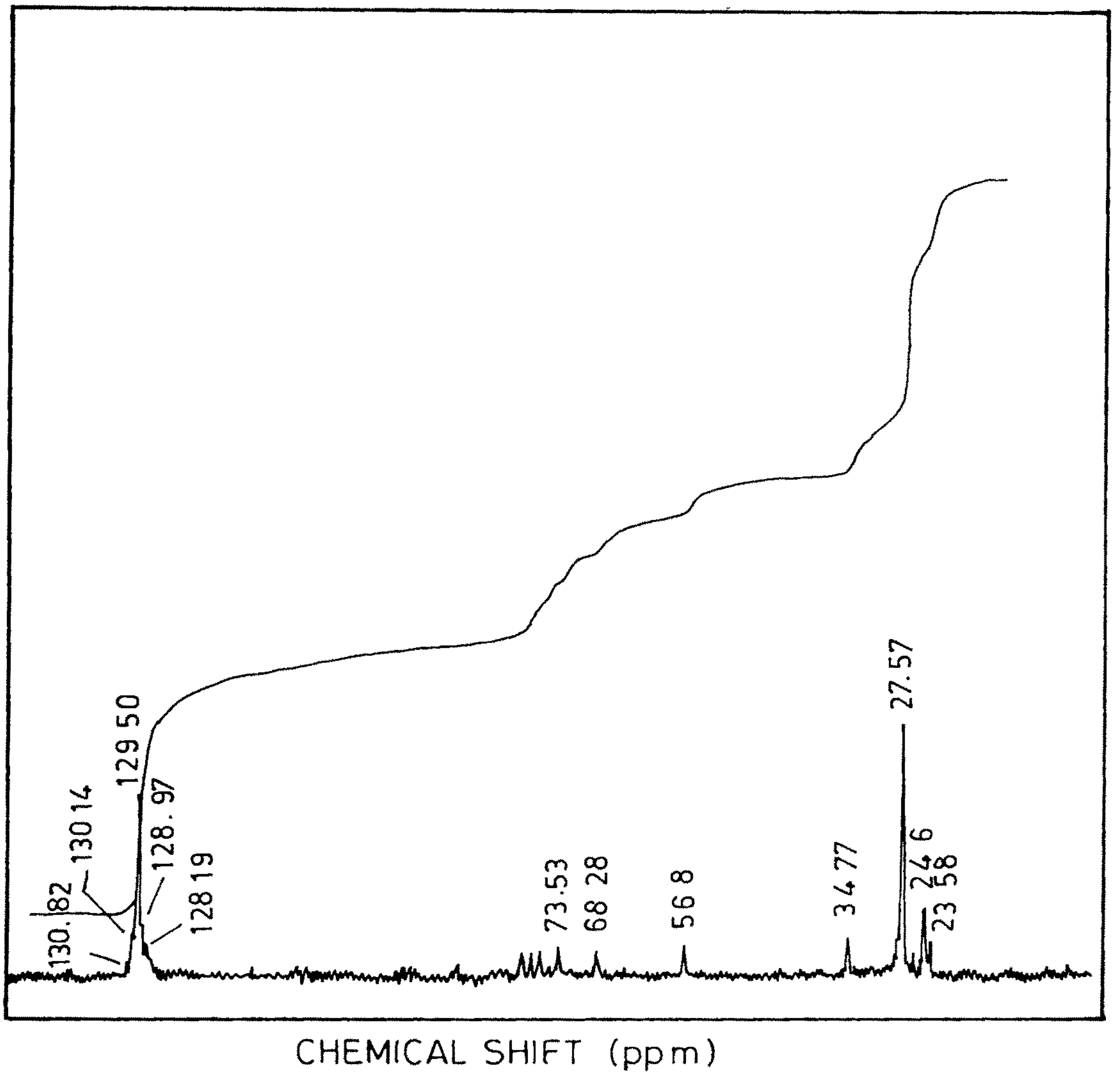


FIG. 2.9 ^{13}C NMR SPECTRUM OF CHLOROHYDRIN DERIVATIVE OF PBR

Novelty of the work since the reference is stated to the support the result

from literature[34]. As in the case of ^1H NMR spectra, epoxy content from the ^{13}C data (Fig. 2.8) was determined using the relationship :

$$\text{mol.\% epoxide} = 100 \left(\frac{A_{56.78}}{A_{56.78} + A_{129.56} + A_{130.19} + A_{128.78}} \right)$$

and the values obtained are given in Table 2.2. In this case also the reproducibility of duplicate measurement was within ± 1 5 mol% in the epoxidation range studied.

In the ^{13}C NMR spectra of chlorohydrin derivative of PBR (Fig. 2.9) two new peaks appeared at $\delta = 68.28$ and $\delta = 73.53$, attributable to carbon atoms bearing OH and Cl substituents. The peaks due to epoxide carbons diminished in intensity showing only partial conversion of epoxy groups.

2.3.4 Elemental analysis:

The epoxy content of the modified PBR was calculated from the % C and % O obtained from elemental analysis of samples dried at 318 K under vacuum. A reproducibility of ± 1 mol% was obtained in both the cases.

The data given in Table 2.2 indicates that the epoxidation level of various samples determined by different methods agree well within the experimental limitations in the epoxidation range studied. The degree of epoxidation values are very close to 5, 10, 15, 20 and 25 mol% and these rounded off values are used in further discussions.

2.3.5 Thermal studies:

The thermogravimetric analysis of PBR and modified PBR samples (Fig. 2.10) shows that chain fragmentation with evolution of volatile products occurs only above 380°C and there is no significant difference in the thermal stability of PBR and modified PBR.

Differential scanning calorimetric studies of some of the epoxidised samples revealed that main-chain modification of PBR leads to enhanced Tg values (Fig. 2.11) due to hindered rotational freedom of the modified repeat unit. Epoxide modification of PBR results in almost a linear increase in Tg with level of modification. The results are in accordance with the literature results, where this method has been employed to estimate epoxy content after independent calibration[31]. Chlorohydrin derivative of PBR shows still higher Tg (Fig. 2.12). Where is the novelty if this has been done before?

It is observed that the progressive increase in Tg parallels a concomitant increase in polymer density as shown in Table. 2.2. A reduction in free volume of the chain segments is indicated by such a variation.

2.3.6 Contact angle measurements :

By studying the spreading of different liquids on the polymer

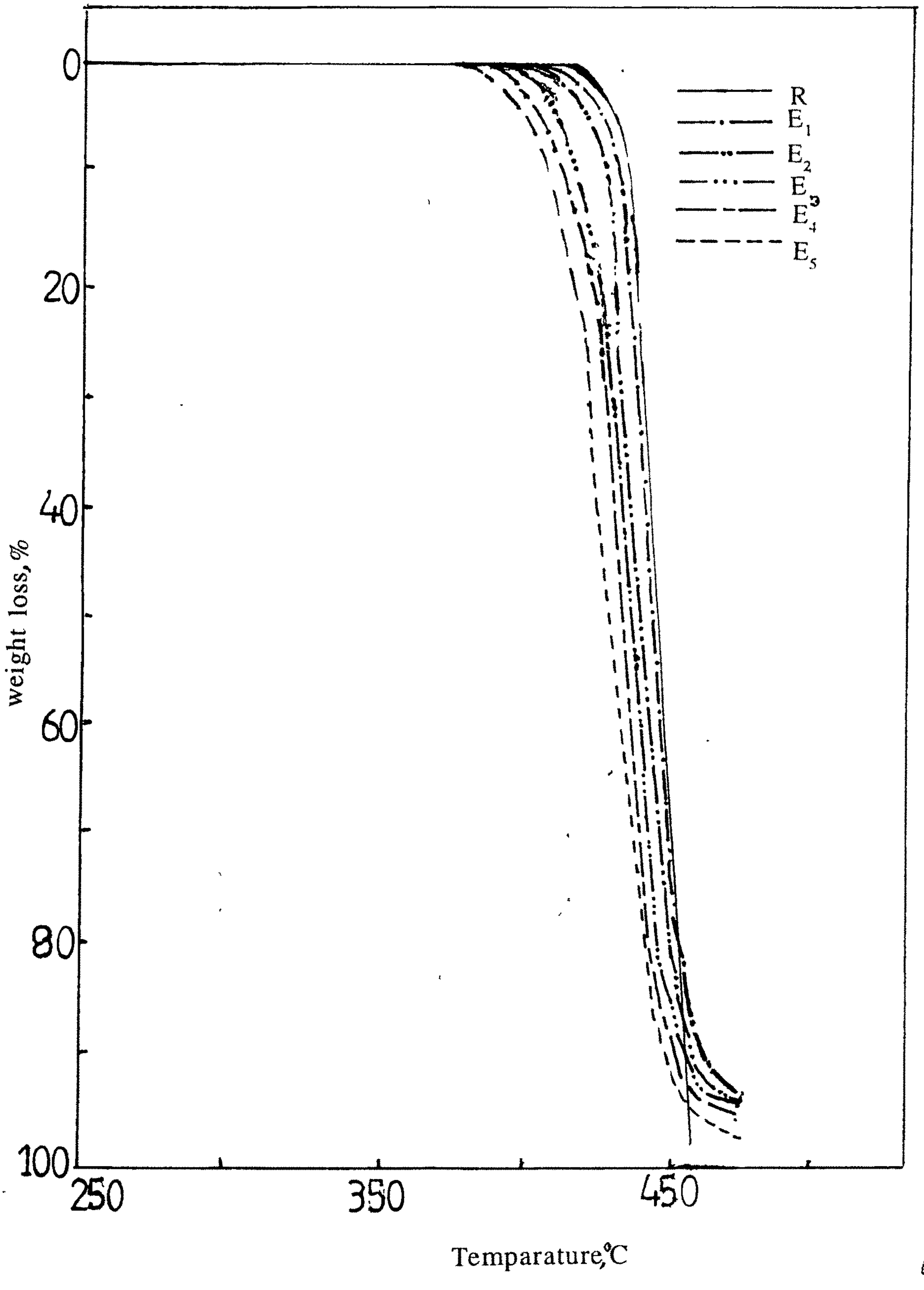
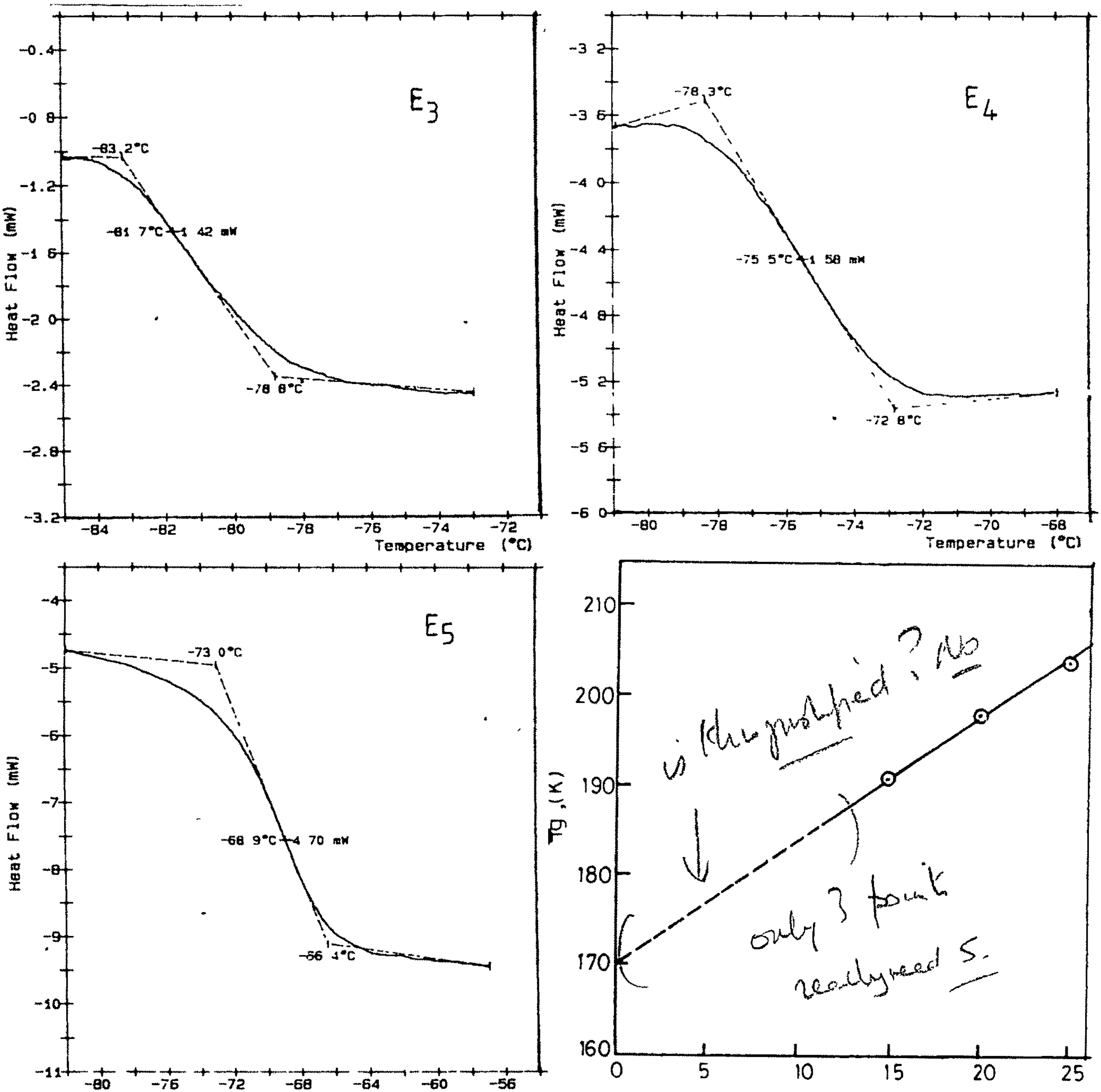


FIG. 2.10 TGA OF PBR & EPBR ($E_1 - E_5$)



is this justified? No

only 3 points really need 5.

FIG 2.11. DSC THERMOGRAMS OF EPBR (E_3 , E_4 AND E_5) AND PLOT OF T_g VERSUS EPOXY CONTENT

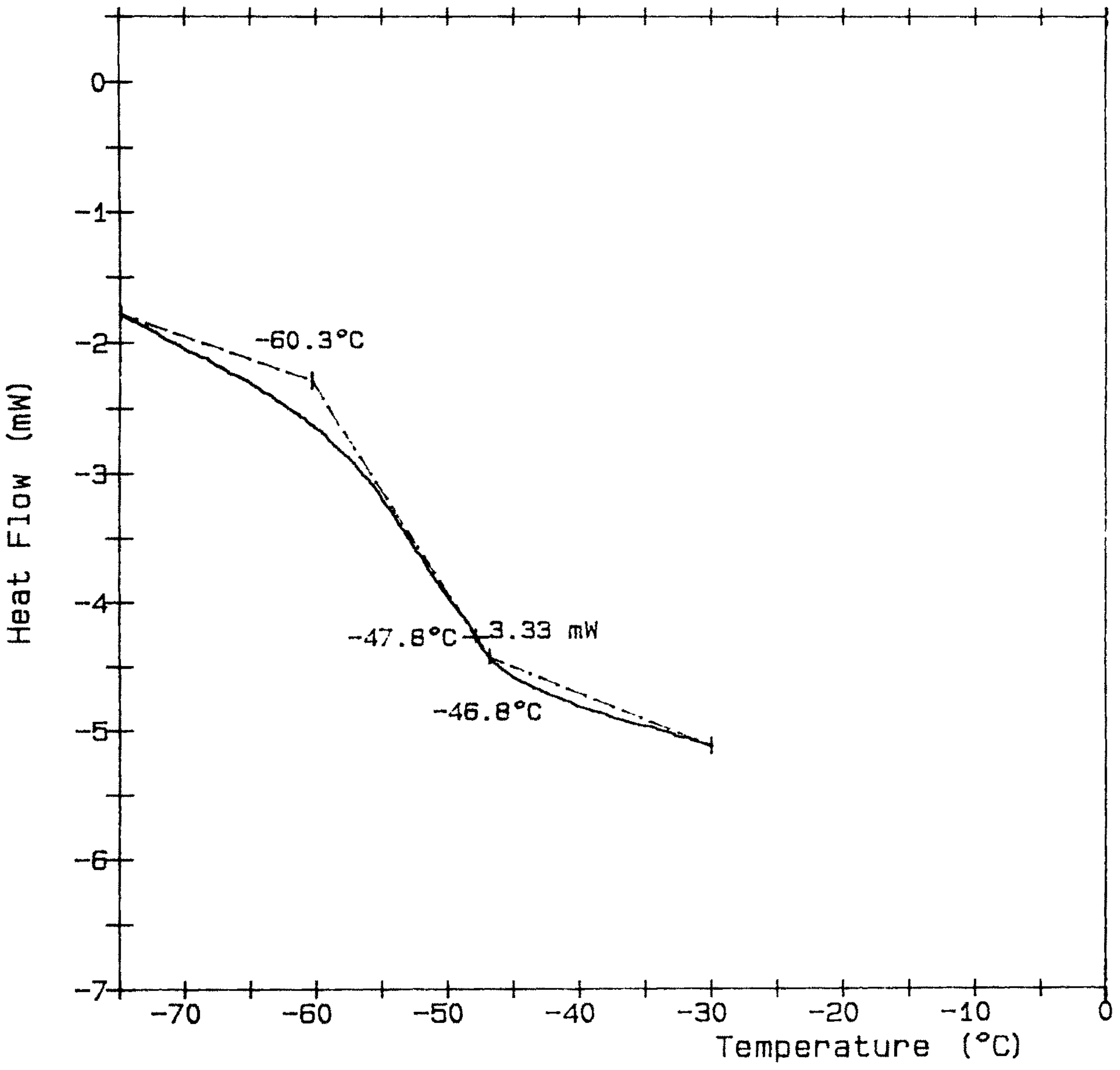


FIG. 2.12 DSC THERMOGRAM OF CHLOROHYDRIN DERIVATIVE OF PBR.

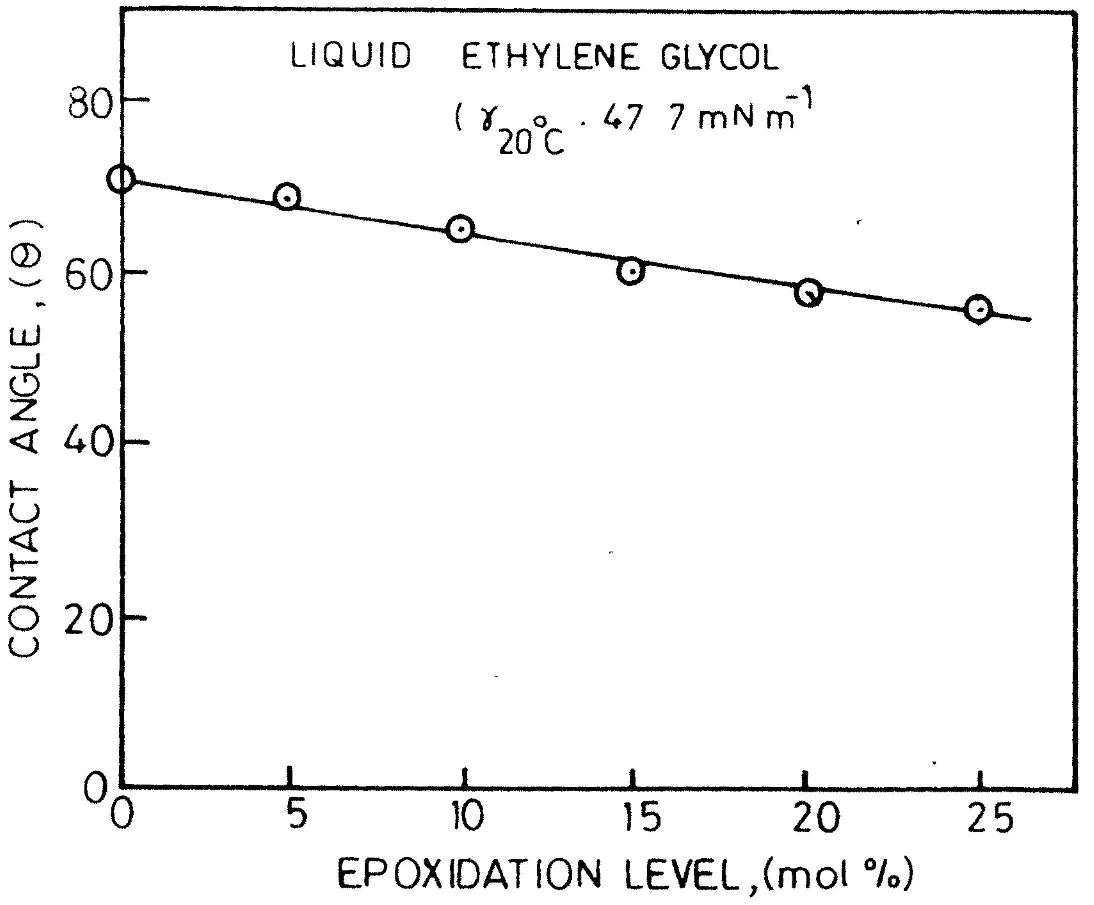


FIG 2.13 **PLOT OF CONTACT ANGLE (Θ) VERSUS EPOXY CONTENT.**

Good

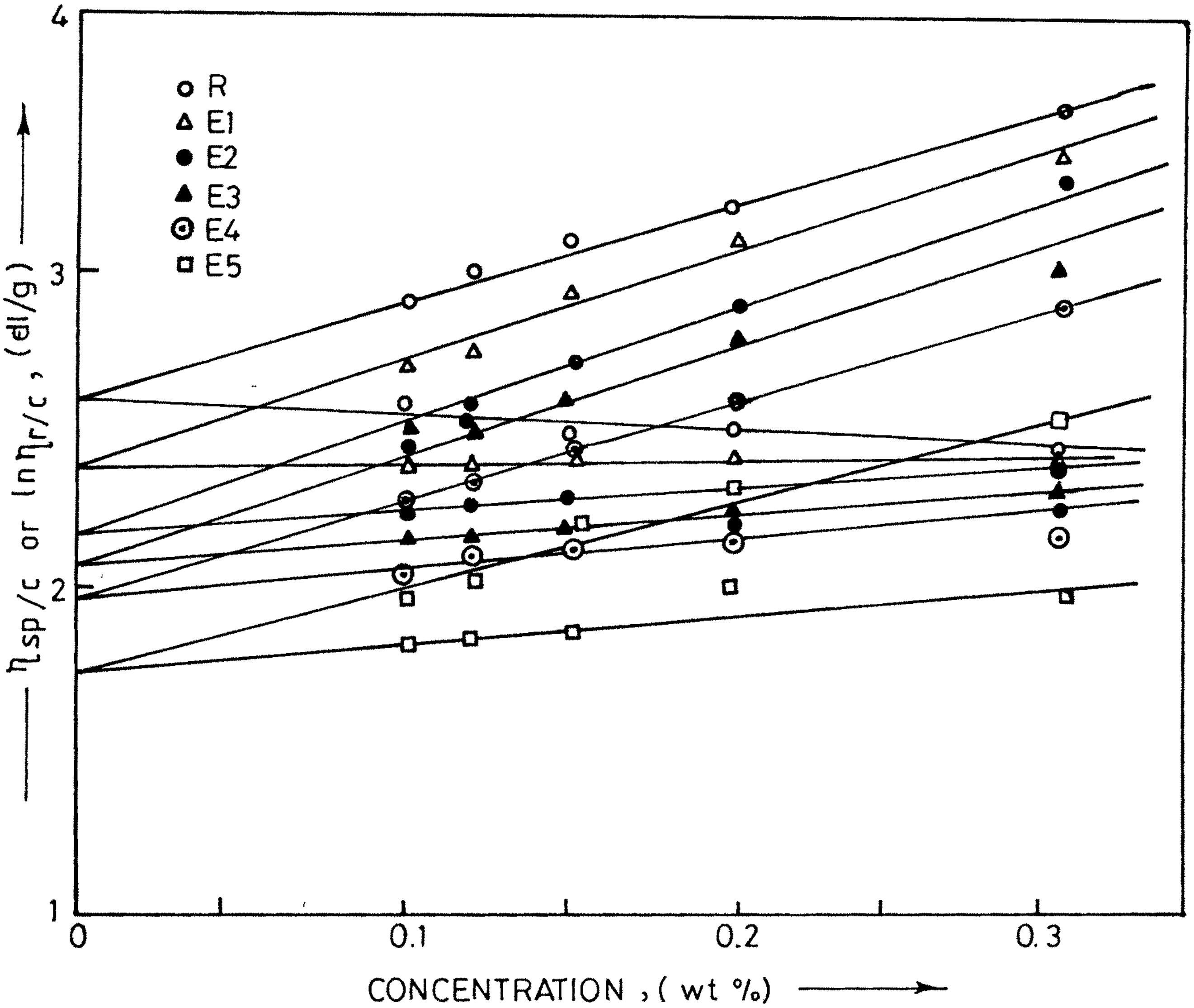
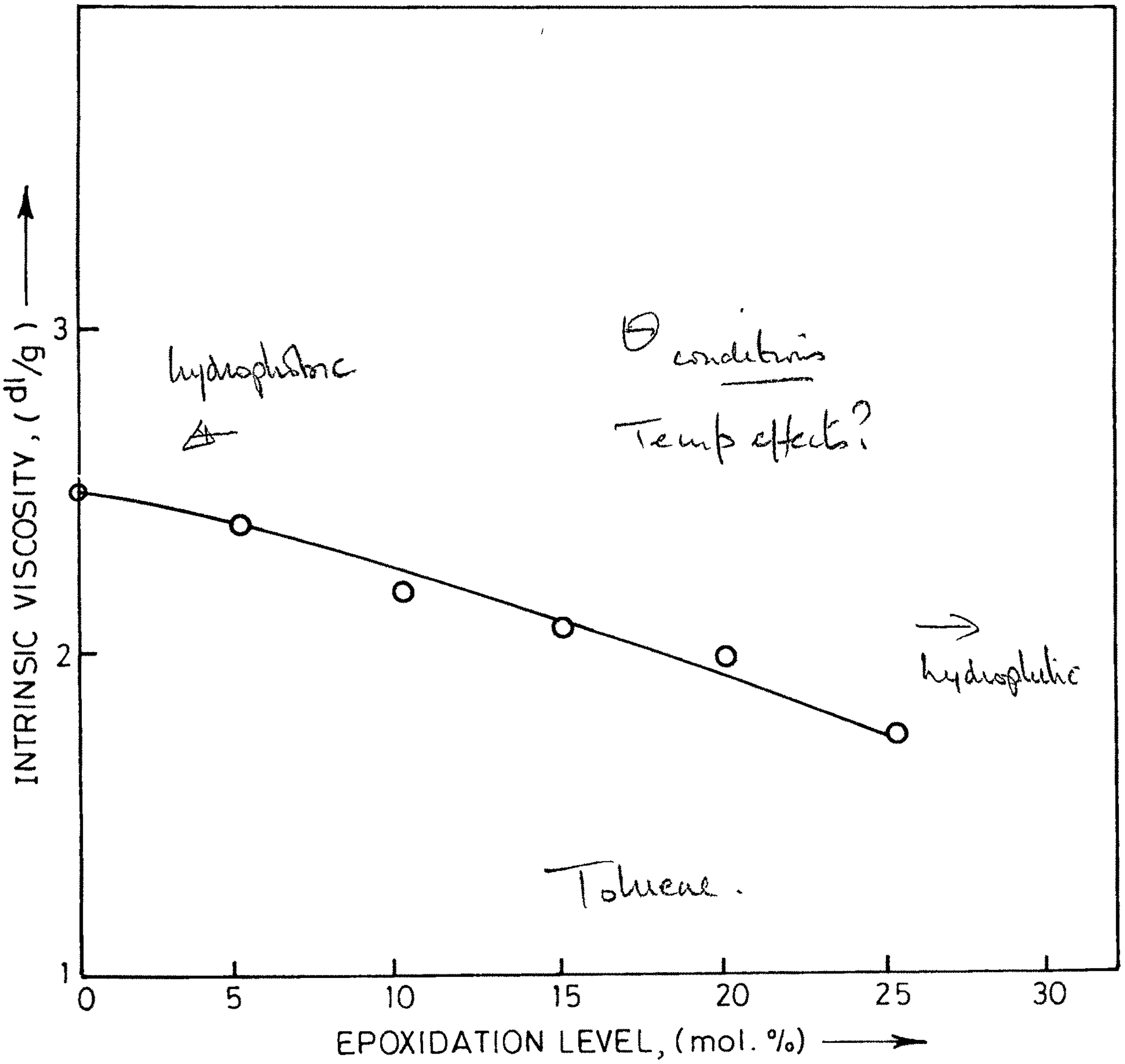


FIG 2.14 PLOTS OF η_{sp}/c VERSUS CONCN. AND $\ln\eta_{r}/c$ VERSUS CONCN. FOR PBR AND EPBR ($E_1 - E_5$)



hydrophobic

Θ conditions

Temp effects?

hydrophilic

Toluene.

FIG 2.15. PLOT OF INTRINSIC VISCOSITY VERSUS EPOXIDATION LEVEL (mol. %) OF PBR AND EPBR SAMPLES surface, the relative polarity of the polymers can be ascertained[35,36]. By using ethylene glycol as the liquid probe, contact angle measurements were made on various EPBR films and the results are shown in Fig. 2.13. The decrease in contact angle with increasing epoxy content is indicative of the gradual increase in polarity of the polymer surface.

2.3.7 Viscosity measurements :

Variation in relative viscosity during the epoxidation reaction as well as the variation in intrinsic viscosity with the degree of epoxidation of EPBR has already been reported[37]. Change in viscosity has been explained on the basis of two effects: first, expansion of polybutadiene coil due to electrostatic repulsion as oxygen is introduced and second, the coiling due to the deterioration of solvent power as oxirane ring structure is formed.

Viscosity of various EPBR samples were determined in toluene at 30° ± 1°C. Intrinsic viscosity was found to decrease with increasing epoxidation level as shown in Fig 2.14 and 2.15. This is indicative of chain shrinkage in non-polar media with the progressive increase in the polar nature of EPBR samples.

Much more discussion and treatment / interpretation could have been given

Huggins constant variation?

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