CHAPTER : 2

CHARACTERIZATION OF POLYMERS AND ADSORBENTS

CHARACTERIZATION OF POLYMERS AND ADSORBENTS

2.1 PREVIEW

Adsorption being a surface phenomenon, requires ultraclean adsorbents and adsorbates. For this, purified polymers and adsorbents, devoid of all surface active impurities, were chosen for the adsorption study. Thorough characterization of polymers and adsorbents therefore becomes a necessity. Hence spectroscopy is used to get information about the chemical structure of the polymers /276/.

Nature of distribution of isomeric units in polyisoprene was investigated earlier by ozonolysis /277-279/, pyrolysis /280,281/ or perbenzoic acid method /282,283/. However, these methods cannot differentiate between cis-1,4 and trans-1,4 units, because both the units are converted into the same reaction products through the main chain scission reaction. Moreover, the results obtained leave some ambiguity for quantitative discussions because of the occurance of side reactions such as recombination and migration /277-283/. Therefore, the spectroscopic methods were adopted, which could accurately and quantitatively determine the correct distribution of various isomeric units in natural and synthetic rubbers.

The success of infrared spectroscopy in the characterization of organic compounds is a result of the almost general validity and applicability of the concept of group frequencies /284/. The characterization of polymers by infrared spectroscopy represents one specific application, a large and important one, of the group frequency concept. The importance of infrared spectroscopy is considerably enhanced by its ability to provide detail information on the microstructure of polymers. This includes the way in which the successive monomer units add on to the existing chain, both in the case of homo and copolymers, the configurational and conformational structure of the chains, the identification of defect structures, and the chain end groups. This type of information is becoming increasingly important in gaining a better understanding of the properties of polymers and in improving their long term stability in commercial usage /285-287/.

In past, infrared methods have been widely used to determine the microstructure of polyisoprenes /288-291/. These methods are satisfactory for the determination of 1,2 and 3,4 addition units but they leave much to be desired in the determination of cis-1,4 and trans-1,4 repeat units /292-295/. The low molar absorptivities of the bands used for the determination of the cis-and trans-1,4 repeat units are the principal sources of error. Slight errors in absorbance measurements produce considerable variations in the final results. But infrared method is still frequently used to determine the cis-1,4 and trans-1,4 repeat units /136,210/.

The last twenty years have seen a spectacular growth in the use of nuclear magnetic resonance spectroscopy [NMR] for the microstructural analysis of polymers. The stimulus for this growth was the demonstration in early 1960's that high resolution ^{1}H NMR spectroscopy could be used to determine the tacticity of some acrylic acid and vinyl homopolymers and to assess the distribution of monomer units within some simple addition copolymers /296/. By the end of 1960's, the use of ^{1}H NMR for microstructural analysis of polymers was well established and the progress made through the decade was comprehensively reviewed by Bovey, the foremost contributor in this field /297/. With the advent of NMR spectrometers capable of operating at 300 MHz, it has been possible to determine the cis-1,4, trans-1,4 and 1,2 contents of polybutadiene and many other polymers /298,299/. In the high resolution NMR method, well resolved bands of high intensity are used for the determination of cis- and trans-1,4 contents of polybutadienes and polyisoprenes /300/. Several papers have been published concerning the determination of the microstructure of polybutadiene by PMR spectroscopy /301,302/. The cis- and trans- contents of polybutadiene have been determined from their olefinic methine resonances and aliphatic methylene resonances at 300 MHz. For polyisoprenes both cis-1,4 and trans-1,4 contents can be determined from their respective methyl proton resonances /303/. However, this type of information is better obtained from ^{13}C NMR spectroscopy /304/. ^{13}C NMR spectroscopy offers several advantages over ^{1}H NMR for a polymer chemist. The much larger range of chemical shifts observed for carbon nuclei in polymer chains compared to those of protons, enables the microstructural differences to be detected more readily by ^{13}C NMR than by ^{1}H NMR.

The rapid progress made in this field can be gauged by comparing the spectra presented by Mochel /305/, with those presented by Randall /306/ five years later. The nearly complete absence of ^{13}C-^{13}C coupling broad band, decoupling of ^{13}C-^{1}H couple, avoidance of saturation using the pulse technique, add to the already numerous advantages of ^{13}C over ^{1}H NMR spectroscopy. The main information that can be obtained from ^{13}C spectra are : identification of specific polymers, branching in macromolecules, analysis of sequences in copolymers, distinction between block and random copolymers, and analysis of microtacticity /307/. ^{13}C NMR spectroscopy has been recognized as a powerful tool for studying the structure of polybutadiene /308,309/. This is because the resonance region of the carbon double bond is very sensitive to small differences in the sequence distribution of cis- and trans- units in the polymer chain. ^{13}C NMR spectra of 1,4 polyisoprenes have been helpful in elucidating the sequence distribution of cis-1,4 and trans-1,4 units in these polymers /310-312/. The ^{13}C spectra of various polyisoprenes have been interpreted quantitatively by several workers /313,314/. Hence, in order to get maximum useful information, nonspectroscopic methods of polymer science should be combined with polymer spectroscopy. This does then give a better understanding about the characteristics of the polymer samples being used.

Thermoanalytical techniques are being extensively used to characterize a polymer, measure the temperature dependence of some mechanical or physical property and correlate it to the structure /315/. They involve a group of techniques in which properties are measured as a function of temperature or time, keeping every other variable constant /316,317/.

Differential thermal analysis [DTA] is a thermal technique in which the temperature difference [$\triangle$T] between a sample and a thermally inert material is recorded as both the sample as well as the inert material are heated or cooled at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic transitions caused by reactions such as phase changes, fusion, boiling, sublimation, vaporization, dehydration reactions, dissociation or decomposition, oxidation or reduction, destruction of crystalline lattice structure and many others.

Generally speaking, phase transitions, dehydration and some decomposition reactions produce endothermic effects, whereas crystallization, crosslinking or polymerization, oxidation and other decomposition reactions produce exothermic effects. The difference between differential scanning calorimetry [DSC] and DTA is in the manner of recording the heat flow. With some exceptions, record of the heat flow is done directly [$\triangle$H/$\triangle$t] in mcal/sec., as a function of temperature is a DSC unit. In DTA, dT is recorded against the temperature.

The sample and the reference material, both are maintained at an isothermal condition in DSC by the required flow of electrical energy, as they are heated or cooled at a linear rate. The area enclosed by either DTA or DSC curve is proportional to the enthalpy change. The proportionality constant is of course independent of temperature in DSC and dependent on temperature, in DTA.

Thermogravimetric analysis [TGA] involves continuous monitoring of the weight of the sample with temperature at a constant rate of change of temperature or time, isothermally. By far, the commonest use of TGA is in measuring the thermal and oxidative stability of polymers under working conditions. To yield useful information with this technique, the sample must evolve a volatile product from the parent compound /318-320/.

Besides the bulk properites surface properties of the polymers are also important and need to be known to properly understand the adsorption process. Contact angle is one such property. When a drop of liquid is placed on a flat solid surface, it may spread completely over the surface or, it may remain as a drop having a definite angle of contact with the solid surface. This angle is known as the contact angle. The zero contact angle results when the forces of attraction between the liquid and the solid are equal to or greater than those between the liquid and liquid, and a finite contact angle results when the liquid adheres to the solid less than it coheres to itself /321/. The solid is completely wetted by the liquid if the contact angle is zero and only partially wetted if the contact angle is finite. Complete nonwetting implies a contact angle of 180°.

A major contribution was made by Zisman and coworkers /322/ to a rational organization of contact angle data. They observed that Cos θ

is usually a monotonic function of γ_L [the surface tension of the respective liquid] for a homologous series of liquids. The line extrapolates to $\theta = 0$ at a certain γ_L value, which Zisman has called the critical surface tension γ_c; a quantity characteristic of a particular solid surface. This concept of critical surface tension has provided a useful means of summarizing wetting behaviour and allowing predictions based on this interpolation. A large amount of work has been done on the wetting behaviour of various liquids on different solid surfaces including polymer surfaces /323-325/.

The solution viscosity is helpful to determine polymer molecular weight and it has been so recognised ever since the early work of Staudinger /326/. Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is empirically related to molecular weight of linear polymers. The simplicity of measurement and usefulness of viscosity-molecular weight correlation are so great that the viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymers /327,328/.

All the above mentioned properties are dependent upon the molecular weight and molecular weight distribution i.e. polydispersity of the polymer. It therefore becomes absolutely necessary to know the molecular weight of the sample under study. Gel permeation chromatography [GPC] is a technique that separates molecules according to their size in solution. The principal use of the method has been to obtain the molecular weight distribution [MWD] of polymers. The use of GPC for the determination of MWD of elastomers is well established, typically using styragel columns with tetrahydrofuran [THF] solvent. The analysis of rubber from 33 plants has been reported /329/. Commercial high cis-polybutadiene was fractionated and each of the fractions was analysed by GPC /330/. A detailed characterization of polybutadiene with high molecular weight and broad MWD has also been reported /331/.

The various above mentioned techniques were adopted for the characterization of the polymer samples used in this study. The polymer samples chosen for the adsorption study were natural and synthetic rubbers.

2.2 EXPERIMENTAL

The synthetic rubber chosen for the adsorption study is cis-1,4 polybutadiene [PBR] obtained commercially. Natural rubbers chosen for the study are [a] natural rubber obtained from Guyana [GR] and [b] natural rubber obtained from Kerala, India [InR]. The various techniques used for the characterization are :

[1] Infrared spectroscopy [IR]

[2] Nuclear magnetic resonance spectroscopy [NMR] : PMR and ^{13}C NMR

[3] Contact angle measurements

[4] Thermogravimetric analysis [TGA]

[5] Differential scanning calorimetry [DSC]

[6] Viscosity study of dilute solutions

[7] Gel permeation chromatography [GPC]

[A] Characterization of Polymers

cis-1,4 polybutadiene [PBR] was obtained from Indian Petrochemicals Corporation Limited [IPCL], Baroda, India.

Guyana rubber [GR] was natural rubber obtained from Guyana, as a gift.

The Indian rubber [InR] was natural rubber obtained from Kerala, India as ribbed smoked sheet [RSS], from the plant RRII 105.

The polymers were purified by well known procedures /332,333/. They were dissolved in toluene and left overnight. The insoluble part was filtered out, though quantitatively not measured. The clear filtrate was poured in excess methanol with constant stirring. The pure white rubber obtained was vacuum dried at room temperature to a constant mass.

The solvents i.e. chlorobenzene [b.p. 132°C], toluene [b.p. 110°C], n-heptane [b.p. 98°C], cyclohexane [b.p. 80°C], methylcyclohexane [b.p. 101°C], methanol [b.p. 65°C] and chloroform [b.p. 61°C] were obtained from Merck, India. Cyclohexane and methylcyclohexane used were of chromatography grade. All the solvents were freshly distilled before use.

IR spectra of the polymer films were recorded on a Shimadzu IR-408 spectrophotometer. The films were prepared by dissolving the polymers in chloroform and pouring the solution over a pool of mercury. The films were obtained by vacuum evaporation of the solvent. Proton NMR of the polymer solutions in $CDCl_3$ were recorded on R-32 Perkin Elmer spectrometer at 90 MHz. They were also recorded on XL 300 MHz for PMR and 75 MHz for ^{13}C NMR, at the Regional Sophisticated Instrumentation Centre [RSIC], Indian Institute of Technology [IIT], Bombay, India.

GPC of the polymers was run in tetrahydrofuran [THF] at ambient conditions [$\simeq$ 27°C] on "Waters" 150C ALC, Millipore Corporation, with a refractive index detector, at the Research and Development Section of IPCL, Baroda, India.

DSC was recorded on a DuPont 2000 system in nitrogen atmosphere at Department of Colour Chemistry, Leeds University, Leeds, UK. TGA in nitrogen and air was recorded on Shimadzu Thermal Analyser 30B.

The contact angle was determined with the help of a contact Θ meter, fabricated at the Department of Colour Chemistry, Leeds University, Leeds, U.K., which was obtained as a gift.

Viscosity studies of different solutions were carried out with the help of an Ubbelohde viscometer, placed vertically in a thermostat, at all the required temperatures [± 0.05°C].

[B] Characterization of Adsorbents

TLC grade silica gel [with 13% $CaSO_4$, mesh size > 100] was obtained from Acme Synthetic Chemicals, Bombay, India. Alumina [acidic, mesh size > 100] was obtained from BDH [Glaxo Laboratories], India. The surface areas of silica gel and alumina were 192.9 m^2/g and 97.1 m^2/g respectively, obtained by BET method [N_2 adsorption]. Both were dried at 125°C for 3 hours before use. The probability of the presence of surface impurities in silica gel and alumina was checked by X-ray photoelectron spectroscopy [Fig.2.1]. No surface impurities were detected. The spectra were recorded on a VG scientific ESCALAB Mk II spectrometer using Mg Kα radiation under vacuum which was better than 5×10^{-7} mbar /334/ at IPCL, Baroda.

The SEM photographs were taken by a JEOL JSM-T3 scanning electron microscope at the Department of Geology of this University. Aluminium studs of particular dimension were made for mounting the adsorbents. The mounting was done using an adhesive. The mounted samples were then uniformly gold coated, the thickness of the coating being $\simeq 100$ Å. The SEM photographs were recorded at different magnifications, to enable correct interpretation.

Surface acidity of the adsorbents was determined by titration method. Excess of standardised NaOH solution was kept in contact with a known amount of adsorbent and the amount of NaOH consumed was then back titrated with standardised HCl. Silica gel has $1.4 \times 10^{14}/cm^2$ surface OH groups. Alumina has $2.1 \times 10^{14}/cm^2$ surface acidity.

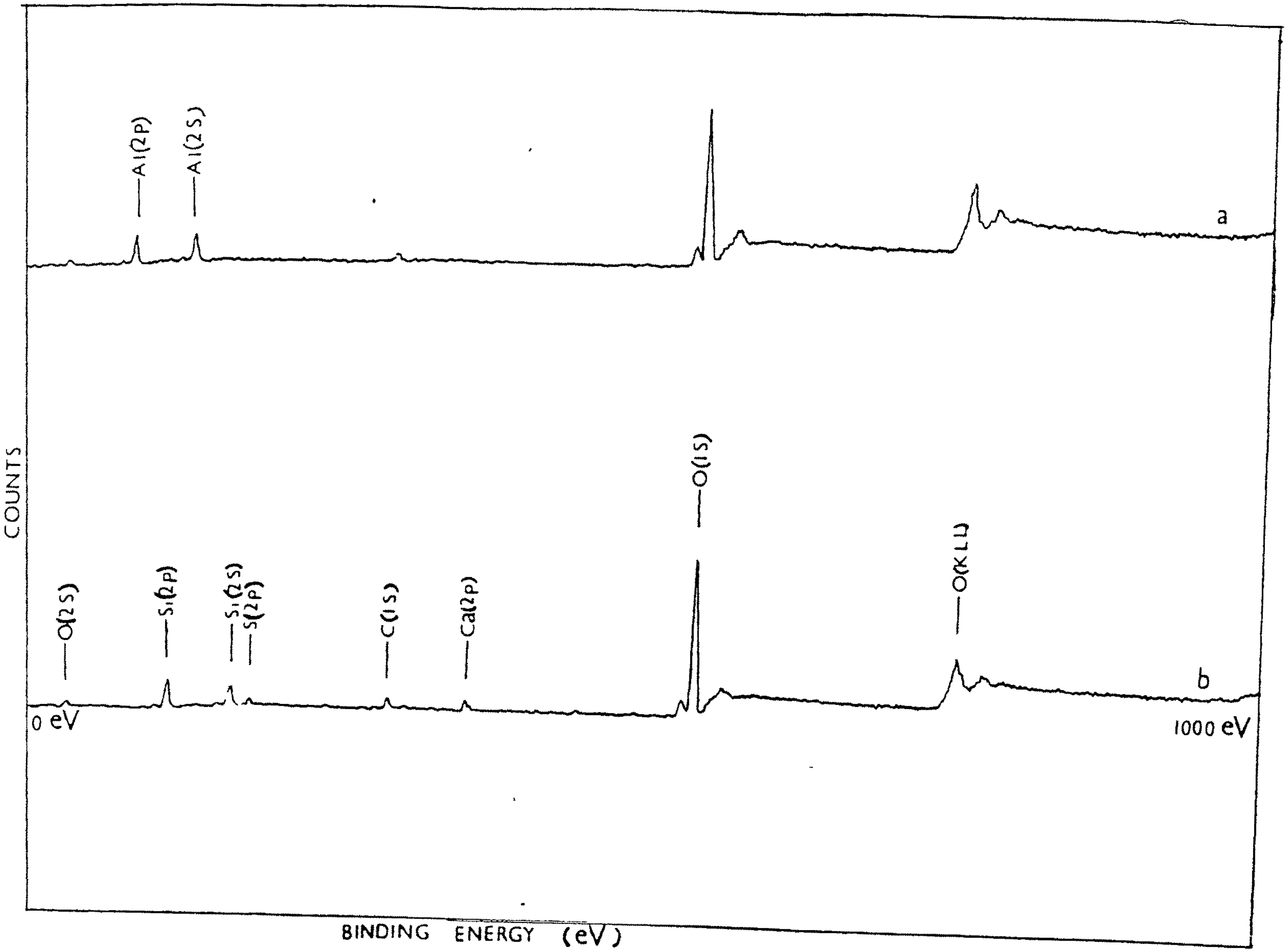

Fig.2.1 ESCA of (a) alumina and (b) silica gel

2.3 RESULTS AND DISCUSSION

[A] IR and NMR Spectra

IR spectra of all the three polymers are given in Fig. 2.2 [a,b&c]. The GR film was opaque, hence the IR spectra was taken in chloroform solution. The spectra of all the three rubbers obtained compare favourably to that in literature. In case of polybutadiene, characteristic bands at 724, 911 and 967 cm^{-1} are obtained, the relative intensities of which depend upon the method of preparation. The band at 967 cm^{-1} is attributed to trans-1,4 polybutadiene /335-337/. The band at 911 cm^{-1} has been similarly attributed to 1,2 polybutadiene and band at 724 cm^{-1} is characteristic of cis-1,4 polybutadiene.

For InR, the bands at 740, 1130 and 1310 cm^{-1} are due to vibrations of cis-$C(CH_3) = CH$- group. For GR, the bands at 1150 and 1325 cm^{-1} are due to vibrations of trans-$C(CH_3) = CH$- group /338/. This suggests that InR is a cis and GR is a trans form of natural polyisoprene. The PBR spectra also compare very favourably with that in literature /338/.

To confirm the configurational differences among the three polymers, PMR and ^{13}C NMR spectra were recorded. The NMR spectra obtained at 90 MHz are not adequate in differentiating the resonance peaks due to different isomeric repeat units. It was not possible to get any difference between the two PMR spectra and hence no figure is

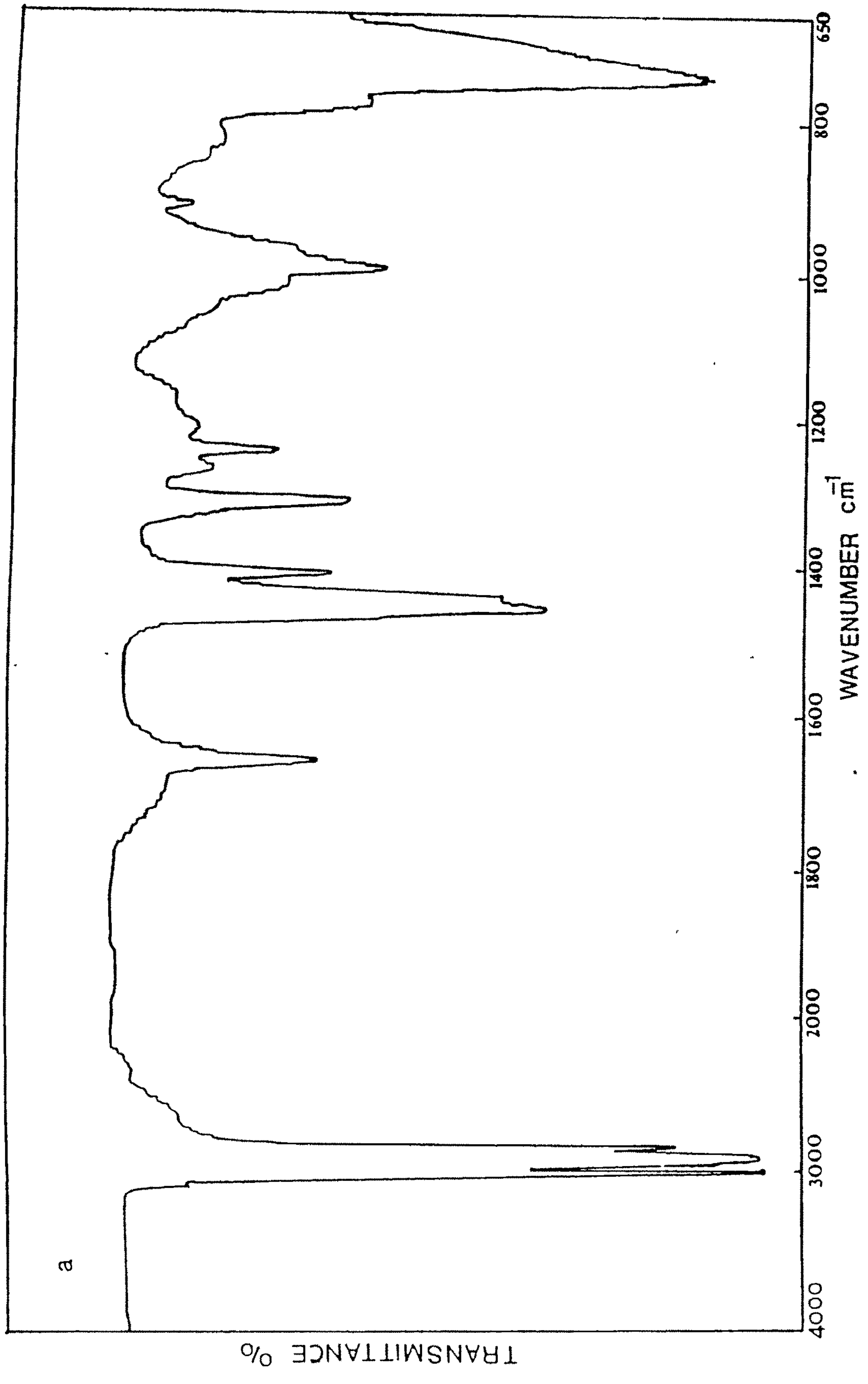

Fig.2.2(a) IR Spectra of PBR

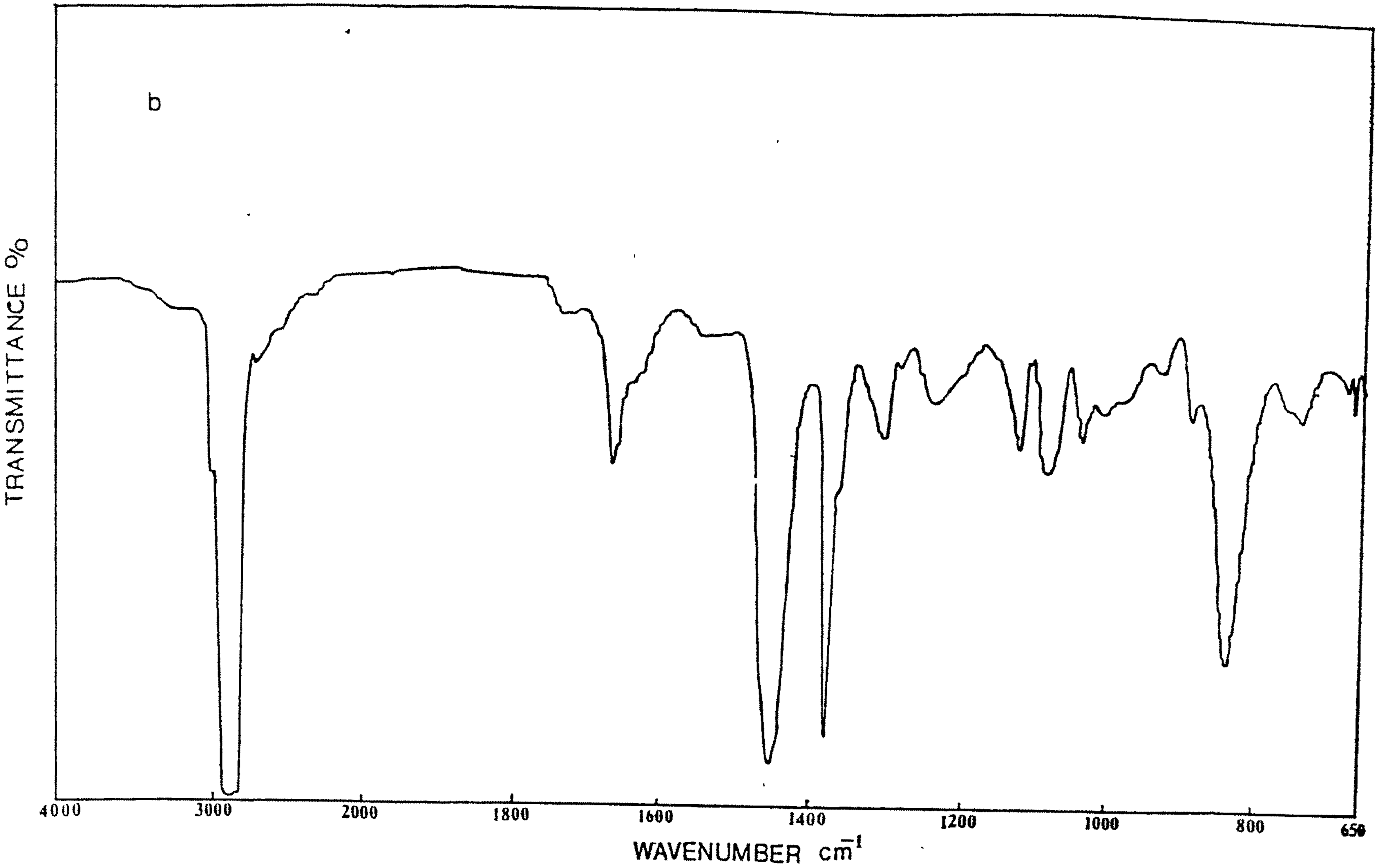

Fig.2.2(b) IR Spectra of InR

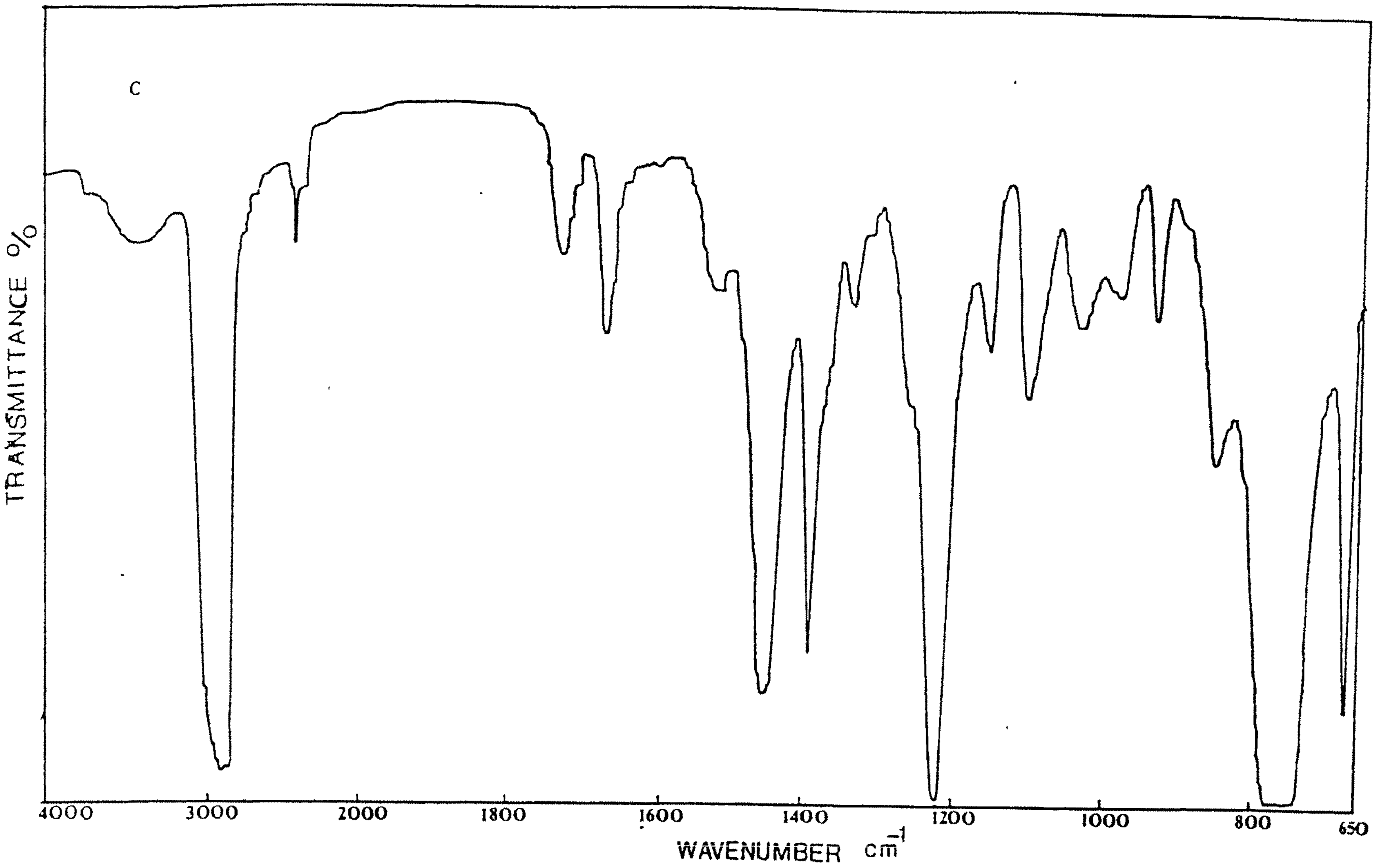

Fig.2.2(c) IR Spectra of GR

included. The PMR spectra of three rubbers at 300 MHz are presented in Fig.2.3 [a,b&c]. The resonance peaks suggest the arrangement of repeat unit as shown in Fig.2.4. The symmetrical units of cis-1,4 polybutadiene [PBR] exhibit one resonance peak from equivalent ethylenic carbons [α peak] and one peak from equivalent methylene carbons [β peak]. InR shows resonance peak at 5.12 ppm indicating that the sample is 1,4 adduct. The peaks at 2.03 and 1.67 ppm are given by α-CH_2 and α-CH_3 respectively. The peak at 1.67 ppm indicates its cis structure. The olefinic peak is observed at 5.12 ppm. In GR, the α-CH_3 peak is observed at 1.59 ppm. This suggests that 1,4 unit is mainly trans in the repeat unit /299,300/.

The ^{13}C NMR spectra of PBR, GR and InR are presented in Fig.2.5 [a,b&c]. ^{13}C NMR further confirms the configurational differences between InR and GR. Both show five clearly distinguishable singlet resonance peaks which are due to methyl, two methylene, and two ethylenic carbon atoms. From Fig.2.4 it can been seen that δ methylene moiety, being in the similar environment in cis and trans-1,4 polyisoprenes, shows similar chemical shift in both the cases /339-341/. The values being 26.4 ppm for natural cis-1,4 and 26.8 ppm for natural trans-1,4 i.e. for InR and GR respectively. Unlike δ carbon, γ methylene carbons resonate at 39.8 ppm for GR and 32.2 ppm for InR i.e. a difference of 7.6 ppm. The methyl carbons [ϵ carbons] also show a difference i.e. 23.37 ppm for InR and 16.03 ppm for GR /339-341/. This confirms that InR is cis-1,4 polyisoprene, GR is trans-1,4 polyisoprene and PBR is cis-1,4 polybutadiene. Literature shows PBR having cis content $> 96\%$, trans-

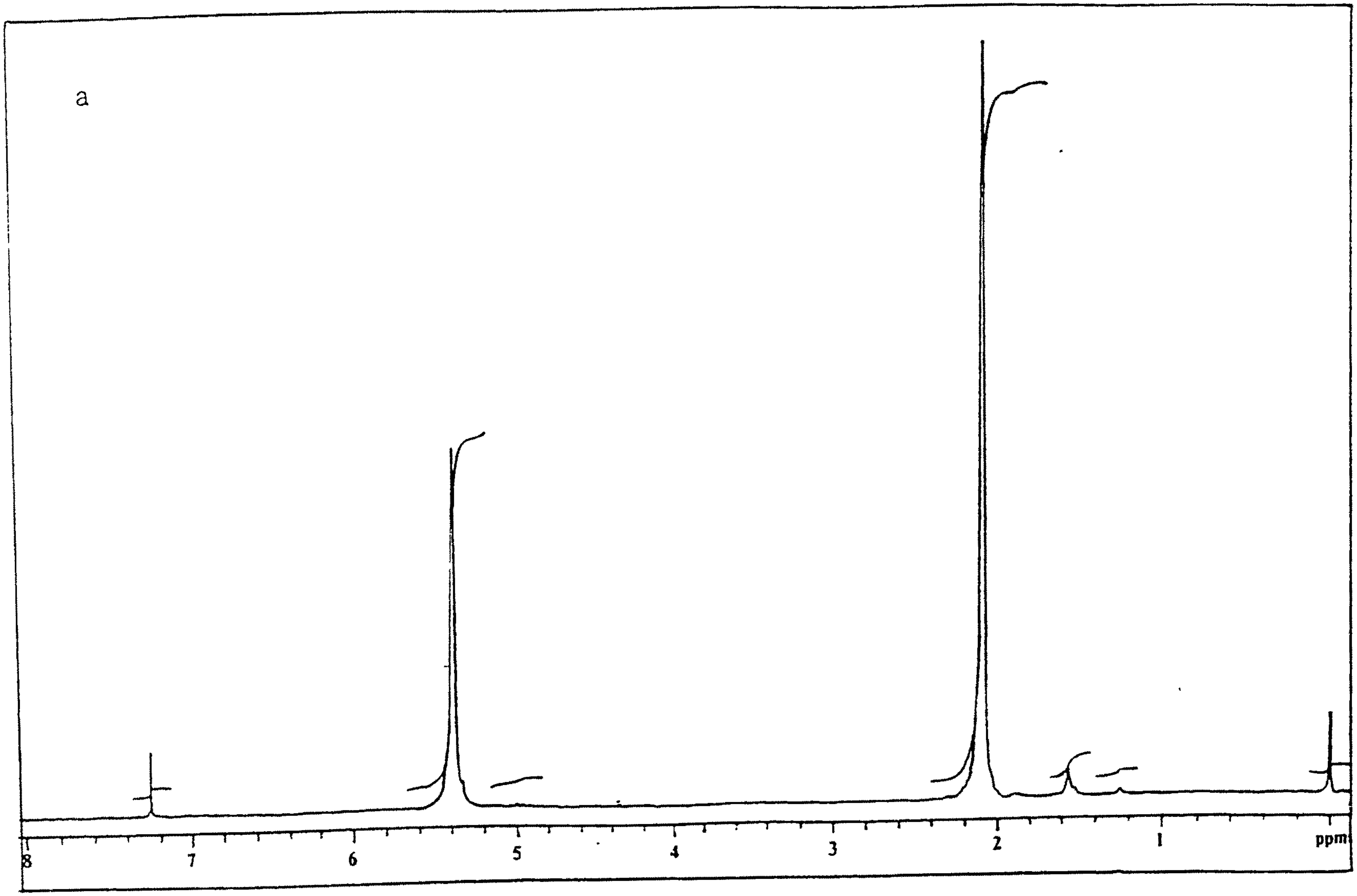

Fig.2.3(a) PMR Spectra of PBR

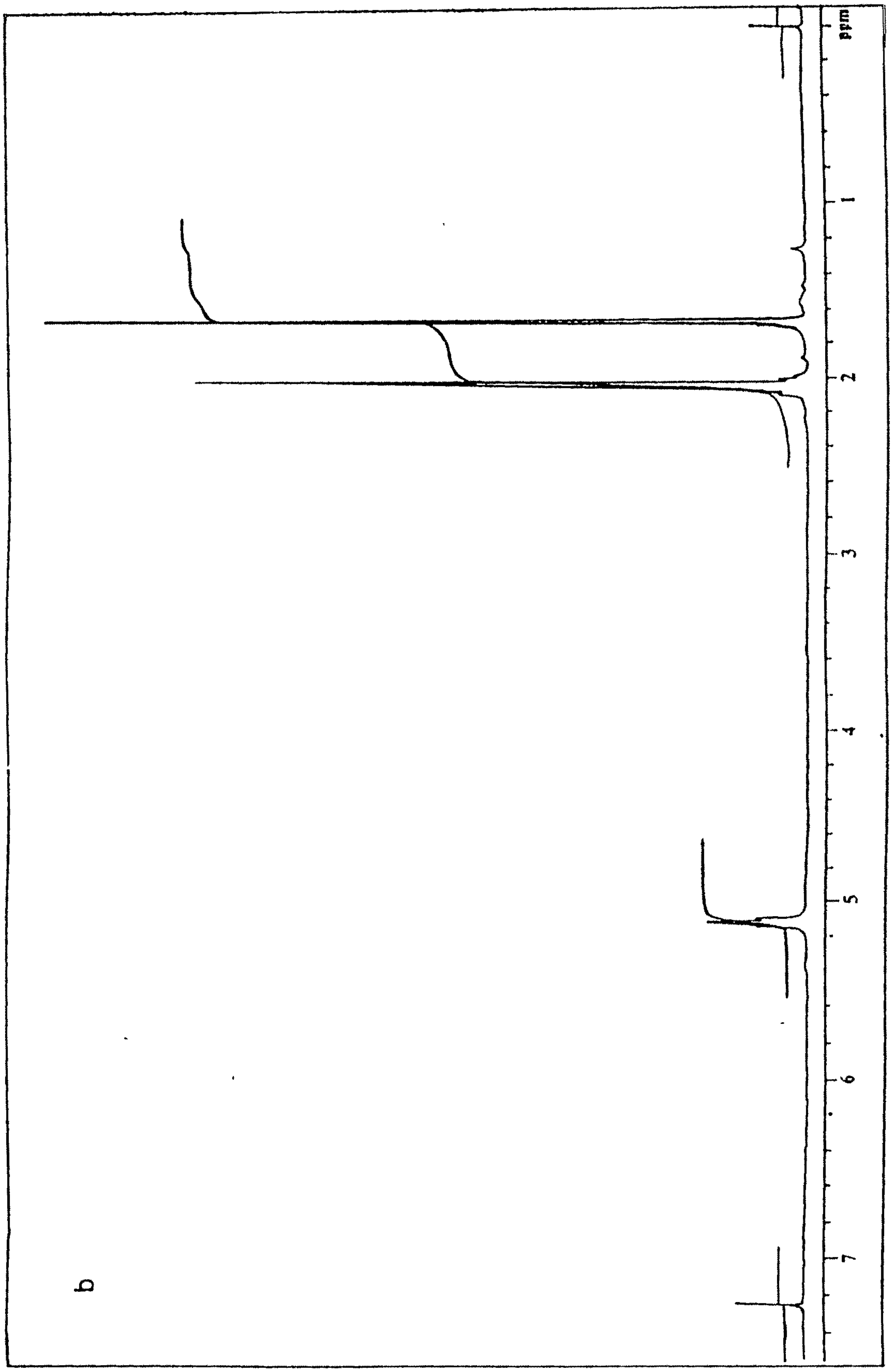

Fig.2.3(b) PMR Spectra of InR

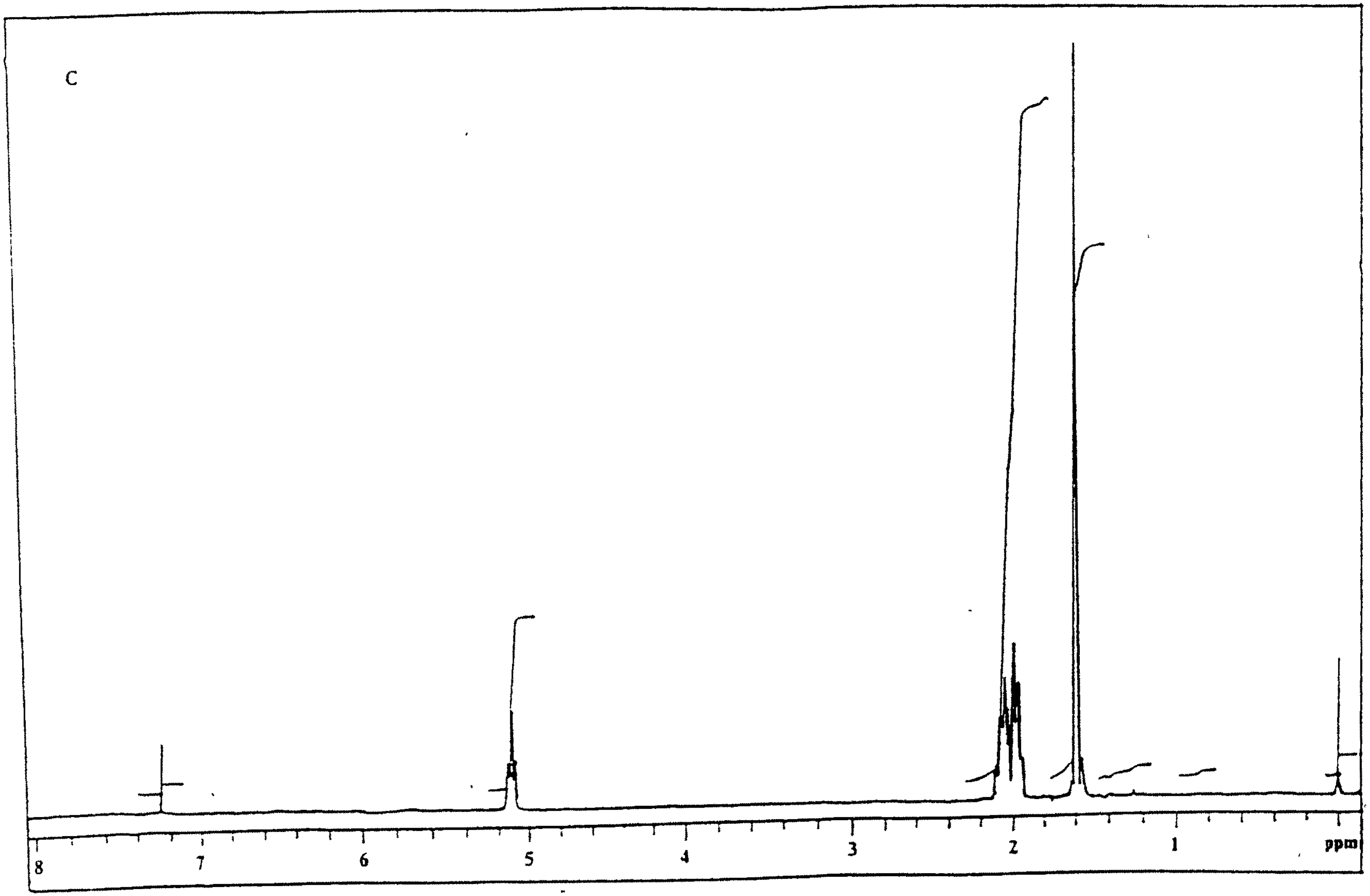

Fig.2.3(c) PMR Spectra of GR

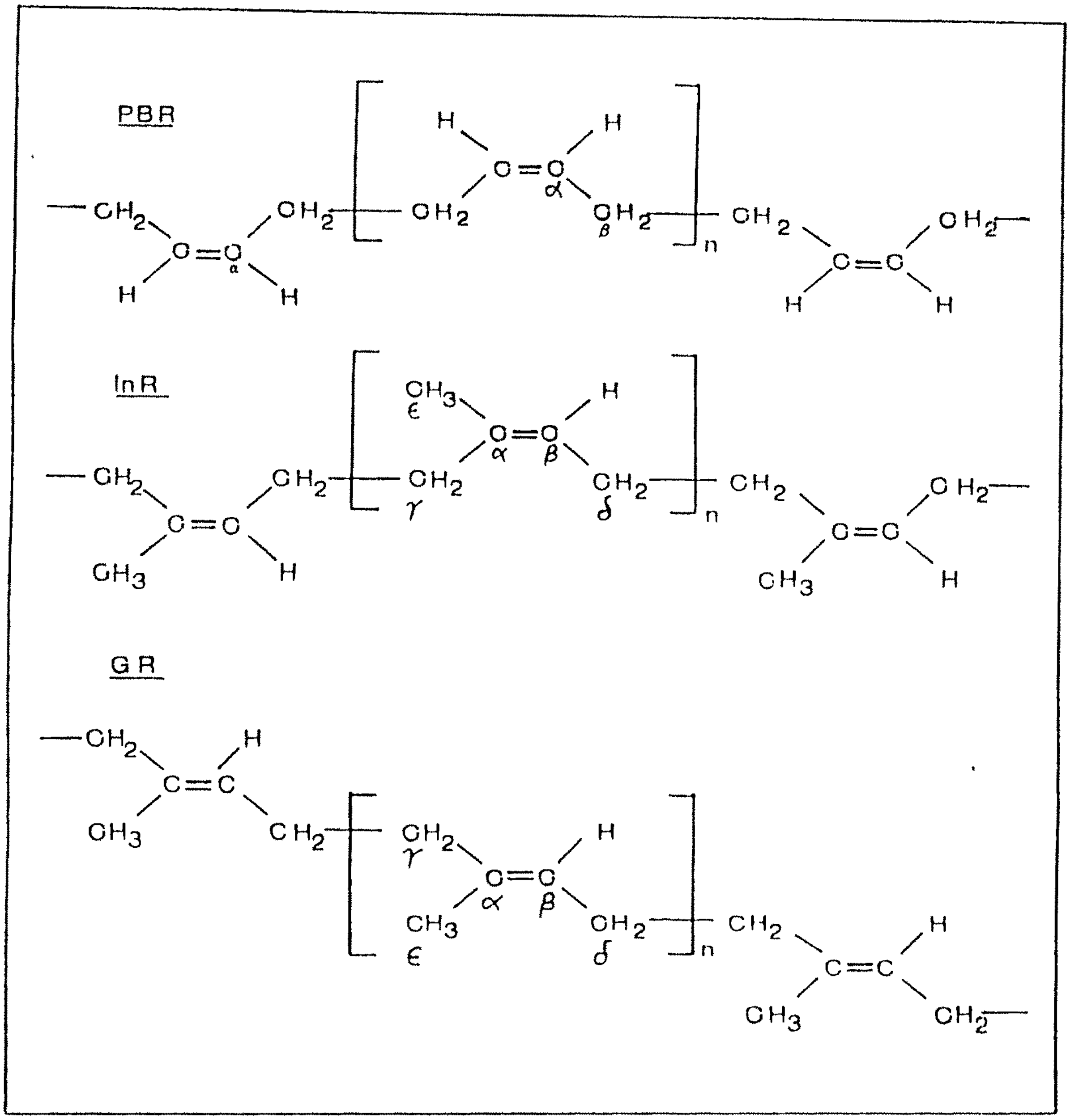

Fig.2.4 Arrangement of repeat units of different rubbers

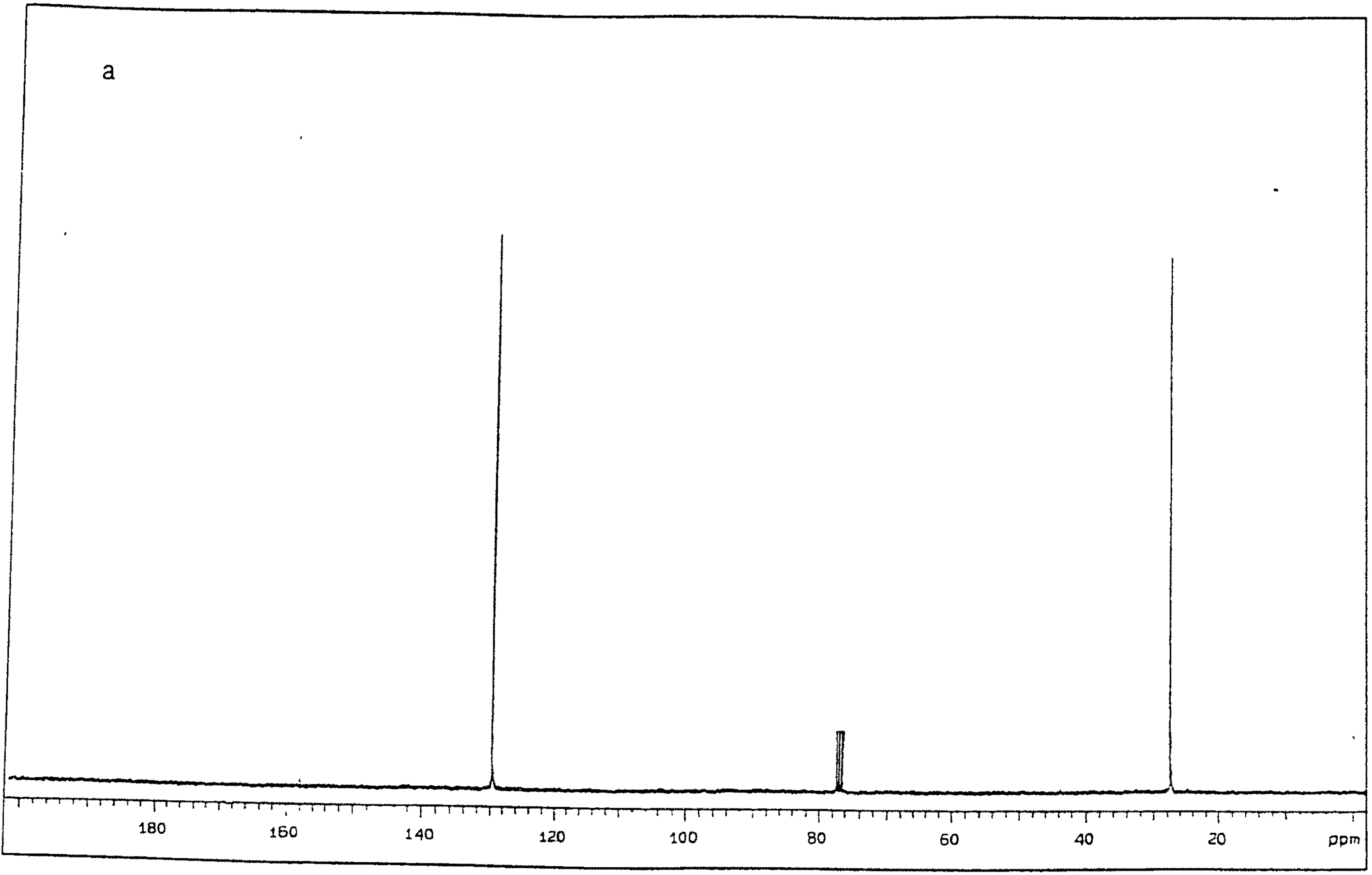

Fig.2.5(a) ^{13}C NMR Spectra of PBR

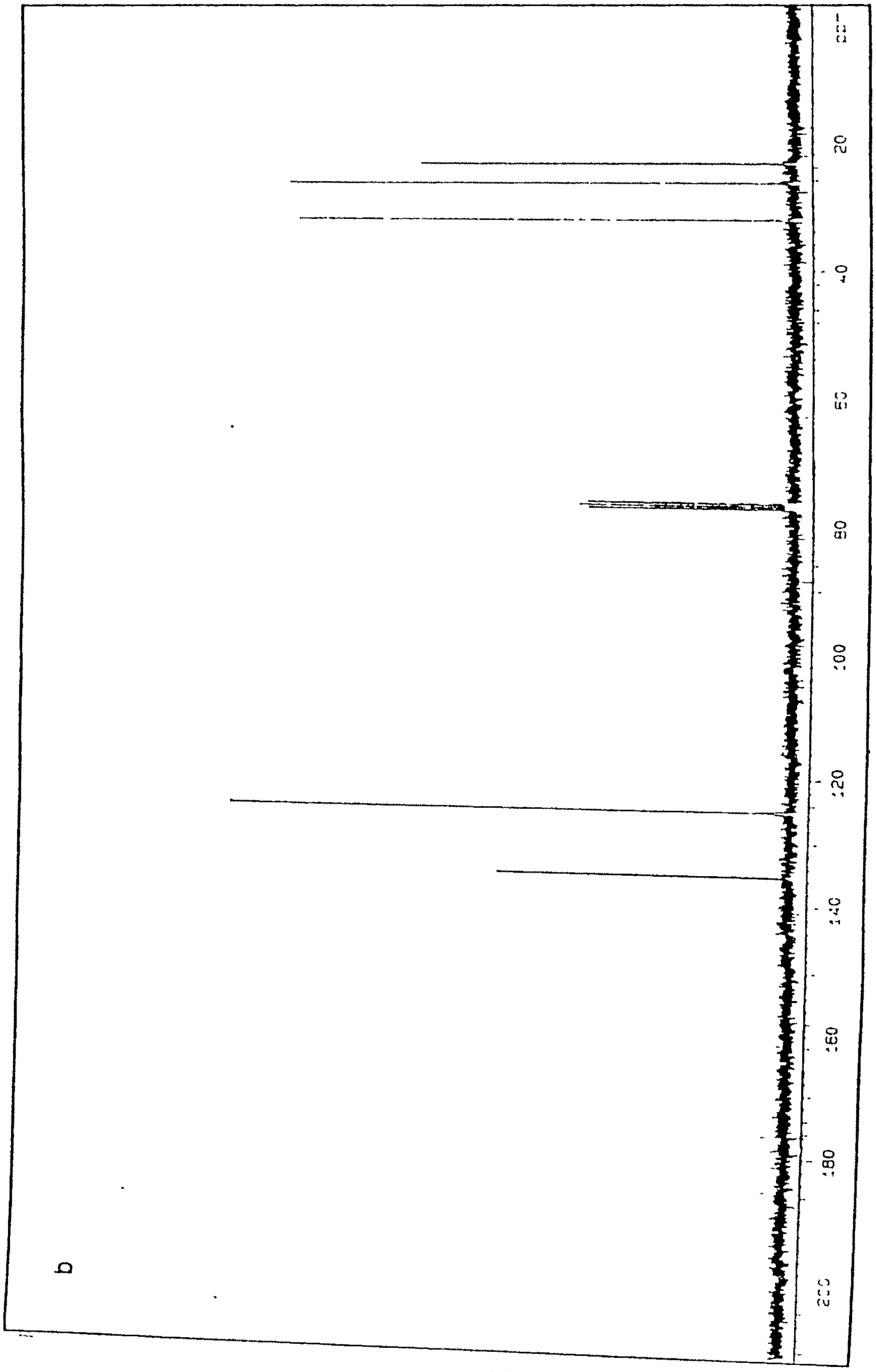

Fig.2.5(b) ^{13}C NMR Spectra of InR

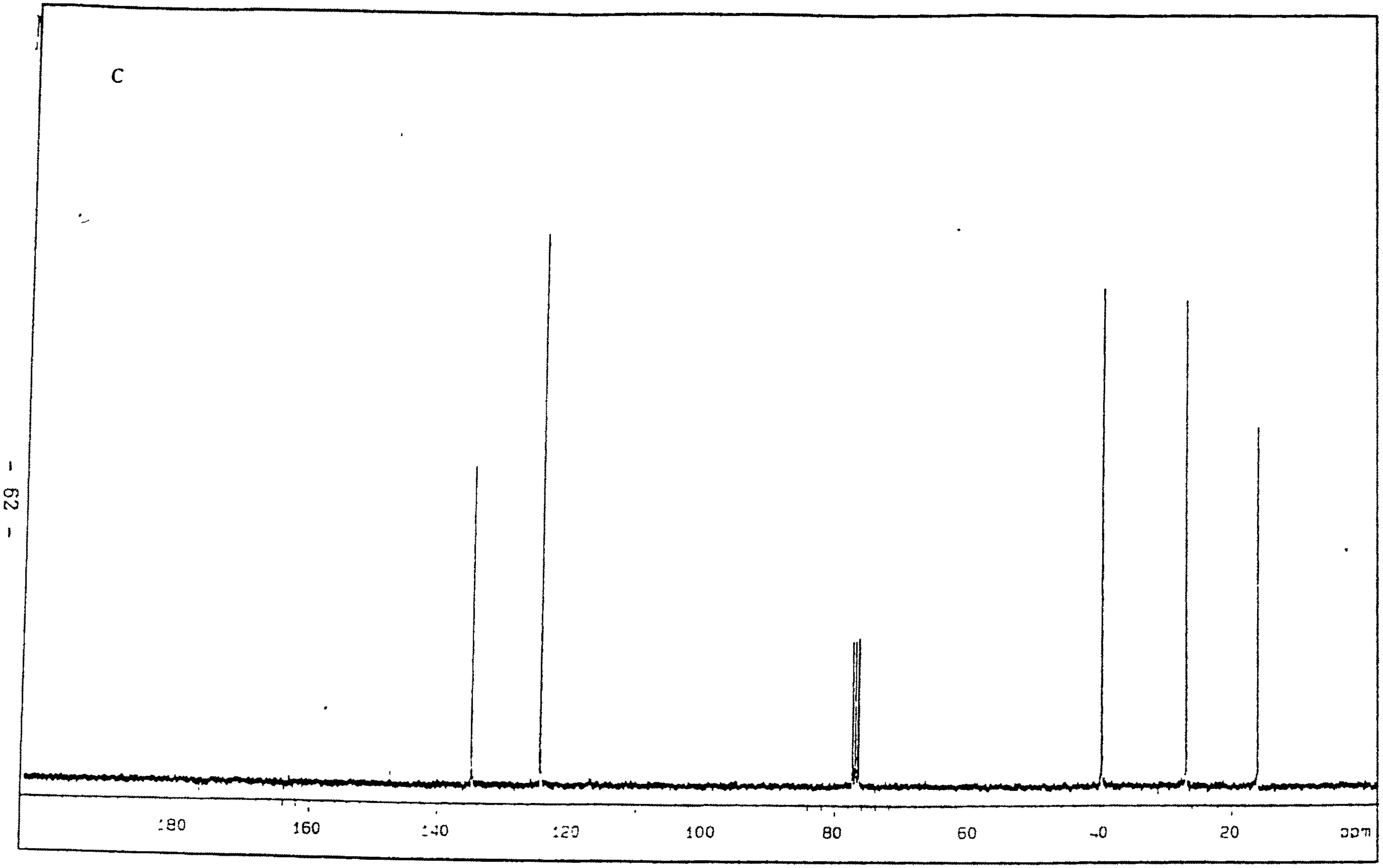

Fig.2.5(c) ^{13}C NMR Spectra of GR

1,4 [1-2%] and vinyl-1,2 [1-2%] /342/.

[B] Contact angle measurements

Surface characterization of the polymers is important and can be done from its wetting behaviour. The critical surface tension of the polymer, characteristic of the respective polymer was determined. Several workers have reported on the relationship between wettability and nature of the surface of polymers /343-347/. The contact angle, θ, of various liquids with the polymers surfaces [films] was determined with the help of a contact 'θ' meter, mentioned earlier. The liquids used are listed in Table 2.1. The surface tension values at 20°C, for different liquids, were taken from literature for determination of γ_c. The Cos θ was plotted against surface tension of the liquids. Linear plot obtained was extrapolated to $\cos\theta = 1$ [$\theta = 0$] and the corresponding surface tension was the critical surface tension, γ_c /348-350/. The plots obtained are shown in Fig.2.6. The values are 16.5, 15.5 and 13.0 mNm^{-1} for PBR, GR and InR respectively.

This indicates that the liquids with surface tension higher than γ_c will not easily spread on polymer surfaces. This also indicates that liquids with hydroxyl or other hydrophilic groups will spread less on these rubbers. It is clear that synthetic polybutadiene and natural polyisoprenes show similar wetting behaviour and are qualitatively of similar hydrophobicity. We can therefore surmise that all the three polymers are very much hydrophobic in nature /351/.

TABLE : 2.1

THE SURFACE TENSION VALUES OF THE LIQUIDS USED FOR DETERMINING γ_C ON VARIOUS RUBBERS

Liquids used	γ 20°C mN m^{-1}	Polymers
Dioxane	32.59	PBR, GR, InR
Nitrobenzene	43.90	PBR, GR, InR
Aniline	41.75	PBR, GR, InR
Acetic acid	27.80	PBR, InR
Acetone	23.70	PBR
Glycerol	63.40	GR
Ethylene glycol	47.70	GR
Formamide	58.20	GR

TABLE : 2.2

ACTIVATION ENERGY OF DECOMPOSITION OF DIFFERENT RUBBERS IN DIFFERENT ATMOSPHERES

Rubbers	Activation Energy E [kJ]	
	Air	Nitrogen
PBR	251.3	270.6
GR	139.8	154.6
InR	148.7	166.2

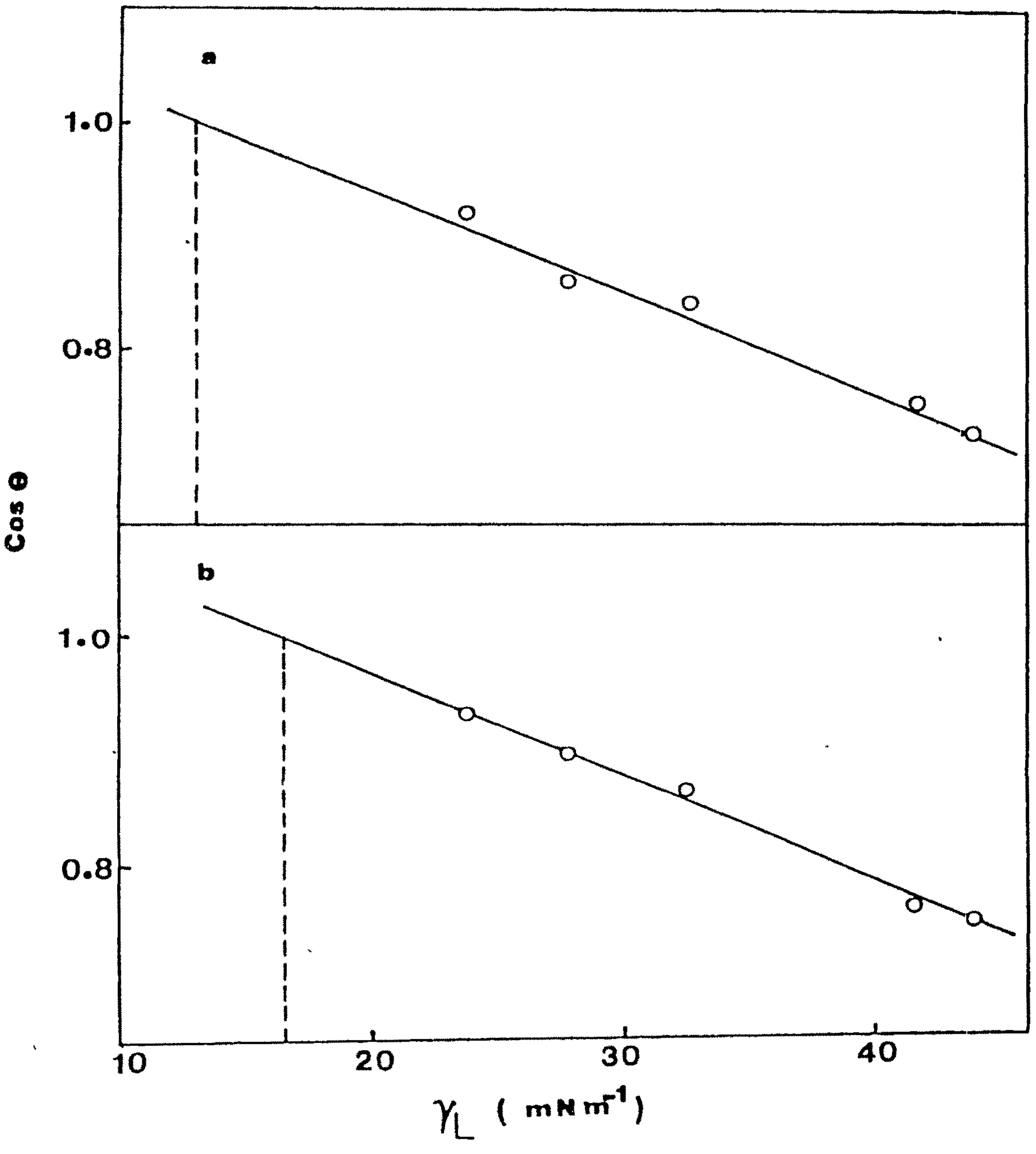

Fig.2.6 Plot of γ_L vs. Cos θ for (a) InR and (b) PBR

[C] Thermal Analysis :

It is seen from TGA of PBR, GR and InR that the maximum weight loss is different for each rubber. From Fig.2.7 it can be seen that maximum weight loss in air is 84%, 90% and 94% for PBR, GR and InR respectively. Fig.2.8 shows the TGA curves in nitrogen atmosphere.

Single stage decomposition was observed in all the cases. Activation energy, associated with this decomposition process has been calculated by the well known Broido method /352,353/. The equation used for the calculation of the activition energy [E] is :

$$\ln \ln [1/y] = [-E/R] [1/T] + \text{const.} \qquad \ldots\ldots [1]$$

where $y = [W_t - W_\infty]/[W_0 - W_\infty]$

i.e. y = fraction of the number of initial molecules not yet decomposed

W_t = weight at any time 't' and
W_∞ = maximum weight loss.

In equation [1], plot of ln ln [1/y] vs. 1/T gives an excellent approximation to a straight line over the range of $0.999 > y > 0.001$. The slope is related to the activation energy of degradation. This can be seen from Fig.2.9 and 2.10. The activation energy values so obtained are compiled in Table 2.2. The values are slightly higher

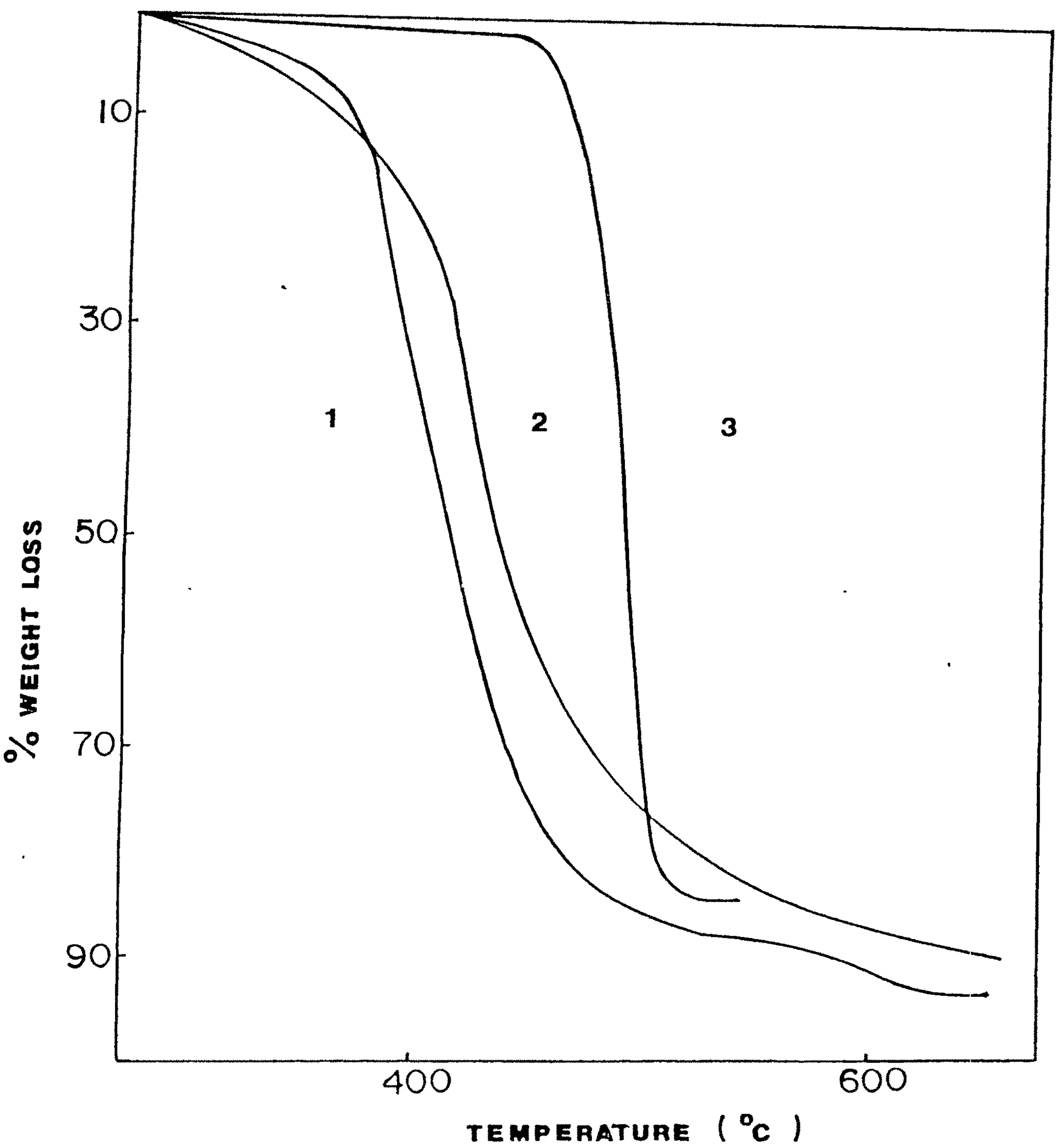

Fig.2.7 TGA Curves of (1) InR, (2) GR, and (3) PBR in air

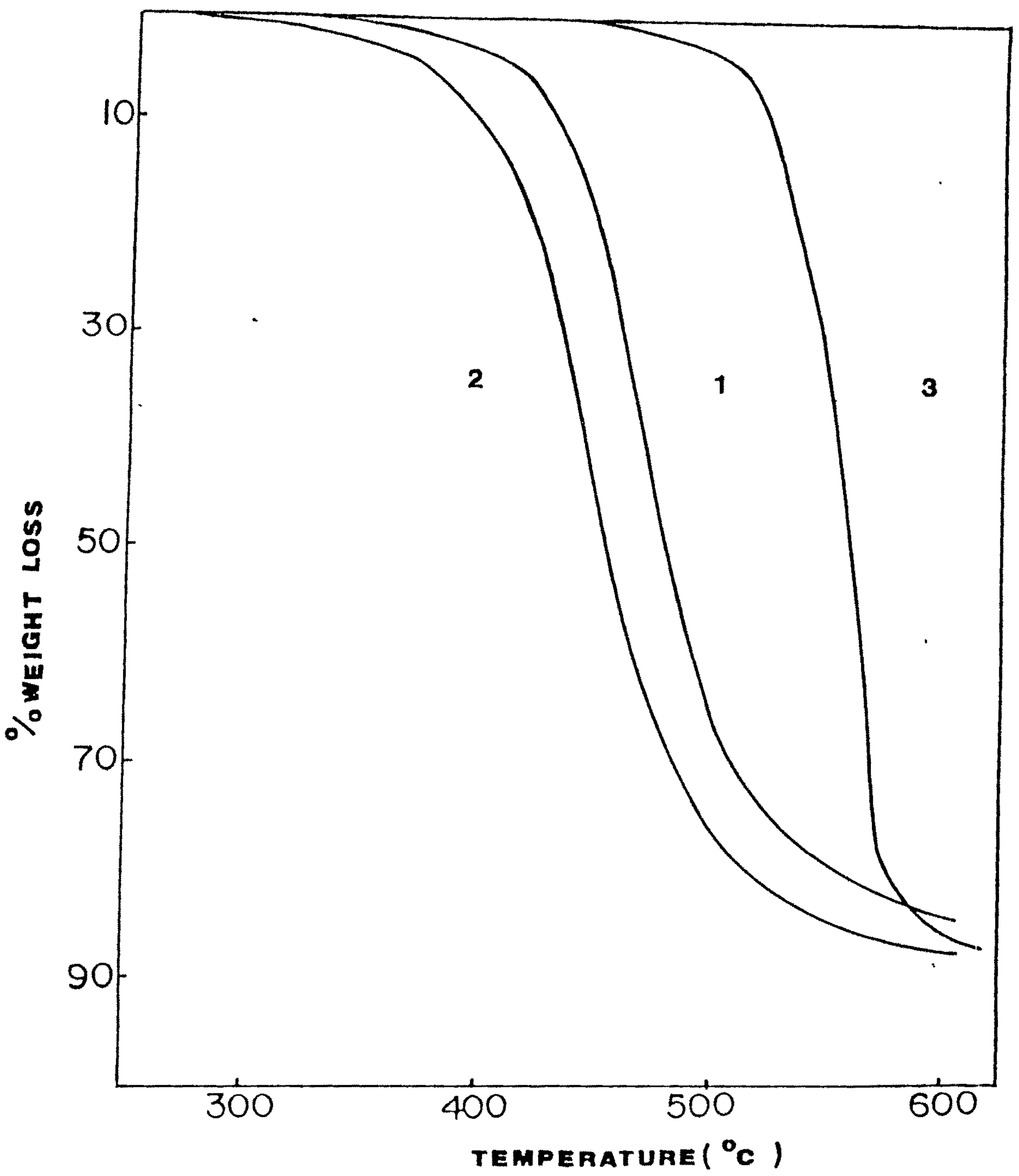

Fig.2.8 TGA Curves of (1) InR, (2) GR, and (3) PBR in nitogen atmosphere

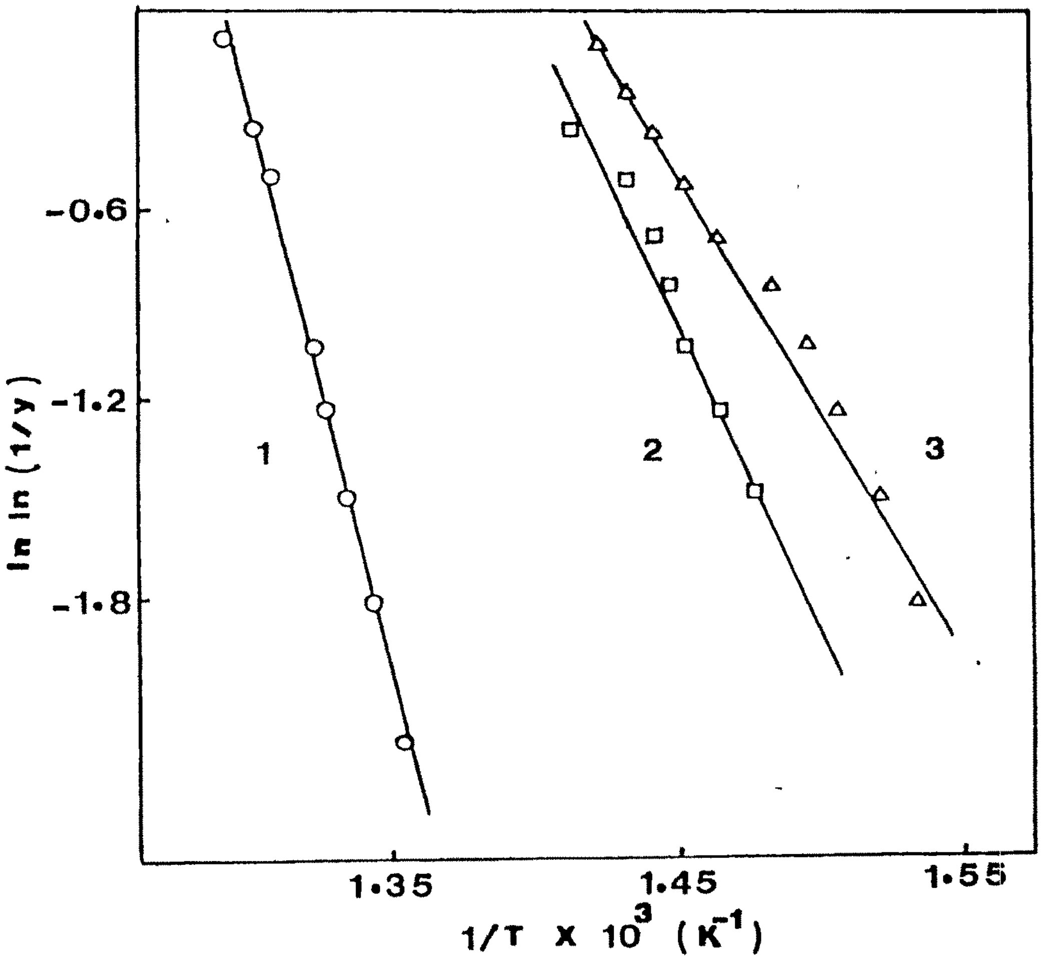

Fig.2.9 Activation energy plot for (1) PBR, (2) GR, and (3) InR in air

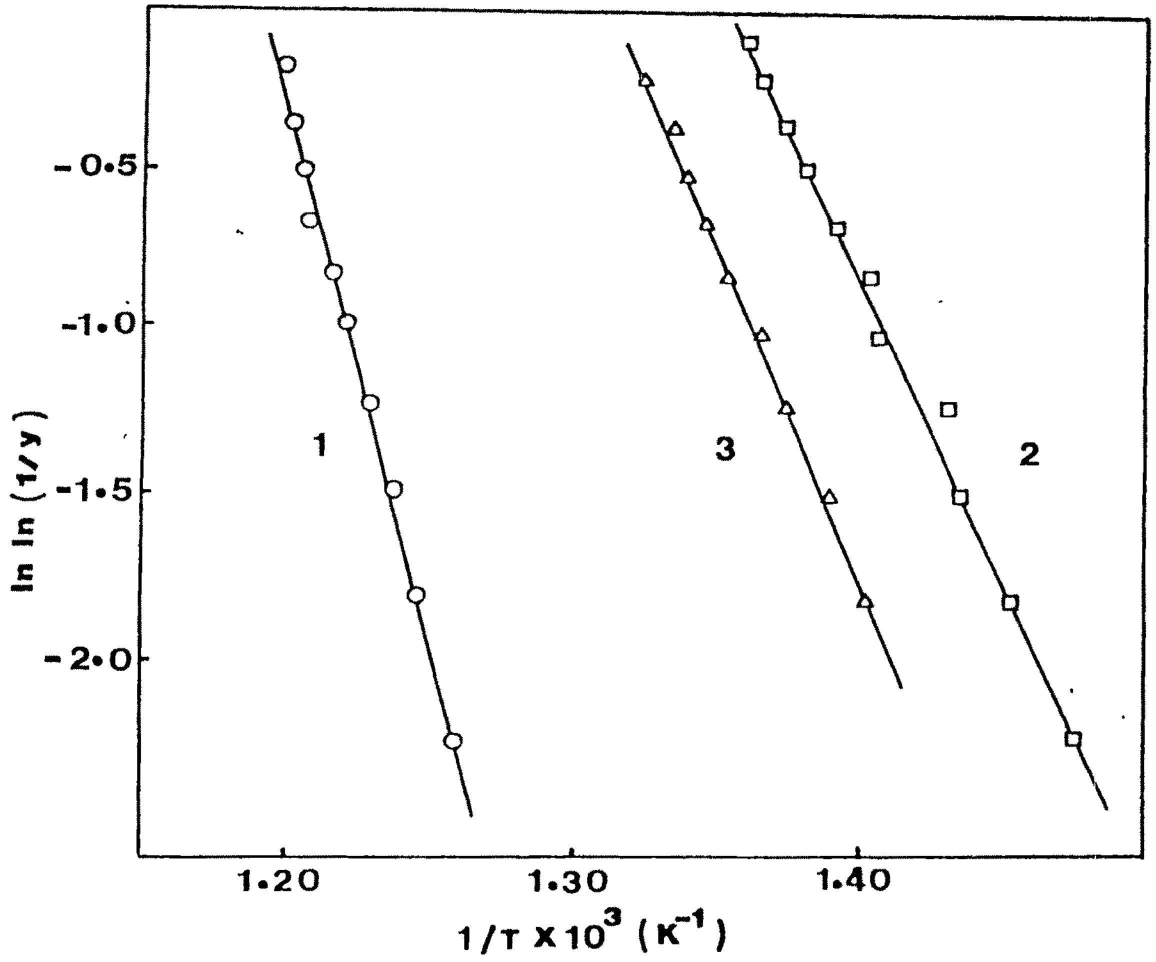

Fig.2.10 Activation energy plot for (1) PBR, (2) GR, and (3) InR in nitrogen

in nitrogen atmosphere, implying higher stability. This is not unexpected, due to the inherent susceptibility of the backbone double bonds to oxidation and crosslinking.

From Fig.2.11 it can be seen that DSC thermograph of PBR differs considerably from those of InR and GR. PBR falls into the class of elastomers showing degradation by exothermic reaction in nitrogen atmosphere. The exotherm peak precludes oxidation and indicates crosslinking and cyclisation reactions /354/. Energy change associated with this is found to be 965.4 J/g. InR and GR fall into another class, degrading both by the exothermic and endothermic reactions in nitrogen /355, 356/. Both of them show a very diffused exotherm upto about 255°C, followed by an endotherm, an exotherm, and finally a devolatalization endotherm between 330°C and 450°C. The absolute values associated with individual transition differ for both the rubbers, being dependent on the molecular structure, configuration and chemical composition.

[D] Viscosity study of polymer solutions

Viscosity of rubbers was studied in different solvents and at different temperatures. This enabled us to calculate the viscosity average molecular weight for different rubbers. The values are listed in Table 2.3. The values obtained from GPC analysis are also cited in Table 2.3. GPC of InR could not be run because of its insolubility in THF. The GPC curves for PBR and GR are shown in Fig.2.12. The intrinsic viscosities of all three rubbers in different solvents and at

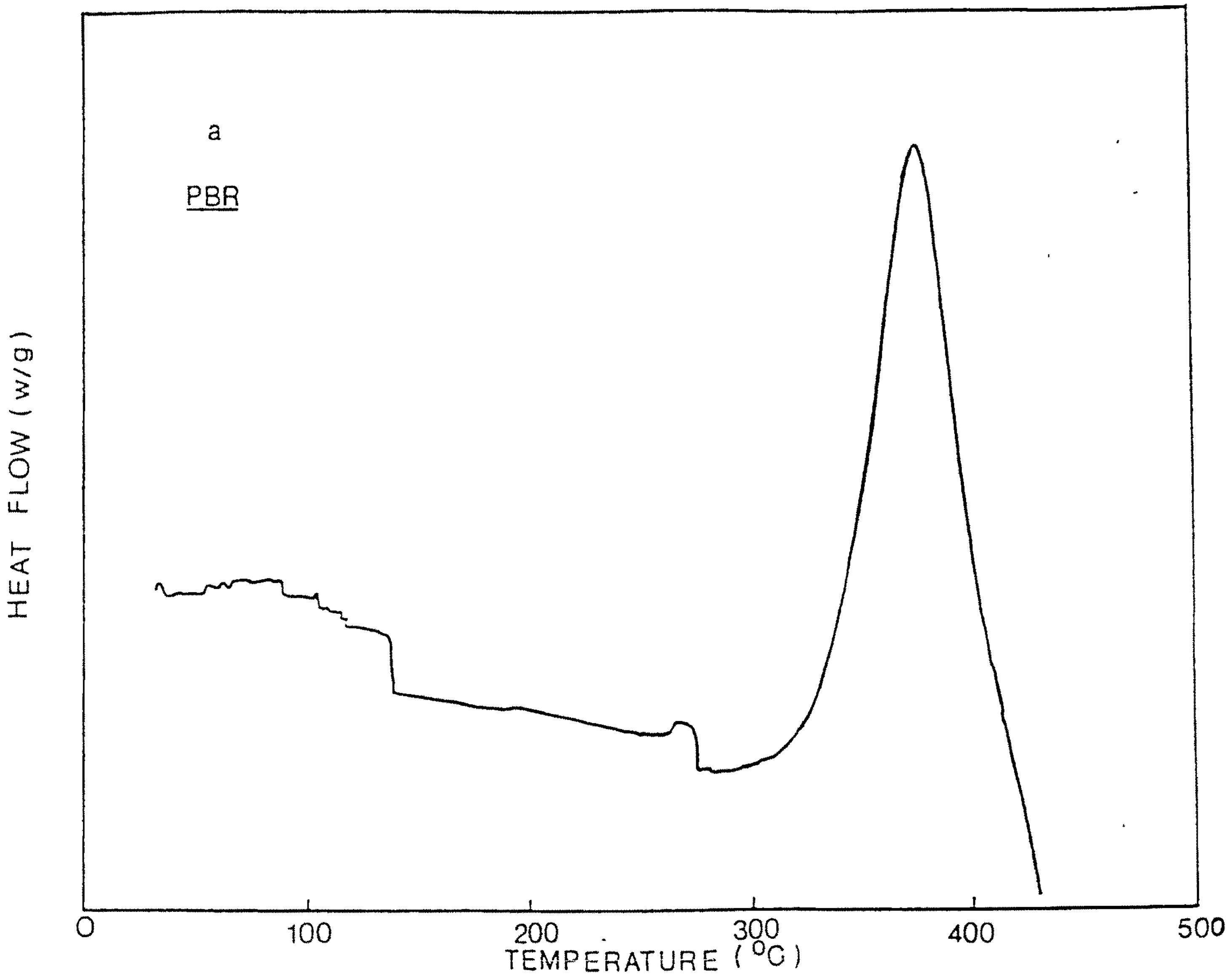

Fig.2.11(a) DSC Curve of PBR

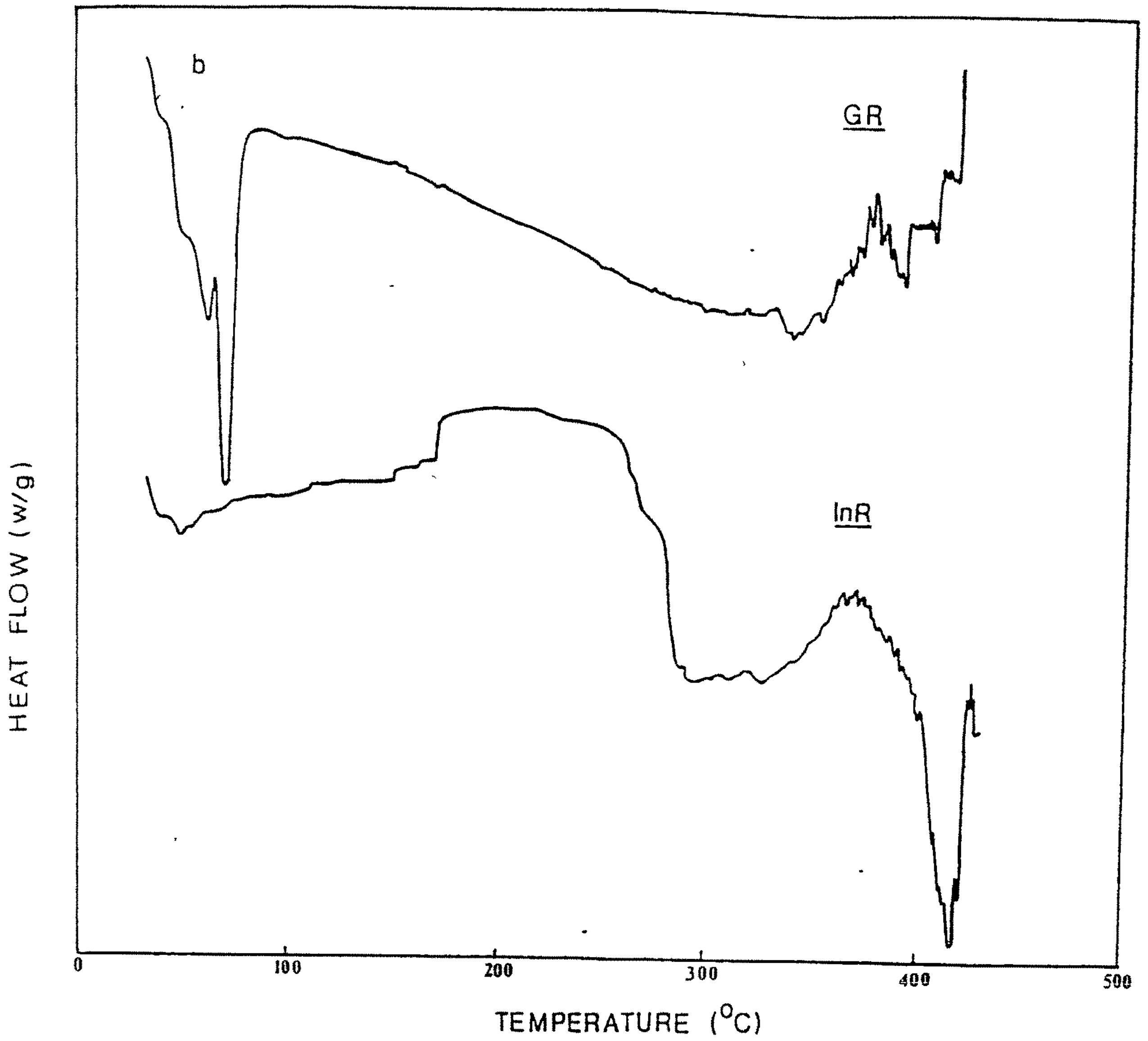

Fig.2.11(b) DSC Curve of InR and GR

TABLE : 2.3

AVERAGE MOLECULAR WEIGHTS AND POLYDISPERSITIES OF RUBBERS

Polymer	$K \times 10^{5*}$	a^*	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_n$	D
PBR	33.9	0.688	4.14×10^5	5.9×10^5	2.3×10^5	2.52
GR	50.2	0.667	2.01×10^5	3.5×10^5	1.4×10^5	2.50
InR	50.2	0.667	9.58×10^5	-	-	-

* Mark - Houwink constants, taken from Ref. 360.

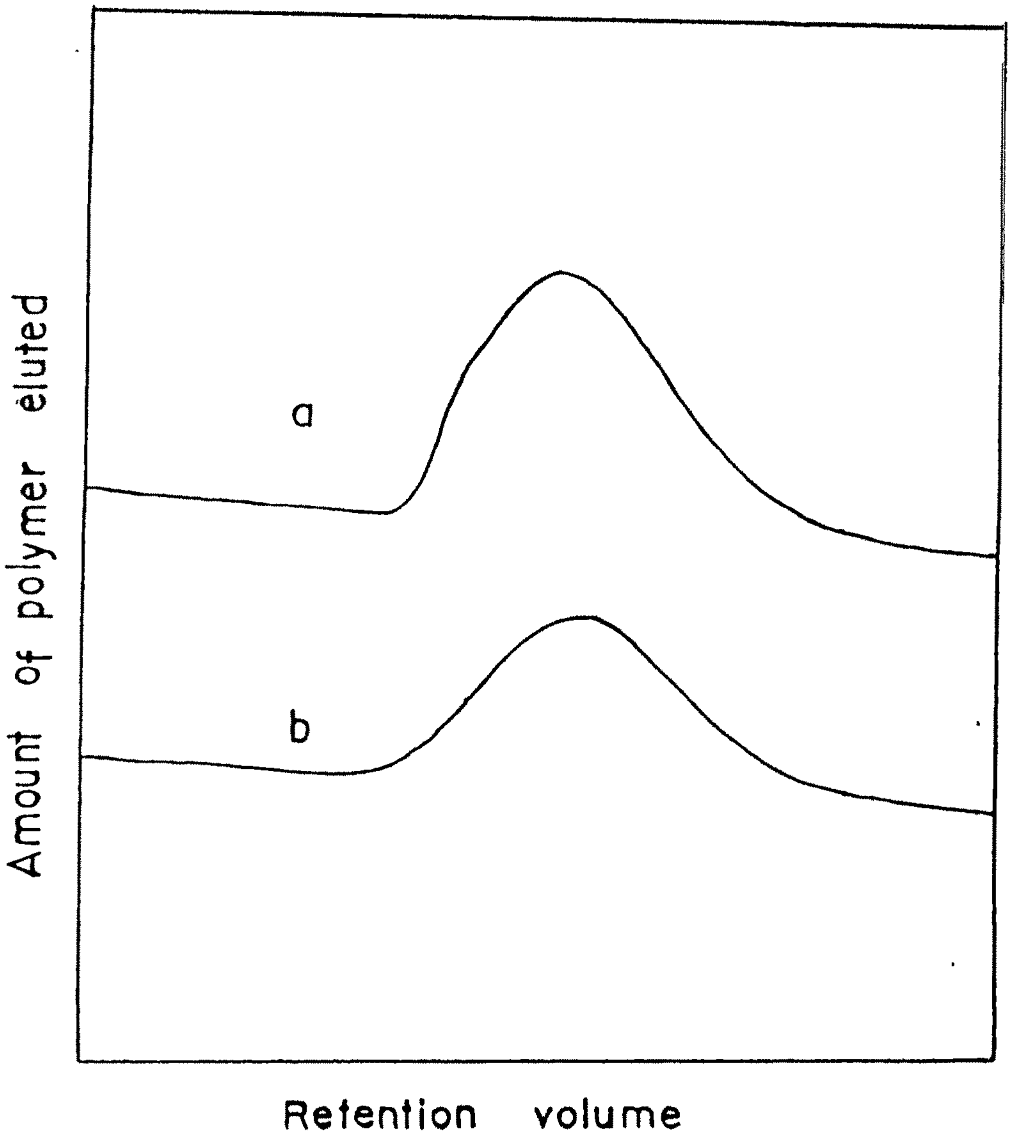

Fig.2.12 Gaussian Chromatograms obtained for (a) PBR and (b) GR

different temperatures are listed in Table 2.4. The intrinsic viscosities were computed by well known procedures/357/. It can be seen that intrinsic viscosity linearly decreases with increase in temperature. The accuracy of the data was checked by calculating K', K" and their difference was 0.5, as expected /358/. The values at various temperatures and from different solvent systems are compiled in Table 2.5. Intrinsic viscosities were plotted against solubility parameter of different solvents, for each of the rubbers. The plots show maxima, which correspond to solubility parameter of the rubber. Solubility parameter of PBR was found to be 8.3 at 35°C. Solubility parameter for GR was found to be 8.5 at 30°C [Fig.2.13]. That for InR was not possible to determine because of lesser number of solvents used for the study.

From the viscosity data, various activation parameters of the viscous flow were evaluated using Frenkel-Eyring equation/359/.

$$\eta = [Nh / V] \exp [\Delta G^{\ddagger}_{vis} / RT] \qquad \ldots\ldots [2]$$

where V is the molar volume of the solvent, N is the Avogadro number, h is the Planck's constant, R is the gas constant, T is the temperature and $\Delta G^{\ddagger}_{vis}$ is the activation free energy change of the viscous flow. Equation 2 can be rewritten as

$$\ln [\eta V/Nh] = \Delta G^{\ddagger}_{vis} /RT = \Delta H^{\ddagger}_{vis} /RT - \Delta S^{\ddagger}_{vis} /R \qquad \ldots\ldots [3]$$

where $\Delta H^{\ddagger}_{vis}$ and $\Delta S^{\ddagger}_{vis}$ are the activation enthalpy and entropy

TABLE : 2.4

INTRINSIC VISCOSITIES OF RUBBERS IN VARIOUS SOLVENTS AND TEMPERATURES

Solvent System	Rubber	Intrinsic Vistosity [η] [dl/g]				
		25°C	30°C	35°C	40°C	45°C
n-heptane [δ* = 7.4]	PBR	1.60	1.56	1.51	1.48	-
methyl cyclohexane [δ* = 7.8]	GR	-	1.53	1.51	1.49	1.47
	InR	-	4.20	4.05	3.85	3.70
cyclohexane [δ* = 8.2]	PBR	2.41	2.37	2.34	2.30	-
	GR	1.55	1.52	1.50	1.47	-
toluene [δ* = 8.9]	PBR	2.56	2.48	2.34	2.06	1.94
	GR	1.73	1.70	1.62	1.58	1.54
	InR	4.90	4.75	4.60	4.45	4.30
chlorobenzene [δ* = 9.5]	PBR	2.44	2.33	2.16	1.84	-
	GR	1.70	1.57	1.50	1.46	-
	InR	4.26	3.12	2.27	2.17	-

* Solubility parameter 'δ' as given in Ref. 360

TABLE : 2.5

$K' - K''$ FOR DIFFERENT RUBBERS IN DIFFERENT SOLVENTS AT DIFFERENT TEMPERATURES

Solvents	PBR					GR					InR				
	25°C	30°C	35°C	40°C	45°C	25°C	30°C	35°C	40°C	45°C	25°C	30°C	35°C	40°C	45°C
Toluene	0.47	0.52	0.46	0.55	0.57	0.57	0.53	0.53	0.55	0.56	0.52	0.50	0.54	0.56	0.55
Chloro-benzene	0.55	0.52	0.54	0.53	-	0.51	0.53	0.55	0.54	-	0.55	0.53	0.57	0.58	-
Cyclo-hexane	0.46	0.47	0.49	0.49	-	0.55	0.53	0.55	0.52	-	-	-	-	-	-
Methyl-cyclo-hexane	-	-	-	-	-	-	0.53	0.52	0.54	0.54	-	0.53	0.57	0.54	0.55
n-hep-tane	0.56	0.51	0.56	0.56	-	-	-	-	-	-	-	-	-	-	-

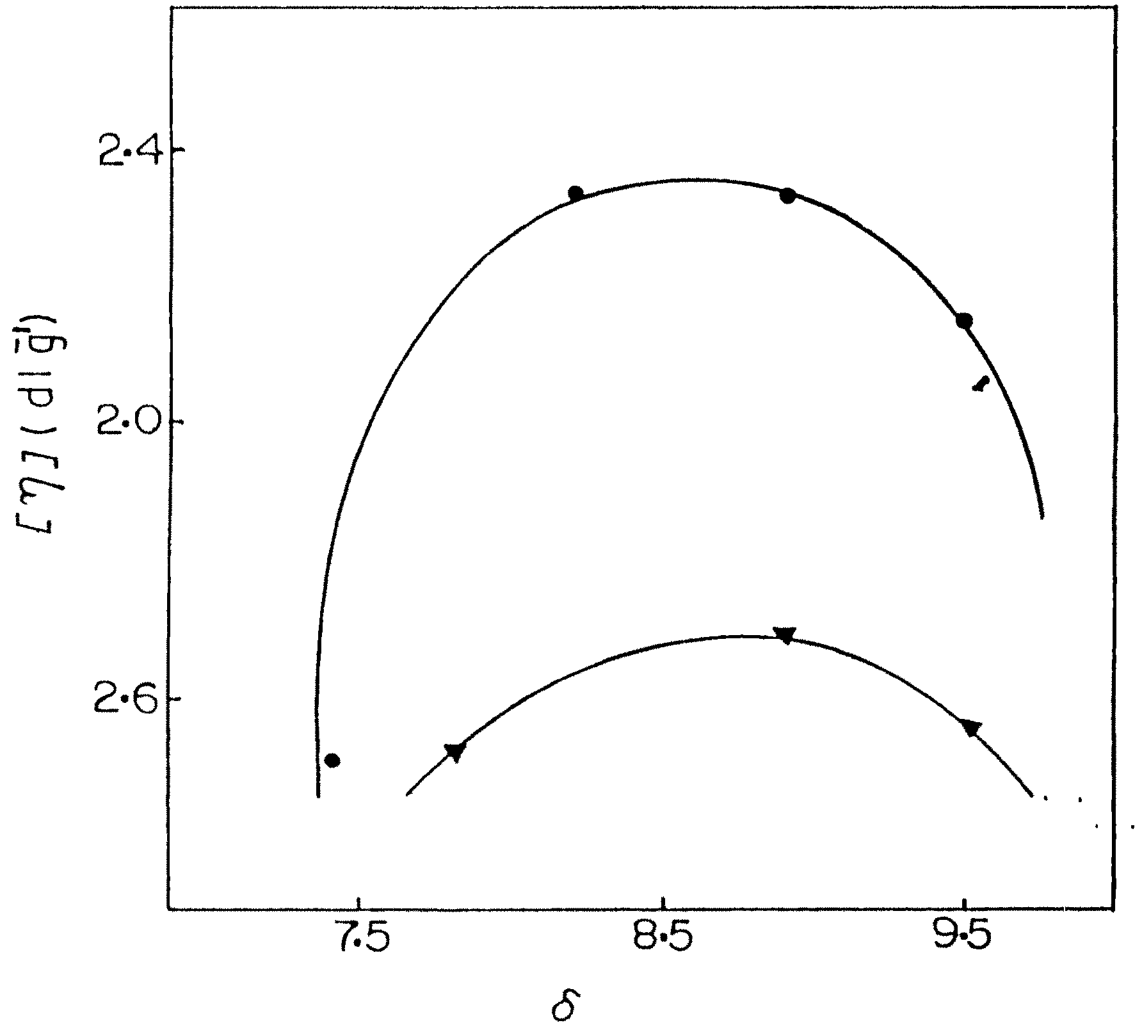

Fig.2.13 Solubility Parameter vs. intrinsic viscosity plot for ● PBR and ▲ GR

change of the viscous flow. The linearity is observed by plotting ln [ηV/Nh] against T^{-1}. The slope and the intercept gave $\Delta H^{\ddagger}_{vis}$ and $\Delta S^{\ddagger}_{vis}$ respectively. On plotting $\Delta S^{\ddagger}_{vis}$ against concentration and extrapolating to C = 0, $\Delta S^{\ddagger o}_{vis}$ values were obtained. $\Delta H^{\ddagger o}_{vis}$ values were also similarly obtained. $\Delta G^{\ddagger o}_{vis}$ values were then computed at 30°C by the well known thermodynamic relation.

$$\Delta G^{\ddagger o}_{vis} = \Delta H^{\ddagger o}_{vis} - T\Delta S^{\ddagger o}_{vis} \qquad \text{.....} [4]$$

All these activation parameters at infinite dilution are compiled in Table 2.6. It was seen that within the range of temperature studied, $\Delta G^{\ddagger o}_{vis}$ values of a particular polymer in a given solvent differed by not more than 200 J, which is rather low. This is due to the small entropy change and rather small temperature range studied. It can be seen that the heats of activation of the viscous flow are positive for all systems. The entropies of activation of the viscous flow are also positive. However, free energy of activation of viscous flow seems to be independent of polymer and solvent.

The relative viscosity data at different concentrations help us in calculation of the voluminosity [V_E] of polymer solutions at a fixed temperature. Recently it has been used /361/ to determine the shape of the protein molecules in solution i.e. the so called 'shape factor'. V_E was calculated by plotting Y against concentration C [in g/ml],

where $$Y = [\eta_r^{0.5} - 1] / [C(1.35\eta_r^{0.5} - 0.1)] \qquad \text{.....} [5]$$

TABLE : 2.6

VISCOSITY ACTIVATION PARAMETERS AT INFINITE DILUTION

Solvents	PBR			GR			InR		
	$\Delta H^{o\ddagger}_{vis}$ [kJ]	$\Delta S^{o\ddagger}_{vis}$ [JK^{-1}]	$\Delta G^{o\ddagger}_{vis}$ [kJ]30°C	$\Delta H^{o\ddagger}_{vis}$ [kJ]	$\Delta S^{o\ddagger}_{vis}$ [JK^{-1}]	$\Delta G^{o\ddagger}_{vis}$ [kJ]30°C	$\Delta H^{o\ddagger}_{vis}$ [kJ]	$\Delta S^{o\ddagger}_{vis}$ [JK^{-1}]	$\Delta G^{o\ddagger}_{vis}$ [kJ]30°C
Toluene	11.4	9.0	8.7	10.1	5.7	8.5	9.6	-1.21	10.0
Chlorobenzene	9.6	3.8	8.4	9.3	2.7	8.5	11.0	9.0	8.3
Cyclohexane	11.8	7.4	9.6	13.0	13.2	9.0	-	-	-
n-Heptane	8.8	2.8	8.0	-	-	-	-	-	-
Methyl cyclohexane	-	-	-	8.6	-0.8	8.6	9.4	1.7	8.9

The straight line obtained was then extrapolated to C = 0 and the intercept yielded V_E. The shape factor ν was obtained from the equation

$$[\eta] = \nu V_E \qquad \ldots\ldots [6]$$

The shape factor gives an idea about the shape of the macromolecules in the solution /362/. Values of shape factor in different solvents and at different temperatures are listed in Table 2.7. It is seen that values for all the systems are around 2.5, suggesting that the macromolecules acquire spherical conformation /363/ in all solvents and temperatures chosen for this study. Moreover, ν values are found to be almost independent of temperature [varying between 2.4 and 2.6] indicating that the ratio between major axis and minor axis varies by about 2%. Therefore we suggest that the conformations of these polymers are independent of temperature.

Some of the molecular parameters of polymers were calculated using solution viscosity data. The expansion coefficient 'α', which is defined as the ratio by which the polymer coil is expanded in solution over its size in the absence of excluded volume effect, can be determined using the relation /364/.

$$\alpha = [\, \bar{M}_V^{(a-1/2)} \,]^{1/3} \qquad \ldots\ldots [7]$$

The mean square end to end length of the polymer chain $[\bar{r}^2]$ is determined by

TABLE : 2.7

SHAPE FACTOR 'ν' AT VARIOUS TEMPERATURES

Solvents	PBR					GR					InR				
	25°	30°	35°	40°C	45°C	25°C	30°C	35°C	40°C	45°C	25°C	30°C	35°C	40°C	45°C
Toluene	2.63	2.54	2.53	2.60	2.54	2.62	2.48	2.54	2.60	2.50	2.60	2.48	2.48	2.43	2.55
Chlorobenzene	2.52	2.50	2.50	2.52	-	2.52	2.53	2.52	2.52	-	2.53	2.53	2.52	2.50	-
Cyclohexane	2.57	2.49	2.55	2.40	-	2.48	2.52	2.47	2.51	-	*	-	-	-	-
Methylcyclohexane	-	-	-	-	-	-	2.53	2.52	2.56	2.58	-	2.53	2.51	2.54	2.55
n-Heptane	2.60	2.54	2.50	2.50	-	*	-	-	-	-	*	-	-	-	-

* were not studied because of insolubility

$$\bar{r}^2 = [KM_V^{(1+a)}/\varnothing]^{2/3} \qquad \text{..... [8]}$$

where $\varnothing$ is a universal constant whose value is 2 x 10^{23}. The mean square end to end length of the polymer chain in unperturbed state, $\bar{r}_o^2$, is calculated using the equation,

$$\bar{r}_o^2 = \bar{r}^2/\alpha^2 \qquad \text{..... [9]}$$

The different values obtained for the three polymers, in toluene, are listed in Table 2.8.

TABLE : 2.8

MOLECULAR PARAMETERS OF THE RUBBERS IN TOLUENE

Polymers	α	$\bar{r}^2$ (cm²)	$\bar{r}_o^2$ (cm²)
PBR	2.25	2.98 x 10^{-12}	5.88 x 10^{-13}
GR	1.97	1.45 x 10^{-12}	3.73 x 10^{-13}
InR	2.15	8.19 x 10^{-12}	1.77 x 10^{-12}