

# Characterization of Natural Polyisoprenes and Synthetic Polybutadiene

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## SYNOPSIS

Synthetic polybutadiene (PBR) and natural rubbers from India (InR) and Guyana (GR) have been characterized in detail. The characterization includes IR, NMR, GPC, DSC, TGA, contact angle, and viscosity measurements. Spectroscopic characterization helped in the differentiation of InR and GR. Viscosity data is used in the evaluation of activation parameters at infinite dilution of the viscous flow. Viscosity data is also used for the determination of the conformation of the macromolecules in various solvents. Surface characterization confirms the total hydrophobic nature of the three rubbers. Thermal analysis shows different degradation pattern for natural rubbers than for the synthetic rubber.

## INTRODUCTION

As a part of our interest in polymer behavior, we decided to study the adsorption of polymers at the solid-liquid interface. The adsorption of synthetic polybutadiene was studied on inorganic substrates, for example, silica gel and alumina from solvents such as toluene and cyclohexane.<sup>1</sup> We are also studying copolymer adsorption, which will be published elsewhere. We are presently studying the adsorption of different natural rubbers on these substrates. The natural rubbers chosen for the study were: (a) natural rubber obtained from Guyana and (b) natural rubber obtained from Kerala, India. To explain and understand the adsorption of all these rubbers on different substrates, detailed characterization is necessary. The characterization includes IR,<sup>2</sup> NMR, contact angle,<sup>2</sup> viscosity,<sup>3</sup> DTA, DSC, and GPC, as were performed earlier. The results are presented and discussed in this article.

## EXPERIMENTAL

Synthetic cis-1,4-polybutadiene (> 96%) (PBR) was obtained from IPCL, Baroda, India. Guyana rubber (GR) was natural rubber from Guyana, and

was obtained as a gift from Dr. J. T. Guthrie, Department of Colour Chemistry, Leeds University, Leeds, UK. The Indian rubber (InR) was natural rubber obtained from Kerala, India, as ribbed, smoked sheet (RSS), from plant RR11 105. The polymers were purified by dissolving them in toluene and leaving them overnight. The insoluble matter was filtered out and the clear filtrate was poured in excess methanol with constant stirring. The pure white rubber obtained was vacuum dried to a constant mass at room temperature.

The solvents, that is, chlorobenzene, toluene, *n*-heptane, cyclohexane, methylcyclohexane, methanol, and chloroform, were obtained from Merck, India. The cyclohexane and methylcyclohexane used were chromatography grade. All the solvents were freshly distilled before use.

The IR spectra of the polymer films were taken on a Shimadzu IR-408 spectrophotometer. The films were made by dissolving the polymers in chloroform and then pouring the solution over mercury. The films were obtained by vacuum evaporation of the solvent. The NMR of the polymer solutions in CDCl<sub>3</sub> were recorded on a Varian XL a 300 MHz for PMR and 75 MHz for <sup>13</sup>CNMR at the RSIC, IIT, Bombay, India. The GPC of the rubbers was run in tetrahydrofuran (THF) at ambient conditions (~ 27°C) on "Waters" (150 C ALC, Millipore Corporation), with refractive index detector. DSC was recorded on a DuPont 2000 system in nitrogen atmosphere. TGA and DTA were recorded on the Shimadzu Thermal

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Analyzer DT 30B. The contact angle<sup>2,3</sup> was determined with the help of a contact  $\theta$  meter, fabricated at the department of color chemistry, Leeds University, Leeds, UK, and was obtained as a gift. Viscosity studies of different solutions were carried out with the help of an Ubbelohde viscometer<sup>3</sup> that was placed vertically in a thermostat at required temperature ( $\pm 0.05^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

### IR and NMR Spectra

The IR spectra of all three polymers are given in Figure 1. The GR films were opaque, hence the IR spectra was taken in chloroform solution. The spectra obtained compare favorably to those in literature.

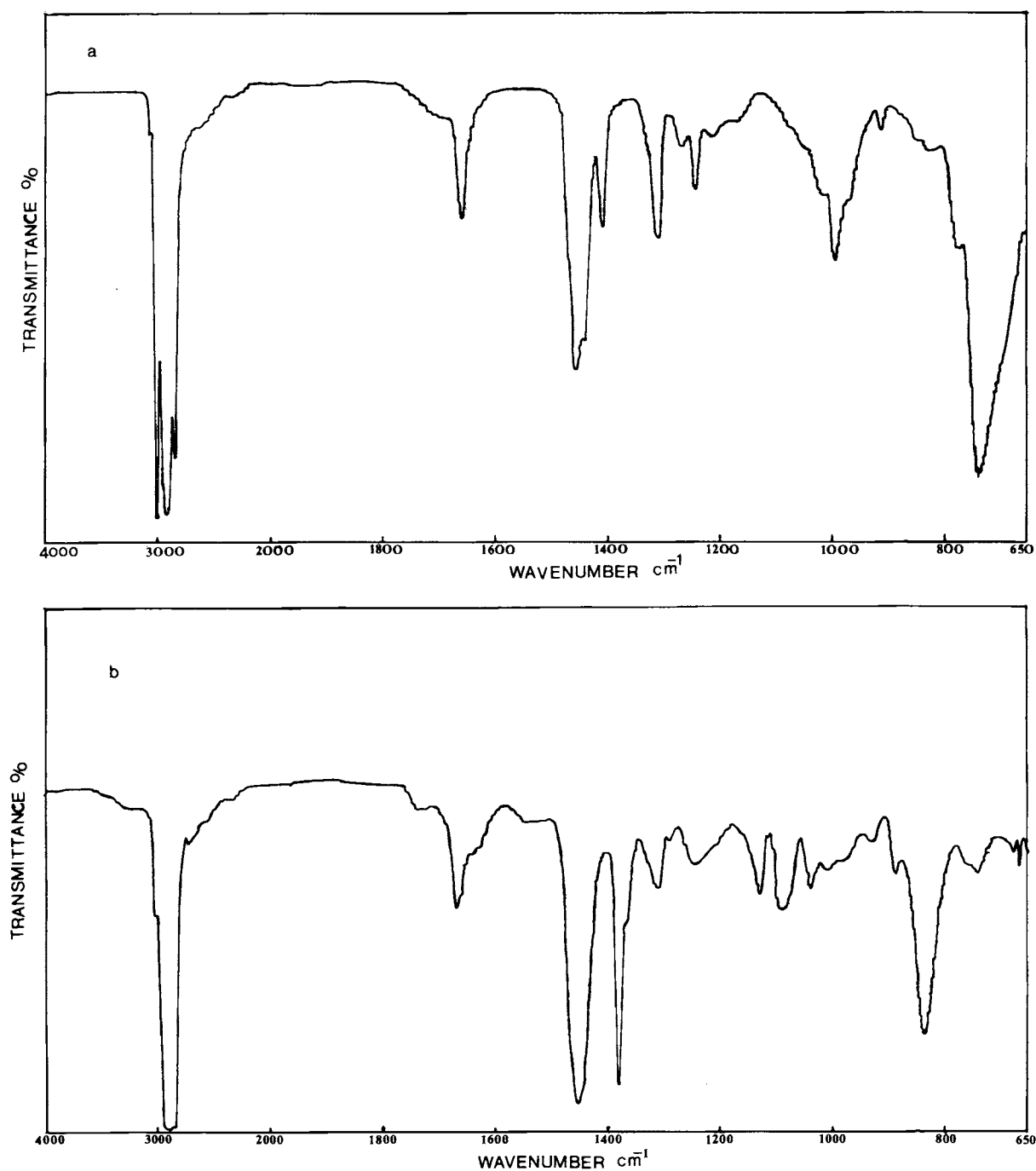


Figure 1 IR spectra of (a) PBR, (b) InR, and (c) GR.

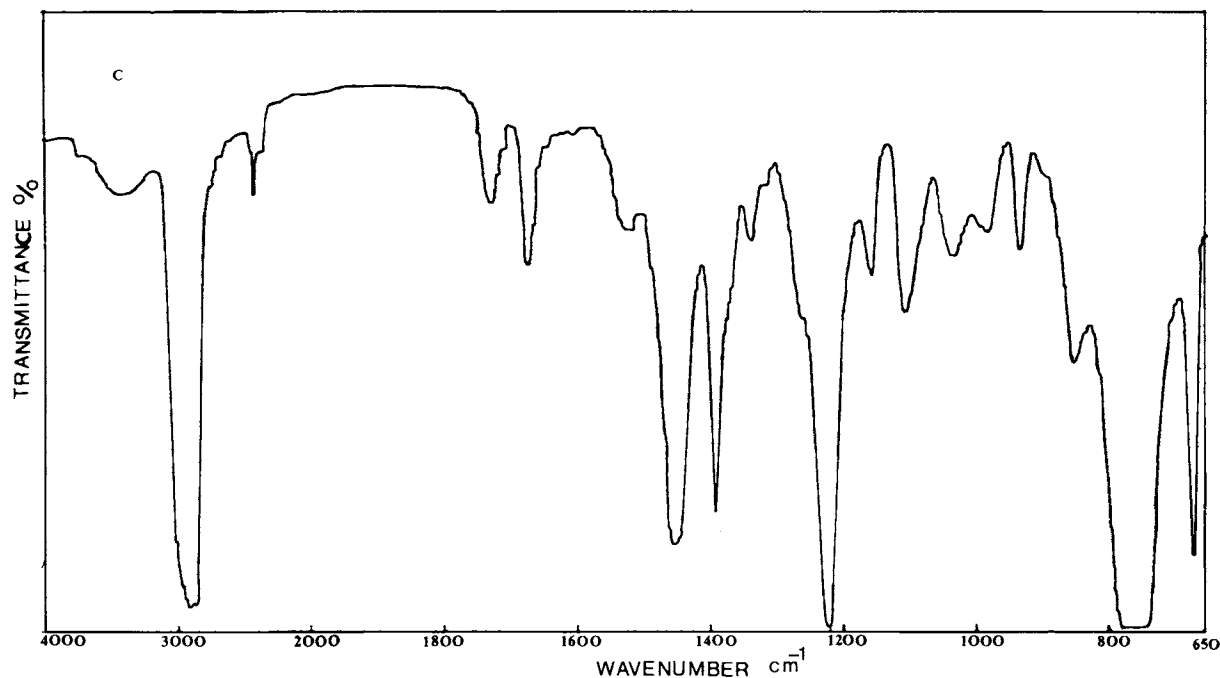


Figure 1 (Continued from the previous page)

For InR, the bands at 740, 1130, and 1310  $\text{cm}^{-1}$  are due to vibrations of *cis*-C(CH<sub>3</sub>) = CH-group.<sup>4</sup> For GR, the bands at 1150 and 1325  $\text{cm}^{-1}$  are due to vibrations of *trans*-C(CH<sub>3</sub>) = CH-group.<sup>4</sup> This suggests that InR is a *cis* and GR is *trans* form of natural polyisoprene. The PBR spectra compare favorably with those in the literature.<sup>5</sup>

The PMR spectra of three rubbers are presented in Figure 2 and their <sup>13</sup>CNMR spectra are presented in Figure 3. The resonance peaks suggest the arrangement of repeat unit, as shown in Figure 4. The symmetrical units of *cis*-1,4-polybutadiene (PBR) exhibit one resonance peak from equivalent ethylenic carbons ( $\alpha$  peak) and one peak from equivalent methylene carbons ( $\beta$  peak). InR shows resonance peak at 5.12 ppm indicating that the sample is 1,4 adduct.<sup>6</sup> The peaks at 2.03 and 1.67 ppm are given by  $\alpha$ -CH<sub>2</sub> and  $\alpha$ -CH<sub>3</sub>, respectively. The peak at 1.67 ppm indicates its *cis* structure. The olefinic peak is observed at 5.12 ppm. In GR, the  $\alpha$ -CH<sub>3</sub> peak is observed at 1.59 ppm. This suggests that the 1,4 unit is mainly *trans* in the repeat unit.<sup>7</sup>

The <sup>13</sup>CNMR spectra of InR and GR further confirms the configurational difference between them. Both show five, clearly distinguishable, singlet resonance peaks, which are due to methyl, two methylene, and two ethylenic carbon atoms. From Figure 4, it can be seen that  $\delta$  methylene moiety, being in a similar environment in *cis*- and *trans*-1,4-polyisoprenes, shows similar chemical shift values in both

cases. These values are 26.4 ppm for natural *cis*-1,4 and 26.8 ppm for natural *trans*-1,4, that is, for InR and GR, respectively.<sup>8</sup> Unlike  $\delta$  carbon,  $\gamma$ -methylene carbons resonate at 39.8 ppm for GR and 32.2 ppm for InR, that is, a difference of 7.6 ppm. The methyl carbons ( $\epsilon$  carbons) also show a difference, that is, 23.37 ppm for InR and 16.03 ppm for GR. This confirms that InR is *cis*-1,4 polyisoprene and GR is *trans*-1,4-polyisoprene.<sup>9</sup>

### Contact Angle Measurements

The contact angle,  $\theta$ , of various liquids with polymer surfaces (films) was determined with the help of a contact " $\theta$ " meter, as mentioned earlier. The liquids used are listed in Table I. The surface tensions at

Table I The Surface Tension Values of the Liquids Used for Determining  $\gamma_c$  on Various Rubbers

Liquids Used	$\gamma_{20^\circ\text{C}}$ mN m <sup>-1</sup>	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

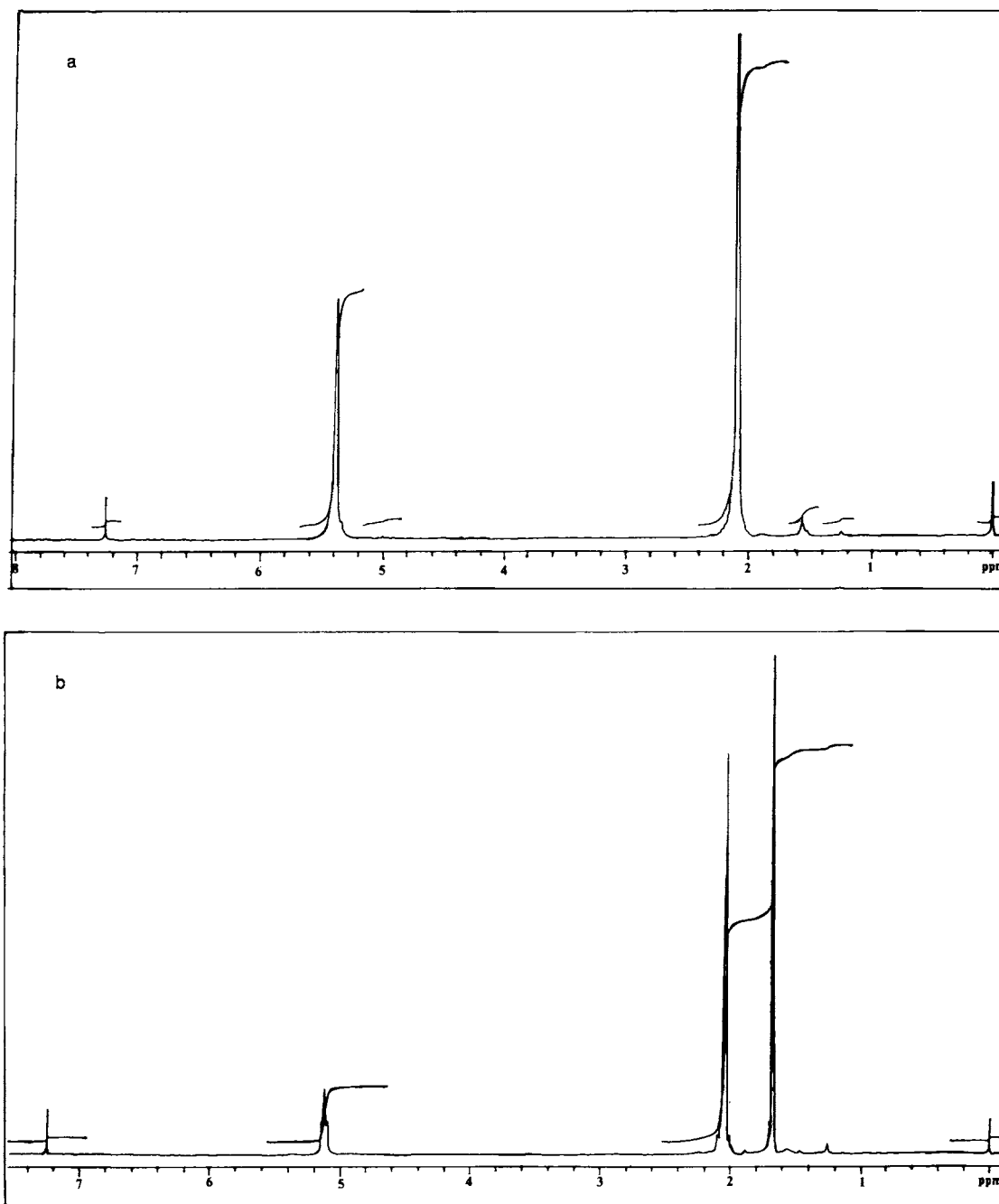


Figure 2 PMR spectra of (a) PBR, (b) InR, and (c) GR.

20°C were taken from the literature and were used for determination of  $\gamma_c$ . The  $\text{Cos } \theta$  was plotted against the surface tension of the liquids. The linear plot obtained was extrapolated to  $\text{Cos } \theta = 1$  ( $\theta = 0$ ) and the corresponding surface tension was taken to be the critical surface tension  $\gamma_c$ . The values were 16.5, 15.5, and 13.0  $\text{mN m}^{-1}$  for PBR, GR, and InR, respectively. This indicates that the liquids with

surface tension higher than  $\gamma_c$  will not easily spread on polymer surfaces. We can surmise that all three polymers are hydrophobic in nature.<sup>10</sup>

This conclusion 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 behaviors.

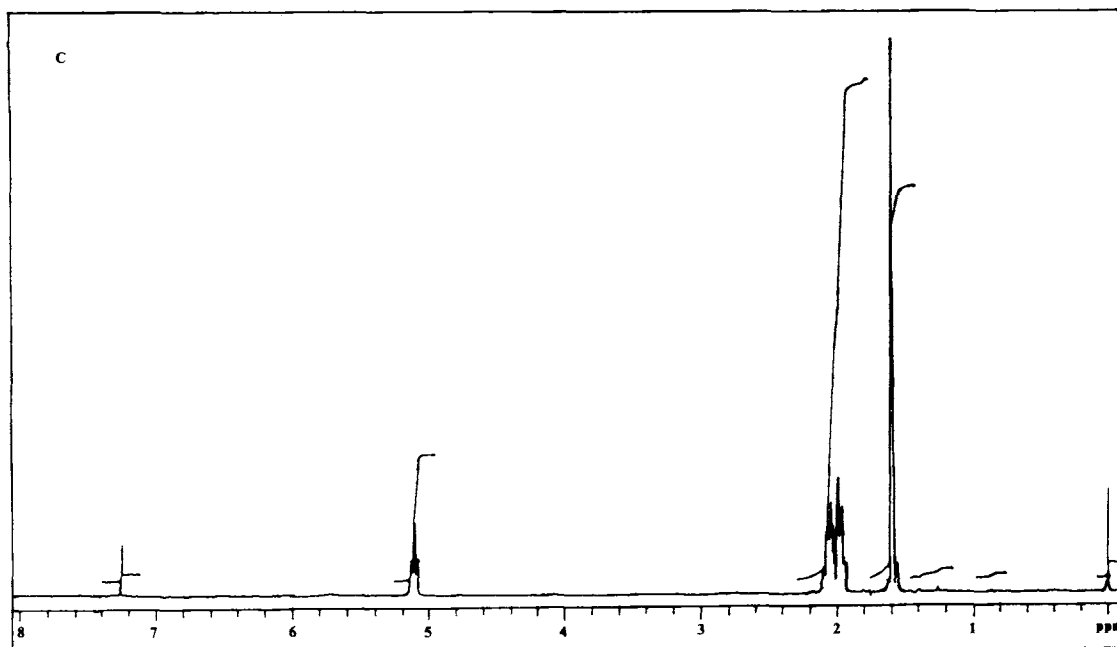


Figure 2 (Continued from the previous page)

### Thermal Analysis

It is seen from the TGA of PBR, GR, and InR that the maximum weight loss is different for each rubber. Weight loss is found to be 84%, 90%, and 94% for PBR, GR, and InR, respectively. From Figure 5, it can be seen that the 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. This exotherm peak precludes oxidation and indicates crosslinking and cyclization reactions.<sup>11</sup> The 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.<sup>12,13</sup> Both exothermic and endothermic reactions show a diffused exotherm up to about 255°C, followed by an endotherm, an exotherm, and finally a devolatilization endotherm between 330°C and 450°C. The absolute values associated with individual transitions differ for both the

rubbers; the values are dependent on the molecular structure, configuration, and chemical composition.

### Viscosity Study of Polymer Solutions

The 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 II. The values obtained from GPC analysis are also cited in Table II. GPC of InR could not be run because of its insolubility in THF. The intrinsic viscosities of all three rubbers in different solvents, and at different temperatures, are listed in Table III. The intrinsic viscosities were computed by a well-known procedure.<sup>14</sup> It can be seen that the intrinsic viscosity linearly decreases with an increase in temperature. The accuracy of the data was checked by calculating  $K'$ ,  $K''$ <sup>15</sup> and their difference was 0.5, as expected.<sup>15</sup> Intrinsic viscosities were plotted against solubility

Table II Average Molecular Weights and Polydispersities of Rubbers

Polymer	$K \times 10^5$ <sup>a</sup>	$\alpha$ <sup>a</sup>	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_n$	$D$
PBR	33.9	0.688	$4.14 \times 10^5$	$5.9 \times 10^5$	$2.3 \times 10^5$	2.52
GR	50.2	0.667	$2.01 \times 10^5$	$3.5 \times 10^5$	$1.4 \times 10^5$	2.50
InR	50.2	0.667	$9.58 \times 10^5$	—	—	—

<sup>a</sup> Mark-Houwink constants.<sup>17</sup>

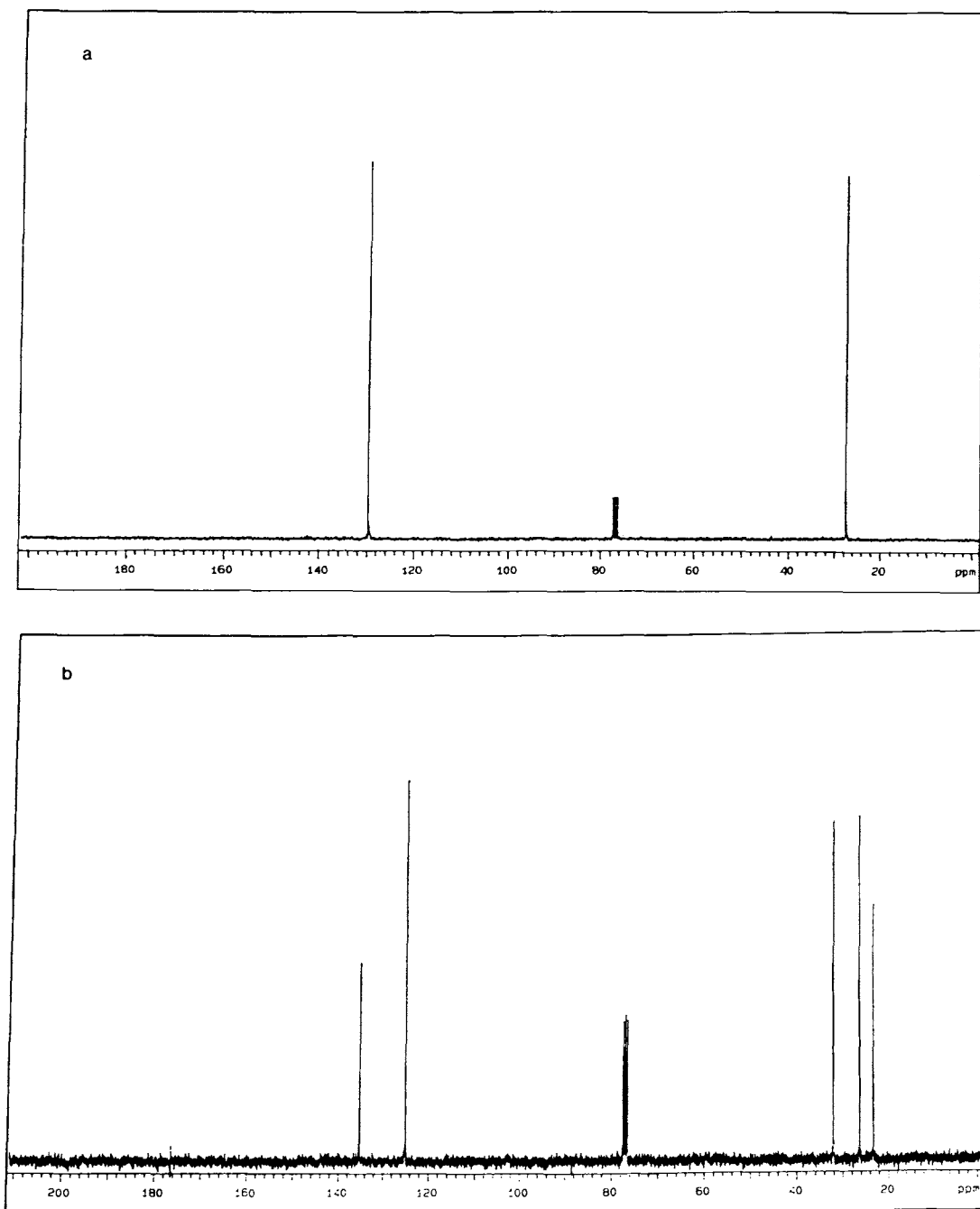


Figure 3  $^{13}\text{C}$  NMR spectra of (a) PBR, (b) InR, and (c) GR.

parameters of different solvents for each of the rubbers. The plots show maxima, corresponding to the solubility parameter of the rubber. The solubility parameter of PBR was found to be 8.75 at 30°C and 8.4 at 35°C. The solubility parameter for GR was found to be 8.8 at 30°C. The solubility parameter for InR was difficult to find because fewer solvents were used.

From the viscosity data, various activation parameters of the viscous flow were evaluated using the Frenkel-Eyring equation,<sup>16</sup> that is

$$\eta = (Nh/V) \exp(\Delta G_{\text{vis}}^{\ddagger}/RT) \quad (1)$$

where  $V$  is the molar volume of the solution,  $N$  is the Avogadro number,  $h$  is the Planck's constant,  $R$  is the gas constant,  $T$  is the temperature, and

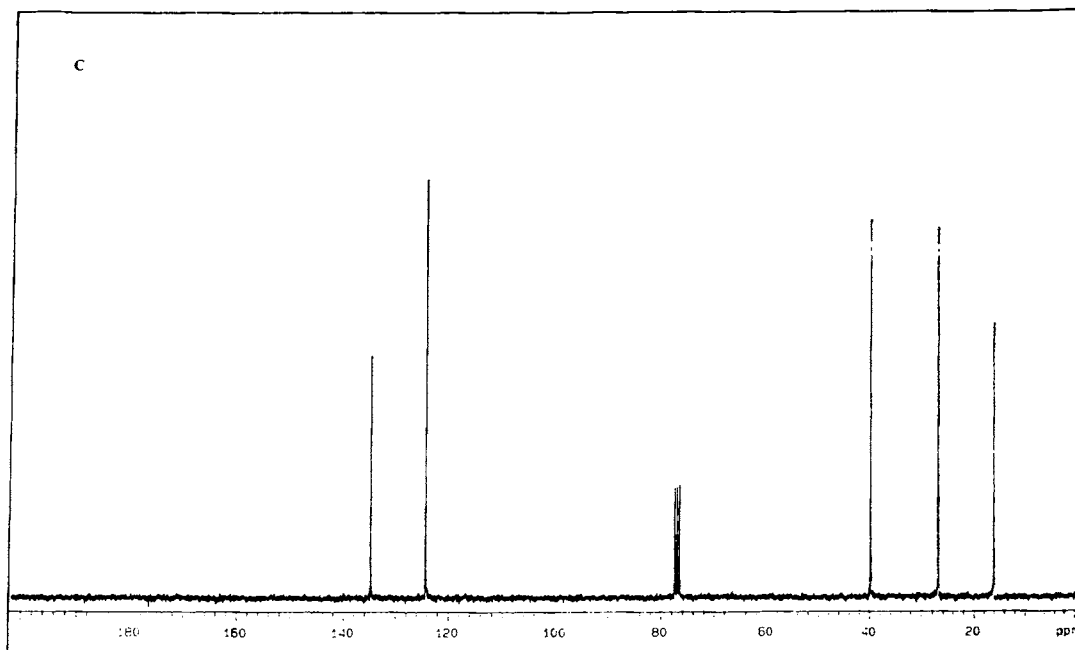


Figure 3 (Continued from the previous page)

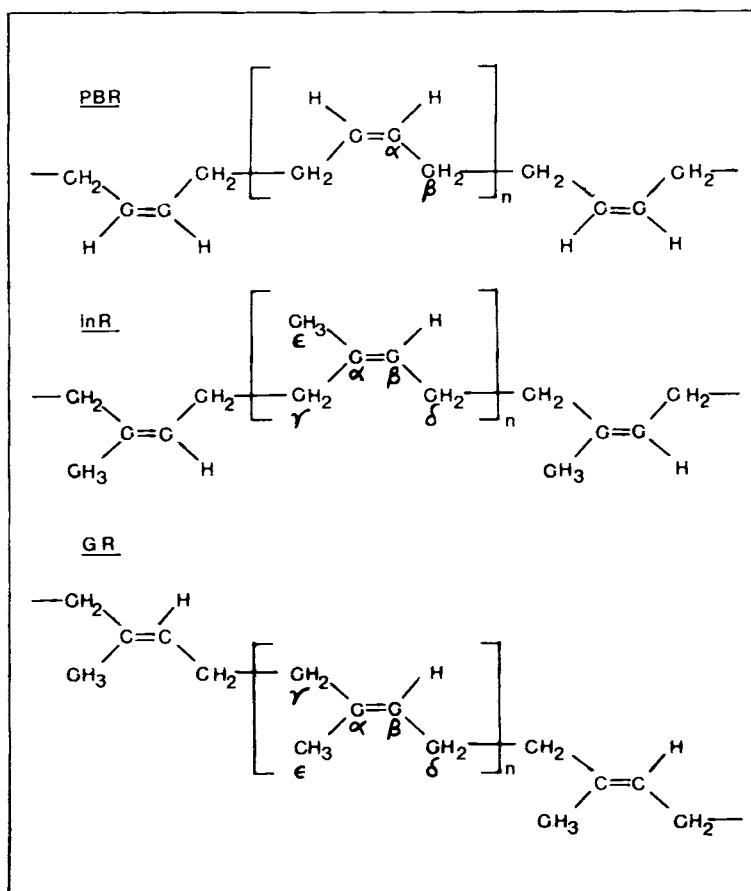


Figure 4 Arrangement of repeat units of different rubbers.

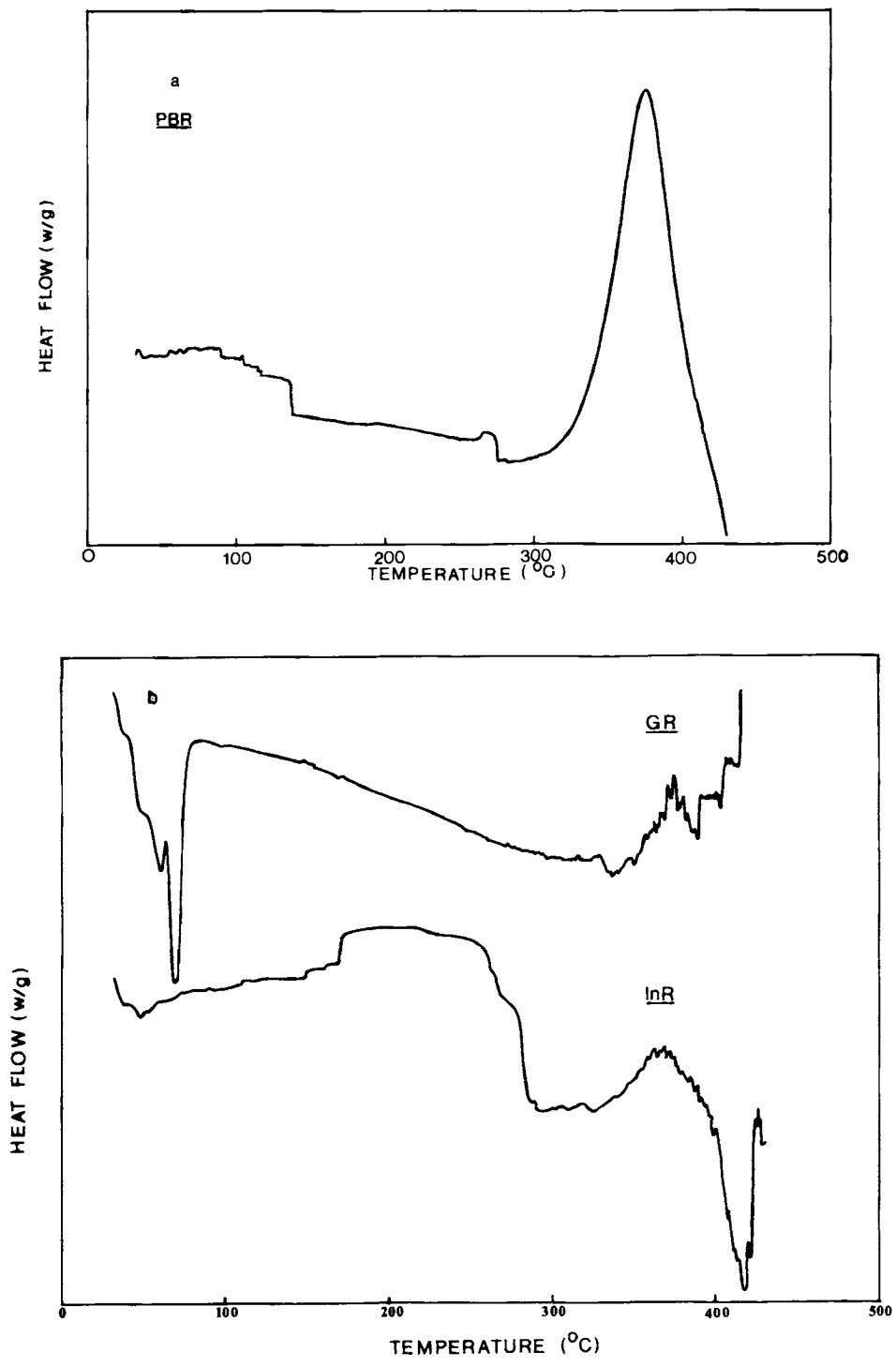


Figure 5 DSC curve of (a) PBR, (b) InR and GR.

$\Delta G_{vis}^\ddagger$  is the activation free energy change of the viscous flow. Equation (1) can be rewritten as

$$\ln(\eta V/Nh) = \Delta G_{vis}^\ddagger/RT = \Delta H_{vis}^\ddagger/RT - \Delta S_{vis}^\ddagger/R \quad (2)$$

where  $\Delta H_{vis}^\ddagger$  and  $\Delta S_{vis}^\ddagger$  are the activation enthalpy and entropy change of the viscous flow. The linearity is observed by plotting  $\ln(\eta V/Nh)$  against  $T^{-1}$ . The slope and the intercept gave  $\Delta H_{vis}^\ddagger$  and  $\Delta S_{vis}^\ddagger$ , respectively. On plotting  $\Delta S_{vis}^\ddagger$  against concentra-



**Table III** Intrinsic Viscosities of Rubbers in Various Solvents and Temperatures

Solvent System	Type of Rubber	Intrinsic Viscosity [ $\eta$ ] (dL/g)				
		25°C	30°C	35°C	40°C	45°C
<i>n</i> -heptane ( $\delta^a = 7.4$ )	PBR	1.60	1.56	1.51	1.48	—
Methyl Cyclohexane ( $\delta^a = 7.8$ )	GR	—	1.53	1.51	1.49	1.47
	InR	—	4.20	4.05	3.85	3.70
Cyclohexane ( $\delta^a = 8.2$ )	PBR	2.41	2.37	2.34	2.30	—
	GR	1.55	1.52	1.50	1.47	—
Toluene ( $\delta^a = 8.9$ )	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 ( $\delta^a = 8.9$ )	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	—

<sup>a</sup> Solubility parameter,  $\delta$ , as given in Ref. 17.

tion, and extrapolating to  $C = 0$ ,  $\Delta S_{vis}^{\ddagger}$  values were obtained.  $\Delta H_{vis}^{\ddagger}$  values were also similarly obtained.  $\Delta G_{vis}^{\ddagger}$  values were then computed at 30°C by well-known thermodynamic relation. All these activation parameters, at infinite dilution, are compiled in Table IV. 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 helps us in the calculation of the voluminosity ( $V_E$ ) of polymer solutions at a fixed temperature. Recently, voluminosity has been used<sup>18</sup> to determine the shape of the protein molecules in solution, that is, the so-called "shape factor."  $V_E$  was calculated by plotting  $Y$  against concentration  $C$  (in g/mL), where

$$Y = (\eta_r^{0.5} - 1) / [C(1.35 \eta_r^{0.5} - 0.1)] \quad (3)$$

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

$$[\eta] = \nu V_E \quad (4)$$

The shape factor gives an idea of the shape of the macromolecules in the solution.<sup>19</sup> Values of shape factor in different solvents are listed in Table V. It is seen that the value for all the systems is around 2.5, suggesting that the macromolecules acquire spherical conformations<sup>20</sup> in all solvents chosen for this study. Moreover,  $\nu$  values were found to be almost independent of temperature, varying between 2.4 and 2.6, indicating that the ratio between the major axis and the minor axis varies by about 2%. Therefore, we suggest that the formations of these polymers are independent of temperature.

**Table IV** Viscosity Activation Parameters at Infinite Dilution

Solvents	PBR			GR			InR		
	$\Delta H_{vis}^{\ddagger}$ (kJ)	$\Delta S_{vis}^{\ddagger}$ (JK <sup>-1</sup> )	$\Delta G_{vis}^{\ddagger}$ (kJ)30°C	$\Delta H_{vis}^{\ddagger}$ (kJ)	$\Delta S_{vis}^{\ddagger}$ (JK <sup>-1</sup> )	$\Delta G_{vis}^{\ddagger}$ (kJ)30°C	$\Delta H_{vis}^{\ddagger}$ (kJ)	$\Delta S_{vis}^{\ddagger}$ (JK <sup>-1</sup> )	$\Delta G_{vis}^{\ddagger}$ (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	—	—	—
<i>n</i> -Heptane	8.8	2.8	8.0	—	—	—	—	—	—
Methyl Cyclohexane	—	—	—	8.6	-0.8	8.6	9.4	1.7	9.9

**Table V** Shape Factor,  $\nu$ , at 30°C

Solvents	PBR	GR	InR
Toluene	2.54	2.48	2.48
Chlorobenzene	2.50	2.53	2.53
Cyclohexane	2.49	2.52	—
<i>n</i> -Heptane	2.54	—	—
Methyl Cyclohexane	—	2.53	2.54

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