

Refractive Index Increments of Natural and Synthetic Polyisoprenes

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Measurements of the refractive index increment of a variety of Hevea rubber samples and a range of narrow distribution synthetic polyisoprenes have been made at a wavelength of 615 nm and a temperature of 40°C. Evidence that the increment decreased with molecular weight at low values (below 100 kg mol⁻¹) was found for both the natural and synthetic materials. Soluble non-rubbers in the natural material were found to act effectively as a diluent. Otherwise there appeared to be little difference between the natural and synthetic polyisoprene; the average values measured for the refractive index increment were respectively 0.135 mlg⁻¹ and 0.133 mlg⁻¹. A high molecular weight fraction of natural rubber gave a figure (0.147 mlg⁻¹) well above that obtained for the other natural polyisoprene samples.

The refractive index increment (dn/dc) is an essential parameter used in the analysis of data obtained from light scattering of polymer solutions. The scattered intensity from a solution depends upon $(dn/dc)^2$, so an accurate determination is particularly desirable. This communication presents the refractive index increments for a series of natural (*Hevea*) and synthetic *cis*-polyisoprenes covering a range of molecular weights. The values were obtained at 615 nm, a wavelength close to the He-Ne gas laser line of 633 nm that is now commonly used in light scattering experiments, but for which there are relatively few (dn/dc) values reported. Studies¹⁻³ at this wavelength for polystyrene, synthetic polyisoprene and polymethyl-methacrylate solutions have recently been reported.

The value of (dn/dc) is obtained experimentally from the intercept of the plot of $\Delta n/c$ versus c , where Δn is the refractive index difference between the solution (of concentration c) and pure solvent, or the slope of the plot of Δn versus c at concentrations low enough for the relationship to be linear, normally assumed to be less than 3% weight/volume⁴.

Theoretical calculations of (dn/dc) can be made using the Lorenz-Lorentz or Gladstone-

Dale equations. The latter expresses the refractive index increment by:

$$dn/dc = v_2(n_2 - 1) - \bar{v}_2(n_0 - 1) \quad \dots 1$$

where v_2 = specific volume of polymer
 $\bar{v}_2$ = partial specific volume of polymer
 n_0 = refractive index of solvent
 n_2 = refractive index of polymer

When additivity of volumes is assumed, *i.e.* $v_2 = \bar{v}_2$, Equation 1 becomes

$$dn/dc = \bar{v}_2(n_2 - n_0) \quad \dots 2$$

The refractive index increments of natural and synthetic *cis*-polyisoprenes have been measured in a number of solvents^{1,5-11}. The linear relationship between (dn/dc) and the refractive index of the solvent, suggested by Equation 2, has been confirmed^{6,9}. The gradient of the line, it should be noted, gives an average value for the partial specific volume of the polymer as this parameter varies with the solvent⁴.

Comparisons of measurements of (dn/dc) made under the same experimental conditions indicate differences between natural and

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synthetic polyisoprenes^{6,9} and variations associated with the source and preparation of *Hevea* rubber samples⁸. The present study includes an investigation of the presence of any such differences.

The value of (dn/dc) has been found to vary with molecular weight in the case of polystyrene¹². This study reveals an asymptotic approach of (dn/dc) towards a limiting value characteristic of a polymer of infinite molecular weight, the limit being reached with fractions above a molecular weight of $5 \times 10^4 \text{ kg mol}^{-1}$. An investigation of the relationship for natural rubber¹¹ and synthetic polyisoprene⁶ both found (dn/dc) to be invariant with molecular weight. However, Hadjichristidis and Fetters¹ using materials covering a wider range of molecular weights found an influence of molecular weight and chain branching on (dn/dc) of synthetic polyisoprenes. The present work looks for any similar effects in natural *cis*-polyisoprene.

As well as the possible influence of molecular weight on (dn/dc) of natural rubber, factors that may be responsible for variations associated with source and preparation were investigated. These are:

- Type of bale rubber providing source material — SMR L and SMR CV were used
- Solvent for dissolution of bale rubber
- Acetone-extractable non-rubbers
- Proteinaceous material.

The results obtained for the natural rubber materials are compared with those for synthetic *cis*-polyisoprenes with narrow molecular weight distribution.

EXPERIMENTAL

Materials

Natural rubber samples were prepared in the following ways. Several samples were obtained by dissolving the original material in tetrahydrofuran (THF) with gentle rolling of the container to produce a homogeneous solution

which included both sol and any gel material present. The sample designated CV was from SMR CV bale rubber, CV/EX from CV bale which had first been acetone extracted to remove soluble non-rubbers, DP from a bale of deproteinised natural rubber and LQ from a low molecular weight, liquid natural rubber.

Various bale rubbers (SMR CV, SMR L and acetone-extracted SMR CV) were separated into sol and gel components by progressive dissolution in dichloromethane. The samples are respectively designated CV/S, L/S and CV/EX/S. A sol component (CV/S/CH) was also obtained from SMR CV bale rubber by progressive dissolution in cyclohexane. The solvent in each case was removed by rotary evaporation.

A sample of sol rubber obtained from SMR CV bale by progressive dissolution in dichloromethane was fractionated by precipitation with methanol. Seven fractions were isolated in this way, five of which were chosen for this study (NRF1–5). One of these fractions (NRF5) contained 22% of acetone-extractable material and therefore an acetone-extracted sample (NRF5/EX) was prepared.

The natural rubber samples tested are listed in *Table 1* together with their molecular weights as measured by GPC in tetrahydrofuran.

The THF used throughout was HPLC grade that had been deoxygenated by purging with dry nitrogen gas. The other solvents were AnalaR grade; the dichloromethane had been redistilled.

The narrow molecular weight fractions (M_w/M_n 1.04–1.15) of synthetic *cis* 1,4 polyisoprene were as supplied from Polymer Laboratories, UK. They ranged in molecular weight from 3.2 kg mol^{-1} to $2.7 \times 10^3 \text{ kg mol}^{-1}$ (*Table 2*).

The synthetic polyisoprenes and the natural rubber samples first prepared with other solvents were dissolved in THF at an initial concentration of approximately 1% weight/volume and left for at least 24 h to ensure complete dissolution. In the case of high molecular weight material, the solutions were

TABLE 1. REFRACTIVE INDEX INCREMENT OF NATURAL RUBBERS IN TETRAHYDROFURAN AT 40°C

Sample	M_w (kg mol ⁻¹)	M_n (kg mol ⁻¹)	N (%)	$(dn/dc)_{615}$ (mlg ⁻¹)
NRF1	2.24×10^3	9.38×10^2	0.29	0.147
NRF2	1.38×10^3	4.80×10^2	0.12	0.135
NRF3	8.29×10^2	3.88×10^2	0.04	0.134
NRF4	4.16×10^2	2.45×10^2	0.03	0.138
NRF5	6.17×10^2	1.93×10^2	0.0	0.121
NRF5/EX				0.136
LQ	26.3	8.13		0.125
CV	9.76×10^2	2.08×10^2		0.136
CV/EX				0.134
CV/S				0.136
CV/EX/S				0.132
CV/S/CH	7.06×10^2	1.24×10^2		0.132
L/S	5.42×10^2	1.56×10^2		0.134
DP	8.76×10^2	1.56×10^2		0.133

TABLE 2. REFRACTIVE INDEX INCREMENT OF LINEAR POLYISOPRENE IN TETRAHYDROFURAN AT 40°C

M_w (kg mol ⁻¹)	M_n (kg mol ⁻¹)	$(dn/dc)_{615}$ (mlg ⁻¹)
3.19	3.07	0.111
34.2	32.8	0.125
60.1	57.7	0.130
1.37×10^2	1.32×10^2	0.133
2.91×10^2	2.81×10^2	0.133
4.53×10^2	4.32×10^2	0.131
1.60×10^3	1.50×10^3	0.135
2.50×10^3	2.22×10^3	0.131

Molecular weight (M_w and M_n) values supplied by Polymer Laboratories Ltd., UK

Method

A Brice-Phoenix Differential Refractometer Model BP-2000-V was used to obtain the refractive index differences between solution and solvent. This was obtained from measurements of the lateral displacement of the slit image in the focal plane of the microscope adapted with a filar micrometer.

The measurements were made at the mercury red line, $\lambda = 615$ nm. The mercury vapour lamp was used with a 72B Wratten filter, which has a narrow transmittance region of 590–650 nm. In this region, the line at 615 nm is over ten times more intense than in any other.

The instrument constant k was determined according to the equation:

$$\Delta n = k \Delta d$$

where Δn is the refractive index difference between a solution and its solvent and Δd is the total slit image displacement. The constant was determined from ten separate measurements of Δd using the two positions of the cell and five potassium chloride solutions of known concen-

left for three days. Five dilutions were made during the course of the experiments yielding a final concentration of approximately 0.1% weight/volume. All the rubber solutions and solvent were stored in the dark, under nitrogen, prior to use.

tration, and hence known Δn . The gradient of the plot of refractive index difference *versus* lateral displacement was calculated by a least squares procedure and gave the calibration constant, $k = (7.7487 \pm 0.0046) \times 10^{-4} \text{ mm}^{-1}$.

The measurements were carried out in tetrahydrofuran at 40°C as this was the solvent system and conditions used in related GPC work. The temperature was maintained by a circulating constant temperature bath. The refractometer cell had to be sealed in order to prevent solvent loss by evaporation. The solutions were equilibrated in the cell for at least 15 min prior to measurements. The lateral shift between solution and solvent was determined for six concentrations (1.0% weight/volume to 0.1% weight/volume) of the different rubbers. Five separate measurements of the shift were made for each concentration at the two positions of the refractometric cell.

RESULTS AND DISCUSSION

The lateral shift was plotted against concentration and the gradient of the slope was obtained by a least squares procedure. The refractive index increment for each rubber was calculated from this slope using the instrumental calibration constant.

Tables 1 and 2 summarise the values of (dn/dc) found for the different types of natural rubber and the polyisoprene standards. Table 2 shows that the value of (dn/dc) for linear polyisoprene reached a limiting value of approximately 0.133 ml g^{-1} at a molecular weight greater than $6.0 \times 10^2 \text{ kg mol}^{-1}$. A similar relationship has been revealed for polystyrene in toluene¹² and polyisoprene in cyclohexane¹.

The values of (dn/dc) for the natural rubbers are shown in Table 1. They correlate fairly well with the limiting value, 0.133 ml g^{-1} , obtained for the narrow distribution polyisoprenes (Table 2), with the following exceptions:

- The low molecular weight liquid rubber (LQ) has a lower (dn/dc) than the limiting value. However, it falls on the M_w *versus* (dn/dc) relationship determined from the narrow distribution polyisoprenes.

- A high content (22%) of soluble non-rubbers resulted in a low value of (dn/dc) for fraction NRF5; the limiting value was obtained after acetone extraction. Similar extraction of other natural rubber samples with a relatively small soluble non-rubber component (5%) did not greatly affect the value of (dn/dc) .
- The high figure of (dn/dc) for NRF1 was the only major deviation from the limiting value. This fraction was the highest molecular weight natural rubber sample, and it possibly contained the highest proportion of branched chains. However (dn/dc) has been found to be essentially independent of branching for polyisoprene¹. The fraction contained much more proteinaceous matter (as shown by percentage *N* in Table 1) than the others and it is possible that this is responsible for the high value. If that were so, it may have been expected that the value for sample 'CV', prepared from whole bale material, would have been at least similarly high.

The comparison (Table 3) between the values given in Tables 1 and 2 and previously published data has to take account of the differences of wavelength and temperature. The wavelength dependence can be adequately described by the first two terms of the Cauchy dispersion relation⁴:

$$\frac{dn}{dc} = B_1 + \frac{B_2}{\lambda^2} \quad \dots 3$$

The refractive index increments in Table 3 have all been corrected to 633 nm, the wavelength of a He-Ne gas laser, using Equation 3. The empirical constant B_2 was determined from the limited data of Angulo-Sanchez *et al*⁹. They gave (dn/dc) for three polyisoprenes in THF at two wavelengths. The average value of B_2 obtained from the three pairs of data is $2.0 \times 10^3 \text{ ml g}^{-1} \text{ nm}^2$.

TABLE 3. COMPARISON OF REFRACTIVE INDEX INCREMENTS FOR NATURAL AND SYNTHETIC POLYISOPRENES IN TETRAHYDROFURAN WITH PREVIOUSLY PUBLISHED DATA ALL SCALED TO $\lambda = 633$ NM AND TO A TEMPERATURE OF 40°C

Reference	Material	Published dn/dc	$(dn/dc)_{633}^{40}$
9	Hevea	$(dn/dc)_{436} = 0.160$	0.157
9	Natsyn	$(dn/dc)_{436} = 0.153$	0.150
10	Polyisoprene	$(dn/dc)_{633} = 0.123$	0.127
15	Hevea	$(dn/dc)_{436} = 0.160^a$	0.145
8	Polyisoprene	$(dn/dc)_{546} = 0.128$	0.130
6	Polyisoprene	$(dn/dc)_{546} = 0.116^b$	0.118
This work	Hevea		0.132 - 0.138
This work	Polyisoprene		0.133
This work	Hevea/Polyisoprene		0.133 ^c

^aThis value reported by Bristow¹⁵ is thought incorrect. It was determined from a plot of (dn/dc) and solvent refractive index using data presented by Schulz *et al.*⁷ Taking $n_{436} = 1.4134$ for THF, a value of $(dn/dc)_{436} = 0.148 \text{ ml g}^{-1}$ should be obtained by extrapolation, and that value is used to determine $(dn/dc)_{633}^{40}$.

^bDetermined from reported data by method used in previous footnote.

^cCalculated from Equation 2.

The correction for temperature can in principle be made by differentiating Equation 2 to give:

$$\frac{d}{dT} \frac{dn}{dc} = (n_2 - n_0) \frac{d\bar{v}_2}{dT} + \bar{v}_2 \left(\frac{dn_2}{dT} - \frac{dn_0}{dT} \right) \quad \dots 4$$

Values of the constants in Equation 4 are listed in Table 4. The figure for $\bar{v}_2$ was obtained

from plots of (dn/dc) against solvent refractive index^{7,9} for natural and synthetic polyisoprenes; an average value from the data for both types of material was taken. The temperature dependence of $\bar{v}_2$ was evaluated by assuming:

$$\frac{d\bar{v}_2}{dT} = \bar{v}_2 \left(\frac{1}{v} \frac{dv}{dT} \right) \quad \dots 5$$

TABLE 4. DATA FOR EVALUATION OF TEMPERATURE VARIATION OF dn/dc

		Reference
Partial specific volume of polymer, $\bar{v}_2$ (ml g ⁻¹)	1.23	7, 9
Coefficient of volume expansion (°C ⁻¹)	6.7×10^{-4}	13
$d\bar{v}_2/dT$ (ml g ⁻¹ °C ⁻¹)	8.2×10^{-4}	
Refractive indices: n_{633}^{25}		
THF	1.4036	3
polyisoprene	1.5097	9
dn/dT (°C ⁻¹)		
THF	-4.5×10^{-4}	14
polyisoprene	-3.7×10^{-4}	13

where $(\frac{1}{v} \frac{dv}{dT})$ is the coefficient of volume expansion. Refractive index data for NR and synthetic polyisoprene^{9,13} do not suggest a reproducible difference between these two materials. An average value from the work of Angulo-Sanchez *et al.*⁹ is quoted after applying a correction based on the Cauchy dispersion relation (Equation 3). The value of $(d/dT)(dn/dc)$ obtained by substituting the figures in Table 4 into Equation 4 is $1.85 \times 10^{-4} \text{ ml g}^{-1} \text{ } ^\circ\text{C}^{-1}$.

A value of (dn/dc) at 40°C and 633 nm was calculated from Equation 2 using the data listed in Table 4 and the above value for the temperature variation.

Table 3 compares the calculated and experimental values of (dn/dc) obtained in this study with other published data all scaled to $\lambda = 633 \text{ nm}$ and 40°C. This reveals a fair agreement between the present calculated and experimental values and certain previous determinations^{8,10}, in particular that by Pearson *et al.*¹⁰, the only study performed in THF at 633 nm. There is, however, quite a large difference from both the values reported by Angulo-Sanchez *et al.*⁹ and that derived from the data of Schulz *et al.*⁷; the discrepancies could result in up to 40% error in determinations of the values of radius of gyration by light scattering. The lack of agreement is as marked for the synthetic as for the natural polyisoprene. Thus, it seems that differences in the (dn/dc) values reported for natural rubbers should not necessarily be ascribed to the variety of source material and sample preparation. Indeed, the present work, with the exception of fraction NRF1, and the data of Angulo-Sanchez *et al.*⁹ show relatively small variations in (dn/dc) between natural and synthetic polyisoprenes and various types of natural material. The factors found to influence (dn/dc) in the present work were molecular weight (in the range below 100 kg mol^{-1}) and, for the natural polyisoprene, soluble non-rubbers which, when present in large amounts, appear to act as a diluent. The reasons for the high value in the natural sample NRF1 remains unclear, though proteinaceous matter is a possibility.

CONCLUSIONS

Values of the refractive index increment for natural and synthetic polyisoprenes for a wavelength of 615 nm and a temperature of 40°C have been obtained. The average figures, 0.135 ml g^{-1} and 0.133 ml g^{-1} respectively, indicate little difference between the two materials. The only samples showing significant departure from these values were those of low molecular weight, whether synthetic or natural, and a high molecular weight fraction of natural rubber.

ACKNOWLEDGEMENTS

Thanks are due to Dr P.G. Mente for supplying the liquid natural rubber sample and Dr D.S. Campbell for helpful discussions.

Date of receipt: November 1989

Date of acceptance: February 1990

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