

## Light-Scattering Measurements on Solutions of Natural and Synthetic Polyisoprenes

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### INTRODUCTION

Comparatively few studies have been published on the light-scattering behavior of solutions of natural rubber,<sup>1-4</sup> and these have been concerned with evaluating the intrinsic molecular properties of the polyisoprene chain. For this purpose it is necessary to remove from the solution under examination all other molecular species and especially those of great size (branched or crosslinked structures, colloidal debris, etc.). Structures of the latter type, for example microgel,<sup>5,6</sup> may influence the general properties of rubber, and it is undoubtedly the case that, for many purposes, all the components of a rubber solution, other than adventitious dirt, are potentially of interest. This is the standpoint of the present communication, in which are described light-scattering measurements on rubber solutions which have been clarified by filtration rather than by ultracentrifugation (which would remove some or all of the larger species present). Included for comparison is a study of a synthetic *cis*-1,4-polyisoprene, whose behavior was expected to be simpler than that of natural rubber.

### EXPERIMENTAL

#### Materials

Solvents were of Analar or reagent grade, distilled where appropriate.

Two samples of natural rubber were used (1) an unmilled pale crepe, and (2) a well-milled pale crepe. The sample of synthetic *cis*-1,4-polyisoprene was obtained from the Shell Development Co.

#### Clarification Procedure

In conformity with the views expressed in the introductory paragraph, all solutions were clarified by filtration through sintered glass filters. The

finest available—Grade 5 (Pyrex)—has a mean pore size of less than 2  $\mu$ . Rubber solutions will not normally pass through a grade 5 filter unless they have been previously filtered through coarser filters. The standard procedure was to pass the solution in turn through filters of grades 3, 4, and 5 under 5-7 psi nitrogen pressure. In several cases extreme difficulty was experienced, and the filters blocked frequently. Once each solution had been put through a grade 5 filter, subsequent passages through this grade were rapid. Concentrations were determined after filtration by evaporating aliquots and heating *in vacuo* to constant weight. Dilutions were performed as appropriate.

#### Measurements

Turbidity measurements were carried out with a Brice-Phoenix Series 1000 photometer, using a small (15 ml.) cylindrical cell with plane end-windows. The wavelength employed was 4358 Å. The calibration data provided by the manufacturers were checked by measuring the 90° turbidity from a 0.5% solution in toluene of standard polystyrene.<sup>7</sup> The standard value for this sample is given as  $3.51 \times 10^{-3}$  cm.<sup>-1</sup>. Six separate measurements over a period of months gave, as an average, precisely this figure with a standard deviation of 0.06, i.e., less than 2%. Measurements of the Rayleigh ratio for purified benzene gave a mean value of  $49.5 \times 10^{-6}$ , slightly higher than the often-quoted<sup>8</sup> values of  $48.5 \times 10^{-6}$ .

Measurements were normally carried out at 10° intervals from 30° to 100° or 120° and at a range of concentrations from about  $3-5 \times 10^{-3}$  g./ml. down to about one-tenth of this. The depolarization factor with unpolarized incident light for natural rubber in cyclohexane was found to be less than 2% and hence no correction was applied. For the refractive index increment the values found by Altgelt and Schulz<sup>2-4</sup> were used. For tetra-

hydrofuran an interpolation was made from their data.

All data were evaluated by the Zimm diagram method in which  $c/\tau$  is plotted against  $Kc + \sin^2 \frac{1}{2}\theta$ , where  $c$  is the concentration (in grams/milliliter),  $\tau$  the turbidity,  $\theta$  the angle of observation, and  $K$  is an arbitrary constant chosen to give a well-spaced array of points. The light-scattering parameters tabulated are weight-average molecular weight  $\bar{M}_w$ , second virial coefficient  $A_2$ , mean-square radius of gyration  $\bar{S}_z^2$ , and  $(\bar{r}^2/\bar{M}_w)^{1/2}$ , where  $\bar{r}^2$ , the mean-square end-to-end distance of the equivalent random coil, is equal to  $6\bar{S}_z^2$ .

## RESULTS AND DISCUSSION

### Effect of Filtration

Useful qualitative information can be obtained from a study of the effect of filtration on polymer solutions. Table I lists the relative changes in turbidity (at  $\theta = 120^\circ$ ) produced by passing rubber solutions through sintered glass filters of decreasing pore size. Solute concentrations were about  $2 \times 10^{-3}$  g./ml., and the turbidities are referred to unity for the grade 5 filter. A polystyrene sample, included for comparison, shows negligible changes as the filtration severity is increased.

Concentrations were little affected by the filtration process. For the milled natural rubber in chloroform the decrease in concentration on pro-

TABLE I  
Relative Turbidities

	Filter grade <sup>a</sup>		
	3	4	5
Milled natural rubber in chloroform	3.12	1.47	(1.0)
“ “ “ “ hexane	1.18	1.09	(1.0)
Synthetic polyisoprene in chloroform	5.27	1.21	(1.0)
“ “ “ “ hexane	1.39	1.32	(1.0)
Polystyrene in chloroform	1.03	1.01	(1.0)

<sup>a</sup> The pore sizes quoted by the makers are: 20–30  $\mu$  (grade 3), 5–15  $\mu$  (grade 4), <2  $\mu$  (grade 5).

ceeding from a grade 3 to a grade 5 filter was 7% and the corresponding decrease in intrinsic viscosity was only 5%. This is to be compared with a reduction in turbidity of more than threefold (Table I). One can deduce from this that the material which is removed by filtration (possibly by an absorption process) is compact in shape, since it has little effect on viscosity. The sample of synthetic polyisoprene also contains a strongly scattering

component. The decrements in turbidity when the rubbers are dissolved in the poor solvent hexane are much less. Only about half of each polymer sample is soluble in hexane, and the turbid component(s) is hence associated with that part of the polymer which is insoluble in hexane but dispersible in the good solvent chloroform. Since both the natural and synthetic polyisoprenes show these effects one cannot attribute them solely to those nonrubber components which are known to occur in natural rubber (proteins, etc.). It might be considered that in both rubbers there exist branched structures which can be in part removed by filtration.

### Measurements with Synthetic *cis*-1,4-Polyisoprene

Samples were masticated under various conditions and their light-scattering behavior examined in chloroform ( $\text{CHCl}_3$ ), tetrahydrofuran (THF), and di-*n*-butyl ether/*n*-butanol 60/40 (theta). This last mixture is a near theta-point solvent for polyisoprene, and the refractive indices of the components are almost identical, as required.<sup>8</sup> Table II lists the results. With the exception of the data for chloroform, the light-scattering behavior of this polymer is regular. Molecular weights measured in a good solvent (tetrahydrofuran) and a near theta solvent are in close agreement.

Figure 1 shows  $\log \bar{M}_w$  plotted against  $\log [\eta]$ , the relations being

$$[\eta]_{\phi\text{CH}_3} = 5.9 \times 10^{-6} \bar{M}_w^{1.01}$$

and

$$[\eta]_{\theta} = 3.0 \times 10^{-4} \bar{M}_w^{0.63}$$

The exponents are substantially greater than the theoretical maximum value of 0.8 and 0.5, respectively. Even higher values have been found for  $\bar{M}_n$  vs.  $[\eta]$  with masticated natural rubber and have been attributed to nonrandom chain fracture resulting in a progressive sharpening of the molecular weight distribution as mastication progresses.<sup>9</sup>

The mastication of natural rubber in nitrogen, rather than in air, produces chain branching leading eventually to gel formation.<sup>10</sup> The data of Table II and Figure 1 do not reveal such an effect with the synthetic polyisoprenes, though the data are rather too limited to be decisive. Prolonged mastication in nitrogen produced a little gel, but the Huggins  $k'$  values, obtained from the viscosity measurements, are reasonably constant.<sup>10</sup>

TABLE II  
 Synthetic *cis*-1,4-Polyisoprene

Mastication treatment	$[\eta]_{\phi_{CH_2}}$	$[\eta]_{\theta}$	Solvent	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$ , ml./g.	$S_z^2 \times 10^6$ , A. <sup>2</sup>	$(\bar{r}^2/\bar{M}_w)^{1/2} \times 10^{11}$
None	6.50	1.69	CHCl <sub>3</sub>	16.8	8.2	9.20	1820
			THF	9.51	9.2	4.46	1680
			theta	10.75	—	2.36	1140
3 min. in air	4.25	1.44	THF	6.52	8.0	3.00	1660
			30 min. in N <sub>2</sub>	4.24	1.41	CHCl <sub>3</sub>	14.5
60 min. in N <sub>2</sub>	3.98	1.42	THF	6.21	8.1	3.48	1830
			10 min. in air	3.00	0.95	THF	6.39
50 min. in air	1.76	0.77	CHCl <sub>3</sub>	7.40	10.2	2.94	1540
			THF	4.45	7.0	2.14	1700
			theta	4.50	—	0.49	810
			THF	2.61	12.3	0.88	1420

The last column of Table II reveals that in tetrahydrofuran  $\bar{r}^2$  is proportional to  $\bar{M}_w$  and there is no variation in the quotient with manner or extent of mastication. This parameter is probably not very sensitive to structural changes. Although the quotient might be expected to decrease if branched structures are introduced, this effect may be swamped by alterations in the molecular weight distribution since  $\bar{r}^2$  is a  $z$ -average and  $\bar{M}$  a weight average. As expected, the quotient is diminished on passing from a good to a near theta-point solvent, as a result of the coiling-up of the polymer molecules. The mean value in the theta solvent ( $970 \times 10^{-11}$ ) is close to that ( $830 \times 10^{-11}$ ) derived by Wagner and Flory<sup>11</sup> from viscosity data. This is much higher than the theoretical figure ( $485 \times 10^{-11}$ ) computed for a polyisoprene chain with free rotation.<sup>12</sup>

For all these samples of synthetic polyisoprene the Zimm diagrams were regular with both the

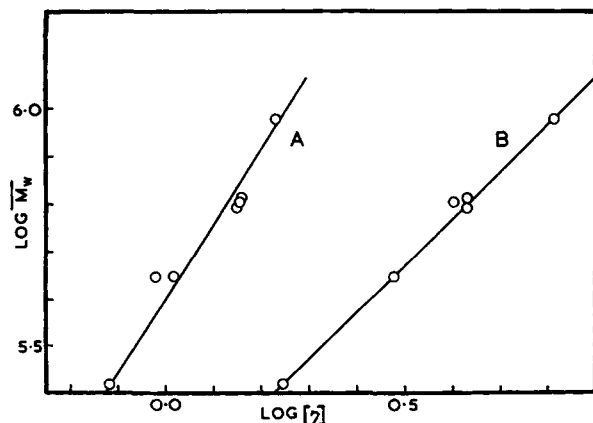


Fig. 1. Relationship between  $\bar{M}_w$  and intrinsic viscosity in (A) theta solvent mixture and (B) toluene for synthetic polyisoprenes.

$c = 0$  and  $\theta = 0$  lines being linear. In this region of molecular weight, curvature of the  $c = 0$  line would not be expected unless the ratio  $\bar{M}_w/\bar{M}_n$  is quite large. Some measurements of  $\bar{M}_n$  for several of the samples indicated that the ratio was only about 1.5. Values of  $A_2$ , derived from the  $\theta = 0$  lines, are typical of those for polymers in good solvents, but no very clear trends can be seen.

No convincing reasons can be put forward to explain the abnormally high values for  $\bar{M}_w$  obtained using chloroform as solvent. It is clear from the filtration experiments (Table I) that chloroform solutions contain a highly scattering substance and it is very likely that, if more drastic filtration (or ultracentrifugation) could be employed, the values of  $\bar{M}_w$  would approach those found with the other solvents.

#### Measurements with Unmilled Natural Rubber

Altgelt and Schulz<sup>2-4</sup> have made extensive use of cyclohexane as a light-scattering solvent for natural rubber. In one respect it is a good choice, since it gives an acceptably large refractive index increment. But, despite the fact that it is thermodynamically a good solvent for rubber, it is usually found that gel contents in cyclohexane are substantially higher than in, for example, benzene. The sample of unmilled pale crepe rubber used here was approximately 50% soluble in cyclohexane. Removal of the macrogel phase by filtration through lens tissue gave an apparently clear solution which could be filtered, with difficulty, through sintered glass filters.

Figure 2 shows the Zimm diagram obtained from the solution. It is very distorted, by contrast with diagrams obtained both with synthetic polyisoprene and with the milled crepe natural rubber. Distorted plots of this form are commonly ascribed

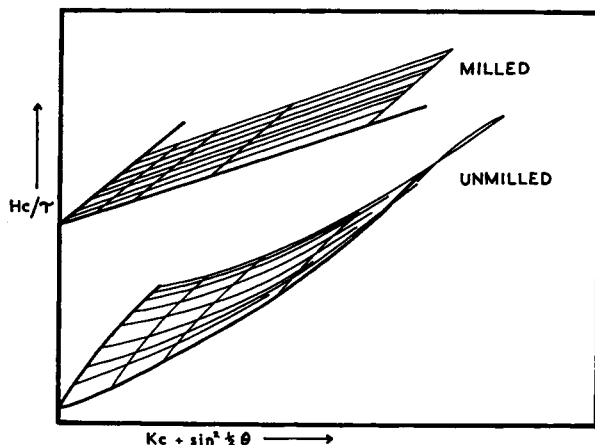


Fig. 2. Zimm diagrams for milled and unmilled natural rubber in cyclohexane. For clarity the individual points are not shown and the ordinates are displaced.

to the presence of microgel,<sup>13-15</sup> and a very similar plot for natural rubber in cyclohexane has been published by Altgelt and Schulz.<sup>3</sup> It is in principle possible to compute the size of the microgel particles from the curvature of the  $c = 0$  line,<sup>3</sup> provided that the molecular weight (and its distribution) of the linear macromolecules is known. One can attempt to obtain  $\bar{M}_w$  by an extrapolation of the linear portion of the Zimm plot, and, from Figure 2 a rough value of  $1.4 \times 10^6$  is obtained, but this procedure is very subjective. By computing theoretical particle scattering factors for linear molecules and for spheres which scatter according to the Mie formula, Altgelt and Schulz estimated the diameter of the microgel particles to be around 5000 Å. The existence of microgel in natural rubber has previously been demonstrated by other methods<sup>5,6</sup> and is confirmed by the light-scattering method.

### Effect of Solvent

In order to investigate the effect of changing the solvent it is necessary to use a sample of natural rubber which is, as far as possible, fully soluble in all the solvents used, otherwise the results may be confused by fractional dissolution. For the experiment of this section, a well-milled pale crepe was employed. The choice of solvent is restricted to those whose refractive index increments are reasonably large and preferably greater than 0.1. Of the four solvents used here, three—chloroform, tetrahydrofuran, and the near-theta solvent (di-*n*-butyl ether/*n*-butanol 60/40)—dissolved virtually all the rubber, while in the fourth—*n*-hexane

TABLE III  
Milled Natural Rubber

Solvent	$[\eta]$	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$ , ml./g.	$\bar{S}_z^2 \times 10^5$ , A. <sup>2</sup>	$(\bar{r}^2/\bar{M}_w)^{1/2} \times 10^{11}$	$\Phi \times 10^{-23}$
Chloroform	3.13	19.6	~0	5.79	1330	0.95
Tetrahydrofuran	2.58	14.8	~0	4.12	1290	0.98
<i>n</i> -Hexane	2.20	7.8	2.8	2.17	1290	1.16
Theta solvent	0.92	4.4	0	0.97	1140	0.91

—the rubber was only about 50% soluble. Table III lists the light-scattering data, together with the universal constant  $\Phi$  given by<sup>12</sup>

$$\Phi = [\eta] \bar{M}_w / (\bar{r}^2)^{1/2}$$

where  $[\eta]$  is the intrinsic viscosity in the same solvent.

In a further experiment a sample of the same rubber was separated into sol and gel fractions by dissolution in cyclohexane for 72 hr. The sol was recovered by freeze-drying and dissolved in tetrahydrofuran for light-scattering measurements. The gel was dispersed in chloroform (Table IV).

TABLE IV  
Behavior of Sol and Gel Fractions

	$\bar{M}_w \times 10^{-5}$	$A_2 \times 10^4$ , ml./g.	$\bar{S}_z^2 \times 10^5$ , A. <sup>2</sup>	$(\bar{r}^2/\bar{M}_w)^{1/2} \times 10^{11}$
Sol fraction in tetrahydrofuran	4.1	6.3	1.83	1640
Macrogel fraction in chloroform	19.5	(-0.8)	3.2	1000

In these experiments the Zimm diagrams were quite regular, showing none of the distortion displayed by the unmilled rubber (Fig. 2). A striking feature is that, as the solvent power of the solvent is increased, so  $\bar{M}_w$  increases and  $A_2$  tends to zero. It is likely that these two effects are interconnected. A consistent explanation is that the rubber contains a highly scattering component. The weight fraction of this component must be quite small, since the samples were virtually (~99%) soluble in three out of the four solvents used. Progressive solubilization of this component as the solvent power is increased would undoubtedly cause  $\bar{M}_w$  to increase; it appears that it is also associated with abnormally low values of  $A_2$ . This component can be retained by the macrogel phase of the rubber which, when separated from the sol phase, actually exhibits a negative value of  $A_2$  (Table IV). This rather unusual behavior could be taken to indicate

dissociation of the structure on dilution, though this interpretation is uncertain.

The behavior shown in Table III is broadly in line with the filtration experiments (Table I). Both indicate the existence of compact, highly scattering components. Further evidence for these comes from the values of  $(\bar{r}^2/\bar{M}_w)^{1/2}$ . The ratio for this parameter between a good and a theta solvent gives<sup>18</sup> the molecular expansion factor  $\alpha$ . For tetrahydrofuran, for example, natural rubber (Table III) gives  $\alpha = 1.13$ , while *cis*-1,4-polyisoprene (Table II) gives  $\alpha \approx 1.5$ . The former value is unreasonably low for a good solvent, while the latter is of the expected magnitude. Expressed in another way,  $\bar{r}^2$  for natural rubber is lower than that of *cis*-1,4-polyisoprene of the same molecular weight. This could be attributed to the existence of branched structures which lower  $\bar{r}^2$ .

An alternative explanation of the effects of Tables III and IV is that it is the progressive solubilization of nonrubber components which increases  $\bar{M}_w$  and lowers  $A_2$ . It is not yet possible entirely to eliminate this possibility but a consideration of the last column of Table II suggests that it is probably not the true explanation. If non-rubber components were dissolved by chloroform, for example, but not by the theta solvent, one would expect  $[\eta]$  and  $\bar{M}_w$  (apparent) in chloroform to be increased by unrelated amounts. In fact, the computed values of the constant  $\Phi$  (which connects  $[\eta]$ ,  $\bar{M}_w$ , and  $\bar{r}^2$ ) are remarkably constant. Strictly speaking  $\Phi$  should only be calculated for polymer fractions, for which it is normally<sup>12</sup>  $2.0\text{--}2.5 \times 10^{23}$ . Heterogeneity will reduce this somewhat, and may perhaps account for the value found. A similar value ( $1.07 \times 10^{23}$ ) was found for the synthetic polyisoprene.

It remains to account for the differences found between milled and unmilled natural rubber. These differences may not, of course, be representative. The proportion of microgel (Fig. 2) may vary considerably from sample to sample,<sup>6</sup> and one should not infer that heavy milling necessarily reduces the microgel content. It is reasonable, however, that the unmilled sample does not exhibit a low or zero value of  $A_2$  since, as we have shown, this effect is due to the macrogel cyclohexane-insoluble fraction (Table IV).

### CONCLUSIONS

Both synthetic and natural polyisoprenes contain a high scattering component(s) which can be partially removed by filtration. With milled natural

rubber this causes  $\bar{M}_w$  to increase and  $A_2$  to diminish to zero as the solvent power of the solvent is increased. From this, from the constancy of  $\Phi$ , and from the differences in  $(\bar{r}^2/M)^{1/2}$  between natural and synthetic polyisoprenes it is considered probable that the component is a compact (and therefore presumably branched) species. The light-scattering behavior of synthetic polyisoprene is essentially normal, except for high values of  $\bar{M}_w$  in chloroform. The possibility cannot yet be entirely excluded that some of these effects are due to nonrubber components. As with other polymers, notably polyethylene and polyacrylonitrile, microgel leads to considerable distortion of the Zimm diagram.

### References

1. Bywater, S., and P. Johnson, *Trans. Faraday Soc.*, **47**, 195 (1951).
2. Schulz, G. V., K. Altgelt, and H. J. Cantow, *Makromol. Chem.*, **21**, 13 (1956).
3. Altgelt, K., and G. V. Schulz, *Kunststoffe-Plastics*, **5**, 325 (1958).
4. Altgelt, K., and G. V. Schulz, *Makromol. Chem.*, **36**, 209 (1960).
5. Bloomfield, G. F., *J. Rubb. Res. Inst. Malaya*, **13**, 18 (1951).
6. Freeman, R., *Proc. Rubber Technol. Conf. 3rd Conf. London*, 3 (1954).
7. Kindly supplied by Prof. P. Debye, Cornell Univ., Ithaca, N. Y.; see I. C. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1624 (1950).
8. Peaker, F. W., in *Techniques of Polymer Characterization*, P. W. Allen, Ed., Butterworths, London, 1959.
9. Angier, D. J., W. T. Chambers, and W. F. Watson, *J. Polymer Sci.*, **25**, 129 (1957).
10. Bristow, G. M., to be published.
11. Wagner, H. L., and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 195 (1952).
12. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.
13. Peebles, L. H., *J. Am. Chem. Soc.*, **80**, 5603 (1958).
14. Nicholas, L., *J. Polymer Sci.*, **29**, 191 (1958).
15. Heyn, A. N., *J. Polymer Sci.*, **41**, 23 (1959).

### Synopsis

The light-scattering behavior of solutions of natural and synthetic *cis*-1,4 polyisoprene is described. For milled natural rubber values of  $\bar{M}_w$  increase as the solvent power of the solvent is increased and, at the same time, the second virial coefficient tends to zero. These effects may be due to compact (e.g., branched) structures. With unmilled natural rubber there is evidence for the existence of microgel. Synthetic polyisoprene shows the behavior expected of a linear polymer.

### Résumé

On décrit le comportement de solutions de 1,4 polyisoprène-*cis* naturel et synthétique par diffusion lumineuse.

Pour le caoutchouc naturel malaxé les valeurs de  $\bar{M}_w$  augmentent avec l'augmentation du pouvoir de dissolution du solvant et, en même temps, le second coefficient viriel tend vers zéro. Ces effets peuvent être attribués aux structures serrées (structures branchées). Pour le caoutchouc naturel non malaxé, il y a présence de microgel. Le polyisoprène synthétique présente le comportement prévu pour un polymère linéaire.

#### **Zusammenfassung**

Das Verhalten von Lösungen von natürlichem und synthetischem *cis*-1,4-Polyisopren bei der Lichtstreuung wird

beschrieben. Bei mastiziertem Naturkautschuk nehmen die Werte von  $\bar{M}_w$  mit der Lösungsfähigkeit des Lösungsmittels zu und gleichzeitig geht der zweite Virialkoeffizient gegen Null. Diese Effekte werden möglicherweise von kompakten (d.h. verzweigten) Strukturen verursacht. Bei nicht-masticiziertem Naturkautschuk bestehen Hinweise auf das Vorhandensein von Mikrogel. Synthetisches Polyisopren zeigt das für ein lineares Polymeres zu erwartende Verhalten.

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