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Intrinsic Viscosity–Molecular Weight Relationship for *cis*-1,4-Polyisoprene

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INTRODUCTION

The intrinsic viscosity, $[\eta]$, of a polymer in solution is a most convenient property with which to characterize polyisoprene with respect to its viscosity-average molecular weight $\bar{M}_v$, to which it is related by the Mark-Houwink equation:[1]

$$[\eta] = K\bar{M}_v^{\alpha} \tag{1}$$

However the constants K and α must be determined empirically for a given solvent and temperature by comparison of $[\eta]$ of several samples with their molecular weights determined by one of the absolute methods (e.g., number-average molecular weight $\bar{M}_n$, determined by osmometry, or weight-average molecular weight $\bar{M}_w$, determined by light scattering).

The intrinsic viscosity–viscosity-average molecular weight relationship for natural rubber (probably 100% *cis*-1,4-structure[2]) in toluene has been determined by Carter, Scott, and Magat,[3] who measured $[\eta]$ and $\bar{M}_n$ of fractions of natural rubber and obtained the equation:

$$[\eta] = 5.02 \times 10^{-4}\bar{M}_v^{0.667} \tag{2}$$

Later measurements of $[\eta]$ and $\bar{M}_n$ of rubber fractions by Bloomfield[4] and by Bywater and Johnson[5] are in general agreement with the data of Carter, Scott, and Magat, although Bywater and Johnson question the precision of eq. (2). Altgelt and Schulz[6] have measured $[\eta]$ and $\bar{M}_w$ for unfractionated natural rubber and obtained results in agreement with eq. (2). More recent light-scattering studies of synthetic *cis*-1,4-polyisoprene by Allen and Bristow[7] appear to be at variance with eq. (2), $\bar{M}_w$ being found to be consistently smaller than $\bar{M}_v$ calculated by use of eq. (2). We see no explanation for this difference between the synthetic and natural polyisoprenes.

In this paper we present our own work on this problem. This work was simplified in two ways. Firstly, we prepared synthetic polyisoprenes of high *cis*-1,4 structure by the use of butyllithium initiator in order to obtain

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linear polymers of narrow molecular weight distribution[8] and so avoid the tedious and difficult preparation of fractions[3,5,6] without introducing additional uncertainty into the experiment. (We have found that samples prepared by the use of Ziegler catalysts are unsuitable for this work because they have broad molecular weight distributions and also contain a considerable proportion of branched and crosslinked molecules which are not separated from the linear molecules by fractionation.) Secondly, we measured weight-average molecular weights by light scattering, and so avoided the necessity for obtaining polymer fractions of extremely narrow number distributions of molecular weight.

EXPERIMENTAL

Polyisoprenes

Samples of polyisoprene were prepared by A. R. Bean, R. J. Ehrig, and H. L. Vincent of this laboratory. Polymerizations were carried out with butyllithium initiator in aliphatic hydrocarbon solvents (e.g., *n*-heptane) under an argon atmosphere. All polymerizations were taken to high conversion. Polymers were prepared having intrinsic viscosities in toluene at 30°C. ranging from 1 to 16 dl./g. and having 85–91% of the isoprene units linked in the *cis*-1,4 configuration (determined by infrared spectroscopy). All were completely soluble in all the solvents used in this work.

Viscometry

Intrinsic viscosities, in several solvents, were measured in modified Desreux-Bischoff viscometers[9] at 30°C. Polymer solutions of 0.5–0.1 wt.-%, depending upon the molecular weight, were filtered through course sintered glass filters before pipetting a known volume into the viscometer, which was mounted in a thermostat held to ±0.01°C. The flow times of at least four dilutions over a concentration range of 4 or 5 to 1 were measured. The intrinsic viscosity was obtained by extrapolating the inherent viscosity to infinite dilution. All our samples were measured in toluene solution, since this solvent was used by Carter, Scott, and Magat. When sufficient polymer was available, measurements were also made in isooctane and in the light-scattering solvent (78 vol.-% *n*-heptane, 22 vol.-% *n*-propanol). Reagent-grade solvents were used.

Where the intrinsic viscosity of the samples exceeds 4 dl./g. the value one obtains becomes sensitive to the shear stress in the viscometer. This effect is particularly important when toluene is the solvent rather than the other poorer solvents. We therefore measured the intrinsic viscosities in toluene in two viscometers of differing dimensions in which the maximum values of the shear stress with toluene were about 3.0 g./cm. sec.^{2} and 0.3 g./cm. sec.^{2}. Both values, denoted by $[\eta]$ (3.0) and $[\eta]$(0.3), are given in Table II. The value of the intrinsic viscosity obtained in the viscometer of lower shear stress was assumed to be identical with the value at zero shear stress for the samples discussed here. Intrinsic viscosities in the other solvents were measured only in the viscometer with higher shear stress.

Light Scattering

Solvent. A mixture of 78 vol.-% *n*-heptane and 22 vol.-% *n*-propanol was used as the light scattering solvent. This mixture was chosen because the components have nearly identical refractive indices; by doing this we avoided errors due to selective absorption of one component on the polymer. The mixture is a poor solvent, and consequently the extrapolations of the light-scattering data to infinite dilution were not difficult to make. During preliminary work we used 2-pentanone as the light-scattering solvent. However, this solvent promoted the degradation of the polyisoprene, presumably due to the presence of peroxides, and its use was discontinued. Degradation of polymers in the mixed solvent was very slow and does not influence our results. Antioxidant, Ethyl 702 (Ethyl Corp., New York 17, N. Y.) 0.05 g./l. of solvent, was added to the polymer solutions.

Purification and Clarification. Reagent-grade solvents were distilled and dried over molecular sieves. Various methods of clarification were examined. Polymer solutions could not be forced through ultrafine sintered glass filters (pore size 0.9–1.4 μ). They could be filtered through Millipore type HA filter membranes (pore size 0.45 μ) (Millipore Filter Corp., Watertown, Mass.), but some polymer from the samples of high molecular weight remained on the membrane surface, suggesting that fractionation of the polymers had occurred. Clarification by high speed centrifugation was found to be effective. We centrifuged for $^1/_2$ hr. at 30,000 rpm in stainless steel tubes in a No. 40.2 head of a Spinco Model L preparative ultracentrifuge. Solutions of 1–2 wt.-% polymer were used, because these solutions are sufficiently viscous to prevent stirback as the centrifuge slows down. Solvents were clarified by filtration through ultrafine sintered glass filters.

Measurements. Light-scattering measurements were made with a Brice-Phoenix light-scattering photometer. Cylindrical cells, painted black on their backs and bottoms and thermostatted at 25.0°C., were used. The calibration of the photometer was checked by measurements of the light scattering of pure benzene[10] and Ludox suspensions.[11] The vertically polarized component of unpolarized light of wavelength 546 mμ was measured at 10 angles between 30° and 135° for each of four or five dilutions.

The refractive index increment of the solution at 25°C. was measured at 546 mμ in the Brice-Phoenix differential refractometer and was found to be 0.162 g./ml.

Calculations. The intensity of light scattered by the polymer was obtained by subtracting the solvent scattering from the solution scattering. Corrections were made for reflection of the primary beam at the exit window of the cell[12] and for the change in scattering volume with angle. The empirical scattering volume correction, determined by using fluorescein solutions,[13] was used in preference to the geometric correction factor sin θ.

The weight-average molecular weight $\bar{M}_w$ was calculated from the equation

$$(\mathrm{Kc}/V_\theta)_{\substack{\theta=0\\c=0}} = 1/\bar{M}_w \tag{3}$$

where c is the concentration of polymer, V_θ is the reduced intensity of the vertical component of scattered light and K is a constant. The extrapolation method of Zimm[14] was used to obtain the left-hand side of eq. (3). We found it convenient to plot Kc/V_θ versus $c + Ac^2$, the value of A being chosen to give a linear extrapolation. (A was actually zero except for the very high molecular weight samples.) The extrapolation at zero angle was made by plotting $(Kc/V_\theta)_{c=0}$ versus $\sin^2 \theta/2$.

Molecular Weight Distribution of the Samples

Before using the rubbers for measurement of $[\eta]$ and $\bar{M}_w$ we thought it best to ensure that the molecular weight distributions were in fact narrow. Accordingly we fractionated several samples by conventional precipitation fractionation. The method we used, i.e., precipitation of fractions from toluene by the incremental addition of methanol, has been described earlier.[15] In this work we found it convenient to add methanol to obtain a first fraction, then to precipitate the next few fractions by lowering the temperature slightly, and finally more methanol to obtain the lowest molecular weight fractions.

The fractionation data for a typical sample are given in Table I.

TABLE I
Fractionation Data

Fraction	Wt.-%[a]	$[\eta]$ (3.0), dl./g.[b]	$[\eta]$ (0), dl./g. (estimated)	$\bar{M}_v \times 10^{-6}$
1	15.6	10.5	11.0	3.22
2	17.2	10.6	11.1	3.26
3	25.2	10.6	11.1	3.26
4	18.7	9.8	10.2	2.87
5	16.0	7.4	7.6	1.85
6	3.7	3.6	3.6	0.60
7	3.6	0.7	0.7	0.05
Original	—	10.2	10.6	3.05

[a] Recovery = 97%.

[b] Weight-average intrinsic viscosity of fractions, $[\eta]$ (3.0) = 9.6 dl./g.

The intrinsic viscosities were measured in the viscometers of high shear stress (3.0 g./cm. sec.$^{-2}$). Data obtained in both the high and the low shear viscometers (see, for example, the data presented in Table II) enable us to correlate these intrinsic viscosities with those at essentially zero shear. (All the data being obtained for polymers with narrow molecular weight dis-

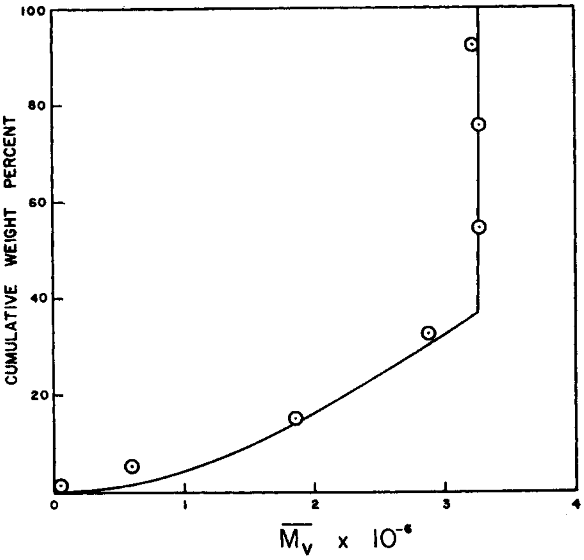

Fig. 1. Molecular weight distribution of a sample of polyisoprene prepared with butyllithium initiator.

tributions.) Intrinsic viscosities at zero shear stress estimated in this way are given in Table I, together with the viscosity-average molecular weight calculated from those values in eq. (2). The integral molecular weight distribution is shown in Figure 1. This distribution is quite similar to that of a monodisperse polymer which has undergone a limited amount of random scission. The curve in Figure 1 is, in fact, calculated from the equations of Montroll and Simha[16] by making the assumption that our sample was originally monodisperse polymer with a molecular weight equal to that of the highest molecular weight fractions and that this monodisperse polymer suffered a drop in $[\eta]$ of 10% because of random scission ($[\eta]$ of the whole polymer after fractionation is some 10% lower than $[\eta]$ of the highest fraction). The agreement of this curve with the experimental data is satisfactory especially when it is borne in mind that that part of the degradation suffered during the fractionation experiment cannot be wholly due to random scission.

Other samples examined had similar molecular weight distributions (e.g., $\bar{M}_z/\bar{M}_w$ calculated from the fractionation data was in the region of 1.1; the data of Table I give $\bar{M}_z/\bar{M}_w = 1.09$). We assume that all our samples had essentially monodisperse molecular weight distributions modified by a tail of lower molecular weight polymer formed, in a large part, by degradation of the high molecular weight material.

Preparation of the Samples for the Measurements

The molecular weight distributions of the samples are such that they could have been used immediately for measurement of $[\eta]$ and $\bar{M}_w$. However, as an additional precaution, each sample was dissolved in toluene and sufficient methanol was added to precipitate about 50% of the polymer. This fraction was mixed with antioxidant Ethyl 702 (1 phr) and dried *in vacuo* (<1 mm. Hg) before preparing the solutions for measuring $[\eta]$ and $\bar{M}_w$.

RESULTS AND DISCUSSION

The results of the intrinsic viscosity and weight-average molecular weight measurements are given in Table II. The values in parentheses after the intrinsic viscosities determined in isooctane and in the mixed solvent are our estimates of the intrinsic viscosity at "zero" shear stress for the samples; we assume that the sensitivity of the intrinsic viscosity to shear stress in these solvents is similar to that found for toluene.

TABLE II
Intrinsic Viscosities and Weight-Average Molecular Weights of Synthetic *cis*-1,4-Polyisoprenes

Toluene			Heptane propanol mixture,	
$[\eta](3.0)$, dl./g.	$[\eta](0.3)$, dl./g.	Isooctane, $[\eta](3.0)$, dl./g.	$[\eta](3.0)$, dl./g.	$\bar{M}_w \times 10^{-6}$
1.11	—	—	—	0.14
1.54	—	1.00	—	0.23
1.66	—	—	—	0.23
2.31	—	1.52	—	0.37
2.58	—	1.56	1.38	0.43
2.63	—	—	—	0.44
4.40	4.55	2.66	2.05	1.0
6.97	7.20	4.00	3.06	1.7
8.7	9.0	5.06 (5.2)	3.73	2.5
10.0	10.4	—	—	2.9
10.3	10.8	5.95(6.2)	4.45(4.6)	3.2
15.1	16.7	9.1(9.4)	6.7(6.9)	5.8

The intrinsic viscosities (at zero shear stress) and the weight-average molecular weights are plotted on log-log scales on Figure 2. The lines drawn through these data were computed by least squares and correspond to the equations

$$[\eta] = 2.00 \times 10^{-4}\ \bar{M}_v^{0.728} \text{ in toluene at } 30^\circ\text{C.} \tag{4}$$

$$[\eta] = 2.22 \times 10^{-4}\ \bar{M}_v^{0.683} \text{ in isooctane at } 30^\circ\text{C.} \tag{5}$$

$$[\eta] = 3.7 \times 10^{-4}\ \bar{M}_v^{0.63} \text{ in the mixed solvent at } 30^\circ\text{C.} \tag{6}$$

Equation (6) is not accurate, since it is based on six points only.

The intrinsic viscosity–molecular weight relationships of eq. (2) and eq. (4) are compared in Figure 3. In the range of interest it is apparent that the two relationships agree within the experimental error of the determinations (say ±5%).

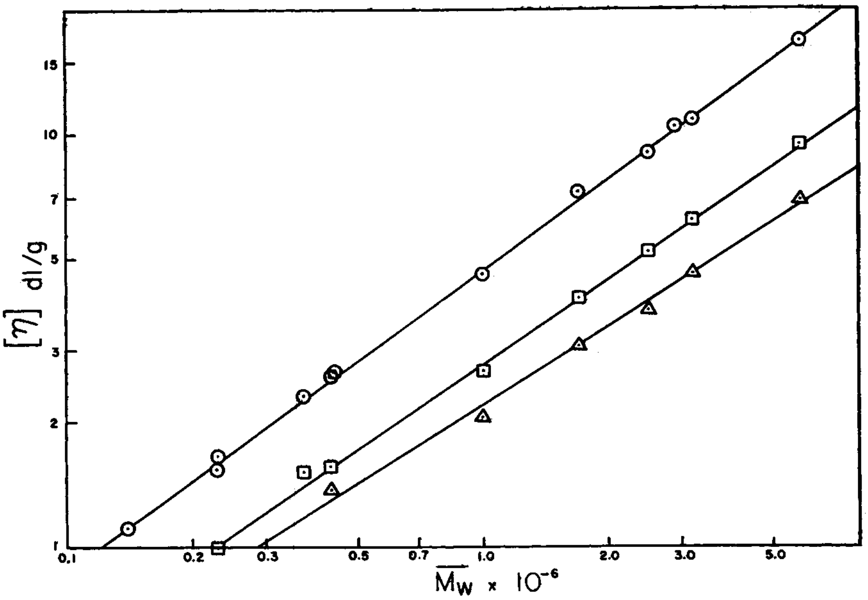

Fig. 2. Intrinsic viscosities and weight-average molecular weights of the polyisoprenes in various solvents: (⊙) toluene; (⊡) isooctane; (◬) heptane–propanol mixture.

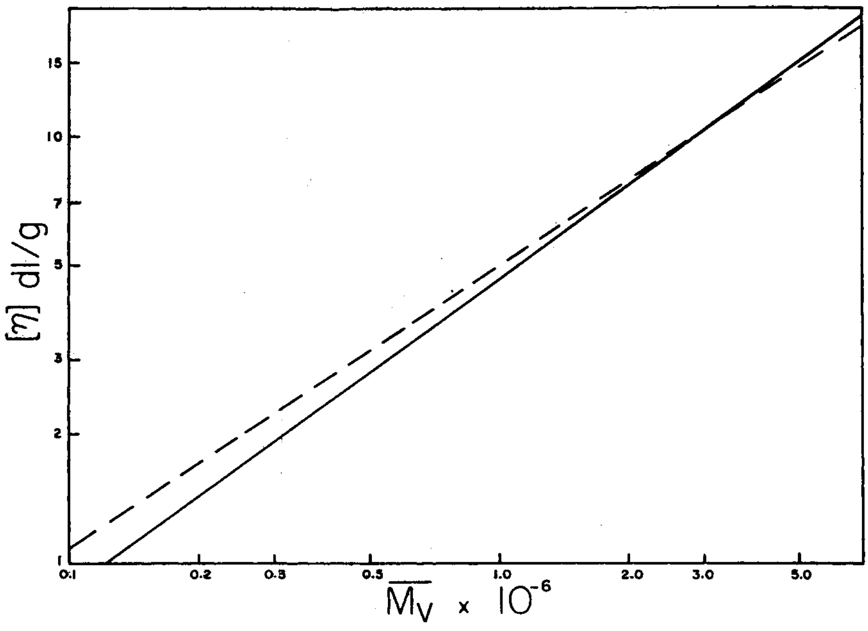

Fig. 3. Comparison of the intrinsic viscosity–molecular weight relationships: (--) Carter, Scott, and Magat; (——) this work.

We conclude that little difference exists between synthetic *cis*-1,4-polyisoprene prepared with the use of butyllithium initiator and natural rubber with regard to their intrinsic viscosity–molecular weight relationships. We also note that our data provide substantial evidence that synthetic *cis*-1,4-polyisoprene prepared with the use of butyllithium is a linear polymer.

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Synopsis

The intrinsic viscosity–molecular weight relationship has been determined for synthetic *cis*-1,4-polyisoprene prepared with butyllithium initiator. The best representation of our results is the equation, $[\eta] = 2.00 \times 10^{-4} (\bar{M}_v)^{0.728}$ for intrinsic viscosities determined in toluene at 30°C. This relationship agrees, within experimental error, with that obtained for natural rubber by Carter, Scott, and Magat.

Résumé

On a déterminé la relation entre la viscosité intrinsèque et le poids moléculaire pour un *cis*-1,4-polyisoprène synthétique préparé en utilisant le butyllithium comme initiateur. C'est l'équation suivante qui donne la meilleure représentation de nos résultats: $[\eta] = 2{,}00 \times 10^{-4} \bar{M}_v^{0{,}728}$ pour des viscosités intrinsèques déterminées dans le toluène à 30°C. En tenant compte de l'erreur expérimentale, cette relation est en accord avec celle obtenue pour le caoutchouc naturel par Carter, Scott et Magat.

Zusammenfassung

Die Viskositäts–Molekulargewichtsbeziehung für synthetisches, unter Verwendung von Butyllithium als Starter hergestelltes *cis*-1,4-Polyisopren wurde bestimmt. Die beste Wiedergabe unserer Ergebnisse bildet die Gleichung $[\eta] = 2{,}00 \times 10^{-4} \bar{M}_v^{0{,}728}$ für die in Toluol bei 30°C bestimmten Viskositätszahlen. Diese Beziehung stimmt innerhalb der Versuchsgenauigkeit mit der für Naturkautschuk von Carter, Scott und Magat erhaltenen überein.

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