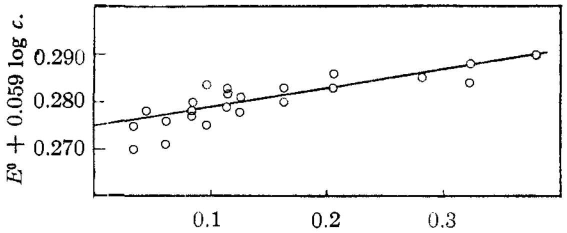

Fig. 1.—The square root of the concentration of potassium azidodithiocarbonate in (mole/liter).

Discussion

Since azidodithiocarbonic acid and azidocarbondisulfide decompose spontaneously,[1] the precision of the results is limited. For this reason it was considered unnecessary to use a thermostat to keep the temperature of the cell constant. Measurements were made at 25 ± 2.0°. The error thus introduced is of the order of magnitude of 0.001 volt, and not significant when compared to the errors brought about by the chemical instability of the above mentioned compounds.

The liquid junction potential between potassium azidodithiocarbonate and potassium chloride in the cell is unknown, but the use of a potassium chloride salt bridge very largely eliminates this effect.

Summary

1. The electrode potential of the azidocarbondisulfide–azidodithiocarbonate electrode was measured and found to be equal to 0.275 volt.

BROOKLYN, N. Y. RECEIVED APRIL 25, 1946

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Viscosity–Molecular Weight Relation for Natural Rubber[1]

BY WALTER C. CARTER, ROBERT L. SCOTT AND MICHAEL MAGAT

Introduction

Houwink[2] and Flory[2] have shown that the Staudinger law in its simplest form, relating the intrinsic viscosity to the molecular weight deduced from thermodynamic properties of the polymer solutions through the equation

$$[\eta] = KM \qquad (1)$$

is not in agreement with experiment.

Both these authors agree that the correct relation is given by

$$[\eta] = KM^a \qquad (2)$$

where in the case of polyvinyl acetate compounds and polymethacrylate $a \backsimeq 0.6$ (Houwink) and in the case of polybutene $a = 0.64$ (Flory). More recently Mark and Bartovics[3] found that a varies from 0.7 to 1.0 for polystyrene prepared at different temperatures in toluene and $a = 0.67$ for cellulose acetate in acetone. However, it seemed to us very important to check the validity of relations (1) or (2) on the very material for which Staudinger deduced his relation, *i.e.*, polyisoprene, (natural rubber), since in this case no argument of the type generally put forward by Staudinger and his co-workers that the deviations from eqn. 1 are due to the specific character of the polymer structure can be made.

Experimental

Molecular Weight Determination. Osmometer.—The molecular weight was determined from osmotic pressure measurements, using a cell identical with that described by Flory[2,4] so that no further description of it is necessary.

Membrane.—It was found, however, that the membranes described by Flory required long and slow measurements and became less and less permeable with time; this is probably due to the difference in solvents used—benzene and cyclohexane in the case of Flory, toluene in our case. It definitely appears that in toluene these denitrated collodion membranes are slowly dehydrated. Following a suggestion of Dr. R. M. Fuoss,[5] we have used collodion membranes without denitration. These membranes proved extremely satisfactory for polymers of molecular weight above 30–40,000 and hydrocarbon solvents. They allow fairly rapid measurements, about one to one and a half hours per solution, and the same membrane, if kept continuously in contact with toluene, can be used over a very long period of time. As a matter of fact, we are still using one of our membranes after twelve months of service. Since this type of membrane proves so successful it seems useful to include the details of its preparation, although it is similar to the one given by Fuoss and Mead.[6] Twenty cc. of solution containing 72% C. P. Merck collodion, 14% ether, 14% ethyl alcohol are poured into an iron ring about 10 cm. in diameter floating on a mercury surface and allowed to dry under a slow current of air. As soon as feasible (prolonged drying decreases the permeability) the film is transferred to water which precipitates the collodion and removes the solvent. The iron ring is disengaged and the membrane stands in water overnight and then is placed successively in water-alcohol, alcohol, alcohol-toluene, and toluene for two hours each. Before the membrane is used, however, it is necessary to age it, by letting it stand for about a week in pure toluene. This precaution is necessary because an unaged membrane was found to give erratic and irreproducible results.

Temperature.—The osmometer was placed in a large thermostat with extremely powerful agitation, controlled within ±0.1°. A better temperature control proved unnecessary, provided the temperature was uniform and the temperature variation in the course of a measurement (1 hour) did not exceed ±0.05°.

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[1] The major portion of this work was done on a grant from the Reconstruction Finance Corporation, Office of Rubber Reserve, for fundamental research in connection with the Government's synthetic rubber program.

[2] (a) R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940–1941); (b) P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[3] A. Bartovics and H. Mark, *ibid.*, **65**, 1901 (1943).

[4] We wish to thank Dr. P. J. Flory for kindly lending us the blueprints of the cell prior to publication of this paper.

[5] Personal communication.

[6] R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

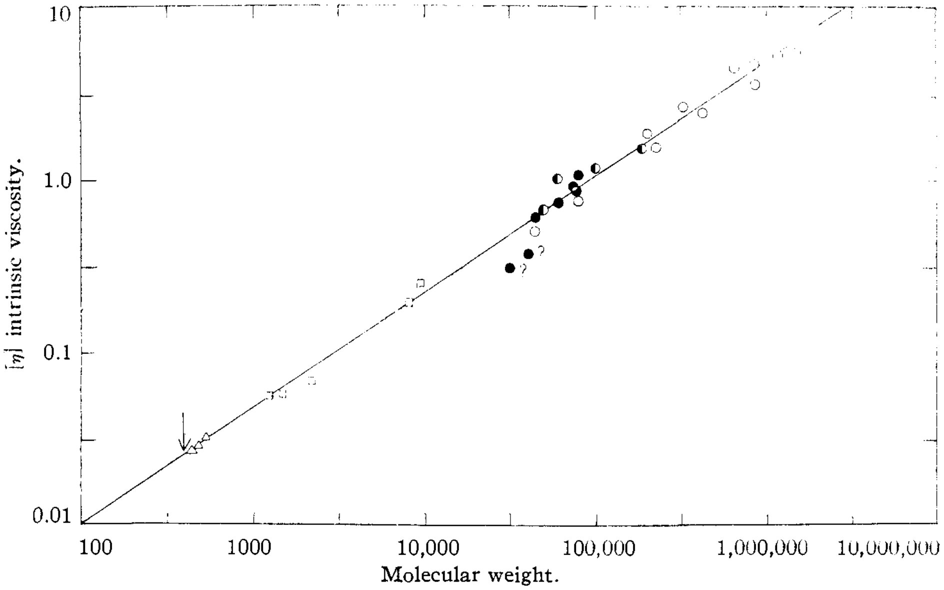

Fig. 1.—Viscosity-molecular weight relation for Hevea: Carter and Magat, ○ Fractionation 1, ◐ Fractionation 2, ● Fractionation 3 (? indicates evidence of possible permeability of the membrane); □ Kemp and Peters; △ Staudinger and Staiger.

Method of Measurement.—The method used is a combination of the dynamic and static method. Equilibrium is approached first from one side and as soon as equilibrium is neared the adjustment is changed and equilibrium is approached from the other side. Measurements are made every few minutes and if necessary the data can be plotted. In general the precision of each equilibrium value is about 3–5%. As soon as the measurement is finished, the solution side of the osmometer is rinsed with toluene and filled with pure solvent. Readings are taken to determine any adsorption by or inhomogeneities in the membrane. The resulting corrections were, without exception, virtually negligible.

Extrapolation to $(\pi/c)_{c=0}$.—Each fraction was measured at several different concentrations, three of them at as many as seven concentrations and π/c was then plotted against c for these three fractions. This relation proved to be linear in the range of concentrations used as is to be expected on the basis of theories of Flory[7] and Huggins.[8] No correction for the difference in density between solvent and solution was applied since control measurements have shown this correction to be almost negligible for the concentrations used, and the curves extrapolate to the same value of $(\pi/c)_{c=0}$ in any case. In the case of the subsequent fractions the slope of π/c *vs.* c was considered identical with the one found above. No discrepancies were found.

Concentration Determination.—The concentration was always determined by high vacuum evaporation of a known amount of the undiluted solution. The determinations were accurate to 1–2%. All concentrations have been expressed in grams of rubber per 100 cc. of solvent.

Viscosity Determination.—The viscosity was determined on a carefully calibrated and systematically checked Ostwald viscosimeter with the usual technique. It was found experimentally, that, provided $\eta_{\text{rel.}}$, the relative viscosity of the solution, is below 1.3, the intrinsic viscosity was independent of the concentration. Repeated checking has shown that the values of the intrinsic viscosity $[\eta]$ determined on solutions of different concentration agreed to 2–3%. All the viscosities have been determined at 25°.

Material.—The hevea used in this experiment was a ribbed smoked sheet kindly supplied by Firestone Tire and Rubber Co., Akron, Ohio. The toluene was the commercial solvent, dried with calcium chloride.

Fractionation.—The extraction and fractionation of hevea proved to be a delicate problem if the oxidative degradation of the high molecular weight fractions was to be avoided and at the same time a narrow fractionation obtained. After repeated failures it was found necessary to extract the soluble fraction in a refrigerator, below 0° under carbon dioxide. All the fractions had to be kept in the dark, in presence of antioxidant and carbon dioxide.

The fractionation method was fractional precipitation by methyl alcohol from toluene solutions. A few of the fractions proved to be fairly large and had to be refractionated but usually the primary fractions were small enough, thus avoiding the necessity of refractionation, a process which always involves the danger of degradation.

Experiments were made on fractions from three different fractionation series; the results lie close together.

Results

The results of the measurement on twenty-two different fractions ranging from 40,000 to 1,500,000 are presented in Fig. 1. The points marked with a question mark correspond to fractions where the possibility of a slight permeability of the membrane cannot be excluded.

As one can see, the results are represented accurately by an expression of the form of eqn. 2, where $K = 5.0 \times 10^4$ and $a = 2/3$.

In order to extend our $[\eta]$ *vs.* M relation toward lower molecular weights, we have used the data of Kemp and Peters[9] on degraded rubber in which they have determined the viscosity and the freezing point lowering of several polyisoprene fractions. An extension of the Flory–Huggins theory of thermodynamical properties of rubber solutions shows that the freezing point lowering ΔT_f of

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(7) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(8) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942).

(9) A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **33**, 1263 (1941).

rubber solutions depends on the concentration according to

$$\left(\frac{\Delta T_f}{c}\right)_{c=0} = \left(\frac{\Delta T_f}{c}\right) - bc \qquad (3)$$

This linear dependence of $\Delta T_f/c$ on the concentration was found experimentally by Kemp and Peters. We have used this relation in order to extrapolate their freezing point lowering data to $c = 0$ and to so obtain the true thermodynamic molecular weights of their fractions. Although it cannot be expected *a priori* that the constants K and a should be exactly the same for toluene and benzene, it was actually found that the points of Kemp and Peters corresponding to molecular weights between 1,000 and 9,000 fall, within the limits of error, on our line extrapolated from the high molecular weight range.[10]

In much the same way the viscosities of pure hydrocarbon (hentriacontane, ethylene, triacontane and ethylidene triacontane) solutions in benzene as determined by Staudinger and Staiger[11] fall exactly on our curve.

It can therefore be stated that the relation derived above is valid for molecular weights ranging from 420 to 1,500,000 and there is no reason to suppose that any change should occur for even higher molecular weights. On the contrary, an extension toward lower molecular weights seems dubious, since it is to be expected that the mechanism of viscosity changes for short hydrocarbon chains.

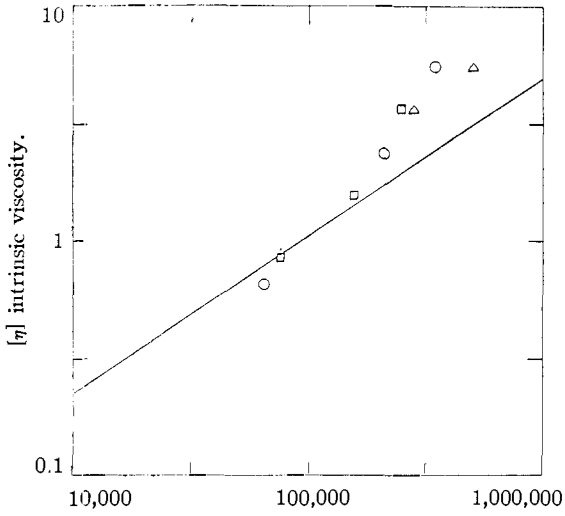

Fig. 2.—Results of previous investigators on poorly fractionated material: ⊙ Gee; □ Staudinger and Fischer; △ Meyer and Wertheim.

If the constants K and a are now revised in order to fit best *all* the data, we find

$$[\eta] = 5.02 \times 10^{-4} M^{0.667} \qquad (4)$$

The limits of error for K are $4.98 < K < 5.02$ and for a: $0.660 < a < 0.673$.

Discussion

Data of Previous Authors.—It is to be expected that for unfractionated or only roughly fractionated samples, the number average molecular weight as determined from thermodynamic data will be much lower than the weight average molecular weight as determined from the viscosity (see also following paragraph). It is, hence, to be expected that the points determined by various authors who did not go through the elaborate procedure of careful fractionation will lie above our curve. This deviation is to be expected to be larger the broader the fractions are, and particularly so for the high molecular weight, difficultly soluble, fractions. The generally narrower, lower molecular weight fractions are expected to lie closer to our curve. That this prediction is realized can be seen from Fig. 2, which includes data of Gee,[12] Meyer and Wertheim,[13] Staudinger and Fisher.[14]

Viscosity Average Molecular Weight.—It was pointed out by Lansing and Kraemer,[15] that the molecular weight determined from the viscosity with help of the Staudinger relation is equal to the weight average molecular $\overline{M}_{\text{w}}$

$$\overline{M}_{\text{w}} = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} \qquad (5)$$

This is no longer exactly true if the Staudinger relation (eqn. 1) is replaced by the more general eqn. 2.

In this case we have to go back to the definition of the average weight. For a relation of the type of eqn. 2 the average weight $\overline{M}_{\text{v}}$ is given by definition as

$$\overline{M}_{\text{v}} = \left(\frac{\Sigma n_i M_i^{a+1}}{\Sigma n_i M_i}\right)^{1/a} \qquad (6)$$

If a is of the order of $^2/_3$ as seems to be the case for most of the polymers so far investigated, $\overline{M}_{\text{v}}$ is still far closer to $\overline{M}_{\text{w}}$ ($a = 1$) than to $\overline{M}_{\text{N}}$ ($a = -1$), although it is no longer identical with it.

Theories of Viscosities of Chain Polymers.—No theory of the viscosity–molecular weight relation of elastomer solutions has been presented so far that represents exactly the observed features. The following remarks, although they do not give a theory, may be of use as a lead for the development of such.

Some years ago Kuhn[16] pointed out that the flow of coiled molecules in solution must follow one of the two following patterns:

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[10] It ought to be noted that Kemp and Peters did not extrapolate their values to infinite dilution and derived from their points a slope of $a = 1$, corresponding to the Staudinger law!

[11] H. Staudinger and F. Staiger, *Ber.*, **68**, 707 (1935).

[12] G. Gee, *Trans. Faraday Soc.*, **36**, 1162 (1940).

[13] K. H. Meyer and M. Wertheim, *Helv. Chim. Acta*, **24**, 217 (1941).

[14] H. Staudinger and K. L. Fisher, *J. prakt. Chem.*, **157**, 19, 158 (1940–1941).

[15] W. D. Lansing and E. O. Kraemer, THIS JOURNAL, **57**, 1369 (1935).

[16] W. Kuhn, *Z. physik. Chem.*, **A161**, 1 (1932).

Mechanism I.—The polymeric molecule and the solvent entrapped, "immobilized," between its segments move together, forming a sphere (or an ellipsoid) to which Einstein's hydrodynamic theory (or its extensions) can be applied.

Mechanism II.—At least a part of the liquid is free and flows between the segments as through the holes of a mesh. In this case the flowing liquid will exert a torque on each individual segment (or a group of such) as in the case of dumbbell molecules. In this case the viscosity mechanism is quite different and the energy lost can be calculated assuming that the sum of the torques has to be zero in order to avoid an infinitely accelerated rotation of the molecule.

Which one of the two mechanisms will predominate depends largely on the degree of separation of segments, that is, on the degree of swelling, the one dissipating the less energy being predominant. It is hard to predict whether the transition from one mechanism to the other will be abrupt or continuous, but it can be safely stated that a mechanism of the first type is to be expected in the case of solutions in poor swelling agents, a mechanism of the second type—if it ever exists in the pure form—in good swelling agents. Kuhn[16–18] has developed mathematical expressions for the viscosities for both mechanisms, but more rigorous demonstrations have been given by Hulburt, Harmon, Tobolsky and Eyring,[19] for mechanism I and by Huggins[20] for mechanism II.

Assuming randomly kinked molecules and applying the formula given by Daniels[21] for the volume occupied by such a molecule, Hulburt, *et al.*,[19] found a relation for mechanism I

$$[\eta] = KM^{1/2} \tag{7}$$

while Huggins found for the second mechanism a relation identical with that of Staudinger

$$[\eta] = KM \tag{8}$$

As shown in preceding paragraphs the experimental results for most rubber-like polymers lead to an expression

$$[\eta] = KM^{0.6-0.7} \tag{9}$$

a power situated between the two values 0.5 and 1 derived theoretically. Two explanations can be advanced for this discrepancy: either in the solvents used we are just in the transition region from one mechanism to the other, or the assumptions concerning the "randomly kinked" shape of the molecule are to be modified. In this connection it ought perhaps to be recalled that previous to Kuhn, Haller[22] has considered the mechanism II assuming that the rubber molecule is not "randomly kinked" but distributed with a uniform density in all the volume occupied, and obtained a relation

$$[\eta] = KM^{2/3} \tag{10}$$

which is exactly correct for hevea and in close agreement with the experiments for other polymers.

Acknowledgment.—The authors wish to thank Professor Hugh S. Taylor for his constant interest and support and for many helpful suggestions, the Firestone Tire and Rubber Company for supplying the rubber samples, and the Reconstruction Finance Corporation (Office of Rubber Reserve) for sponsorship of the research program.

Summary

The osmotic molecular weight–intrinsic viscosity relation for hevea has been determined and found to correspond to the relation: $[\eta] = 5.02 \times 10^{-4}M^{0.667}$.

PRINCETON, N. J. RECEIVED[23] AUGUST 29, 1944

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[17] W. Kuhn, *Z. physik. Chem.*, **A161**, 427 (1932).

[18] W. Kuhn, *Kolloid Z.*, **62**, 269 (1933).

[19] H. M. Hulburt, R. A. Harmon, A. V. Tobolsky and H. Eyring, *Ann. N. Y. Acad.*, **44**, 371 (1943).

[20] M. L. Huggins, *J. Phys. Chem.*, **42**, 910 (1938); **43**, 439 (1939); *J. Appl. Phys.*, **10**, 700 (1939).

[21] H. E. Daniels, *Proc. Camb. Phil. Soc.*, **37**, 244 (1941).

[22] W. Haller, *Kolloid Z.*, **56**, 257 (1931).

[23] This manuscript was originally received on August 29, 1944, and after examination by the Editorial Board, was accepted for publication in the JOURNAL. It was, however, referred to the War Production Board and at their request was withheld from publication, in a confidential file, until clearance was granted on April 20, 1946, by the Reconstruction Finance Corporation.