

Reprinted from the *Transactions of the Faraday Society*, No. 270,
Vol. XL, Part 6, June, 1944.

THE MOLECULAR WEIGHTS OF RUBBER AND RELATED MATERIALS.

V. THE INTERPRETATION OF MOLECULAR WEIGHT MEASUREMENTS ON HIGH POLYMERS.

BY GEOFFREY GEE.

Received 2nd February, 1944.

(Communicated at the Meeting.)

The Indian Rubber Board,
KOTTAYAM,
TRAVANCORE-COCHIN.

The relative merits of the osmotic and viscosity methods for the determination of the molecular weights of high polymers have been widely discussed. The purpose of this paper is to present a new theoretical justification for the osmotic method, and to draw attention to the conditions under which the viscosity method may be employed.

Osmotic Pressure Measurements.

The experimental details of osmotic pressure measurements on high polymer solutions have been described recently by a number of authors.¹ The results obtained give the osmotic pressure π of the solution as a function of the polymer concentration C . The problem to be considered here is that of deducing the molecular weight M of the polymer from these data. The classical osmotic pressure equation is that of van't Hoff

$$\frac{\pi}{c} = \frac{RT}{M} \quad (1)$$

according to which π/c should be independent of C and equal to $\frac{RT}{M}$.

In general, polymer solutions do not obey this law, but π/C increases approximately linearly with C , the slope depending on the nature of the solvent. An illustration of this behaviour is given by Fig. 1, showing some of Dobry's measurements of the osmotic pressure of nitrocellulose in various solvents.^{1(a)} These results show that the limiting value of π/C at infinite dilution is the same for all the solvents examined. No case has been reported in which this has been proved to be untrue, but in the case of polymers of very high molecular weight it is not usually possible to demonstrate it with certainty, owing to the difficulty of extrapolating data showing a large slope. This problem of extrapolation furnishes one of the

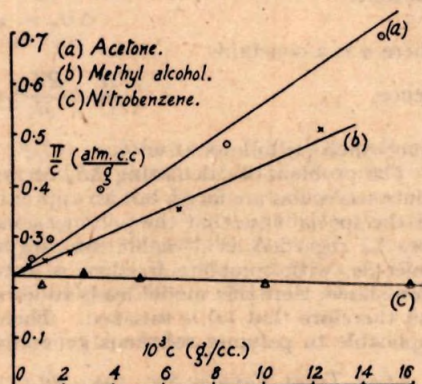


FIG. 1.—Osmotic Pressures of Nitrocellulose Solutions at 22° C.

¹ (a) Dobry, *J. chim. physique*, 1935, **32**, 50; *Koll. Z.*, 1937, **81**, 190. (b) Carter and Record, *J.C.S.*, 1939, 660. (c) Gee, *Trans. Faraday Soc.*, 1940, **36**, 1162; 1942, **38**, 147. (d) Flory, *J.A.C.S.*, 1943, **65**, 372. (e) Fuoss and Mead, *J. Physic. Chem.*, 1943, **47**, 59.

major experimental difficulties of the osmotic method, and is perhaps best dealt with by choice of a solvent which reduces the dependence ² of Π/C on C . Having estimated the limiting value $(\Pi/C)_0$, we write

$$\left(\frac{\Pi}{C}\right)_0 = \frac{RT}{M} \quad (2)$$

Before one can place any reliance on molecular weights derived from (2) it is necessary to consider its theoretical basis. By thermodynamic reasoning, it may be shown that, for dilute solutions of *any* solute,³

$$\Pi V_0 = -\Delta G_0 = T\Delta S_0 - \Delta H_0 \quad (3)$$

where V_0 is the molar volume of the solute and ΔG_0 , ΔS_0 , ΔH_0 are the increases in Gibbs' free energy, entropy and heat content when one mole of solvent is added to a large bulk of solution. For ideal solutions, $\Delta H_0 = 0$, and equation (3) gives a relation between the osmotic pressure and the entropy of dilution ΔS_0 . Now it is possible to calculate ΔS_0 statistically for simple systems by making use of Boltzmann's equation⁴ relating the entropy S of a system with its probability P :

$$S = k \ln P \quad (4)$$

Thus, if the solute and solvent molecules are of similar size, we may calculate P , and therefore S , by considering the number of ways of arranging the molecules on a pseudo-crystal lattice. It is readily shown in this way that the entropy of dilution is given by⁵

$$\Delta S_0 = R \ln \left(1 + \frac{N_s}{N_0}\right) \quad (5)$$

where N_s , N_0 are the numbers of solute and solvent molecules in the mixture. For dilute solutions, the log. term may be expanded, giving

$$\Delta S_0 \simeq RN_s/N_0 \simeq \frac{RV_0}{M}C \quad (6)$$

If $\Delta H_0 = 0$, substitution of (6) into (3) leads at once to van't Hoff's law. If ΔH_0 is not negligible, it may be shown statistically* that, for dilute solutions,

$$\Delta H_0 = \alpha V_0 C^2 \quad (7)$$

where α is a constant.

Hence,

$$\frac{\Pi}{C} = \frac{RT}{M} - \alpha C \quad (8)$$

from which (2) follows at once.

The problem of calculating ΔS_0 becomes much more difficult when the solute molecules are large, but an approximate solution has been obtained⁷ for the special case that the polymer consists of long flexible chains which may be regarded as divisible into segments, each the size of a solvent molecule, with complete freedom of rotation between segments. It has been shown that this model leads to an equation of the same form as (8), and therefore that (2) is satisfied. This model is clearly too simple to be applicable to polymer solutions generally, but in the next section it will

² Gee, *Trans. Faraday Soc.*, 1940, **36**, 1171.

³ Guggenheim, *Modern Thermodynamics* (Methuen, 1933), p. 97.

⁴ Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge, 1939), p. 62.

⁵ *Ibid.*, p. 163.

* This has been confirmed experimentally.⁶

⁶ Hildebrand, *Solubility of Non-electrolytes* (Reinhold, 1936), ch. 3.

⁷ Flory, *J. Chem. Physics*, 1942, **10**, 51. Huggins, *Ann. N.Y. Acad. Sci.*, 1942, **43**, 1. Miller, *Proc. Camb. Phil. Soc.*, 1942, **38**, 109; 1943, **39**, 131.

be shown that equation (2) is in fact applicable to solute molecules of any size and shape.

Limiting Form of the Entropy of Dilution.

We consider the arrangement, on a lattice of $N_0 + nN_s$ sites, of N_0 solvent molecules, each occupying one site, and N_s polymer molecules, each requiring n sites, and we confine our attention to highly dilute solutions, so that $nN_s \ll N_0$. The lattice is to be filled by arranging the polymer molecules first, and it is evident that all the sites are available to the first segment of the first polymer molecule. Having fixed the first segment, the number of ways of arranging the remaining segments of this molecule will be some definite number, p_1 , say, which will depend on the size, shape and flexibility of the polymer molecule. The total number of arrangements of the first polymer molecule on the lattice will thus be $p_1(N_0 + nN_s) \doteq p_1 N_0$. If the solution is sufficiently dilute, there will be very nearly the same number of ways of arranging each remaining polymer molecule, since interference of one polymer with another will be negligible. Hence the total number of ways of arranging the N_s polymer molecules will be approximately $(p_1 N_0)^{N_s}$. The number of ways of arranging these N_s polymer molecules on nN_s sites (i.e. in the pure polymer) is unknown, but we may write it as p_2 . Using Boltzmann's equation, the increase of entropy $\Delta S_{N_0}^m$ on mixing the N_s polymer molecules with N_0 solvent molecules is seen to be

$$\Delta S_{N_0}^m \doteq k\{N_s \ln(p_1 N_0) - \ln p_2\}. \quad (9)$$

Repetition of this calculation with the number of solvent molecules increased by δN_0 gives for the entropy of mixing $\Delta S_{N_0 + \delta N_0}^m$ of N_s polymer molecules with $(N_0 + \delta N_0)$ solvent molecules:

$$\Delta S_{N_0 + \delta N_0}^m \doteq k\{N_s \ln p_1(N_0 + \delta N_0) - \ln p_2\}. \quad (10)$$

Now, by definition,

$$\Delta S_0 = N \lim_{\delta N_0 \rightarrow 0} \frac{1}{\delta N_0} (\Delta S_{N_0 + \delta N_0}^m - \Delta S_{N_0}^m) \quad (11)$$

where N is Avogadro's number.

Substituting from (9) and (10) in (11)

$$\Delta S_0 \doteq R \frac{N_s}{N_0} \doteq R \frac{V_0}{M} \cdot C. \quad (6)$$

Since it has already been assumed that the solution is so dilute that polymer-polymer contacts are negligible, it follows that further dilution does not change the number or nature of the intermolecular contacts, so that $\Delta H_0 = 0$. A better way of expressing this conclusion is to say that it is evident from this model that at sufficiently high dilution ΔH_0 becomes negligible compared with $T\Delta S_0$. It follows, therefore, that van't Hoff's law is the correct limiting law at infinite dilution, whatever may be the size and shape of the solute molecules.

If we write van't Hoff's equation in the form

$$\Pi = \frac{kT}{V} \cdot N_s \quad (12)$$

where V is the volume of solvent in which N_s solute molecules are dissolved, it is evident that what we actually obtain by osmotic measurements is the number of solute molecules, i.e., the number of kinetically distinct units of solute. If each of these is associated with a number of solvent molecules, the latter will not be included in the molecular weight. If,

however, two or more solute molecules are associated with each other, the molecular weight found will be that of the complex. Association of the solvent will have no effect on the result, which is also independent of the nature of the solvent. It will be shown in a subsequent publication that this is also true of mixed solvents.

The above discussion shows that the theoretical basis of the osmotic method is firmly established, and that if $(\Pi/C)_0$ can be found accurately, the absolute molecular weight of the solute—as dispersed in the solvent which has been employed—may be calculated from it with complete confidence.

The Viscosity Method.

Much the simplest and most widely used method of obtaining the molecular weight of long chain polymers depends on the measurement of the viscosity of a dilute solution. The theoretical and experimental basis of this has been widely discussed,⁸ and all that can be done in this brief paper is to indicate the author's own views as to the usefulness of viscosity measurements.

Various attempts to calculate the viscosity of polymer solutions have led to equations of the general form

$$[\eta] = KM^\beta \quad (13)$$

where $[\eta]$, the intrinsic viscosity is the limiting value at infinite dilution of η_{sp}/c , η_{sp} being the specific viscosity of the solution. K , β are constants, the latter being assigned various values between 0 and 2, according to the shape of the polymer molecule in solution, and the particular model used in the analysis. Staudinger's well-known equation is seen to be a special case of (13), with $\beta = 1$. In the present state of the theory, it does not seem possible to calculate absolute values of either K or β for any particular polymer solution, although the theory gives good ground for believing that an equation of the form (13) should hold for a series of polymers differing only in molecular weight. The most convenient way of treating this is to plot $\log. [\eta]$ against $\log. M$, and in Fig. 2 some recent data on fractionated polymers are presented in this way. It is evident that the equation holds over a wide range of M , giving the following values of β :—

Cellulose acetate in acetone ⁹	$M = 25,000$ to $125,000$	$\beta = 0.67$.
Polyisobutylene in Cyclohexane ¹ (d)	$M = 6,000$ to $1,300,000$	$\beta = 0.64$.
Rubber in benzene ^{* 2}	$M = 7,000$ to $350,000$	$\beta = 0.96$.

The value of β found for rubber in benzene is, within experimental error, unity, so that Staudinger's law holds, whereas it clearly does not hold for the other solutions. It is, however, to be noted from Fig. 2 that squalene ($M = 410$) does not fall on the straight line drawn to represent the data for the rubber fractions, so that equation (13) evidently breaks down for sufficiently low values of M . Similar behaviour has been reported for other homologous series,¹⁰ and the empirical relationship

$$[\eta] = KM + \alpha \quad (14)$$

found to fit. It seems quite probable that a similar correcting term α

⁸ See, for a summary : Gee, *Ann. Repts. Chem. Soc.*, 1942, 7.

⁹ Bartovics and Mark, *J.A.C.S.*, 1943, **65**, 1901.

^{*} The point at $M = 7,000$ refers to a fractionated polyisoprene prepared by my colleague, Dr. Bolland. Further materials of this kind are under examination in order to fix the lower part of the curve more precisely. It is hoped to report the results shortly.

¹⁰ Baker, Fuller and Heiss, *J.A.C.S.*, 1941, **63**, 2142. Flory, *ibid.*, 1940, **62**, 3032.

may need to be added to the more general equation (13) in order to extend its application to low molecular polymers.

The discussion so far has been confined to polymers which are believed to be essentially linear in structure, and approximately homogeneous. For such materials it appears that viscosity measurements can be used to measure molecular weights, once values of K and β have been found by calibration against the osmotic method. It is to be noted that K (and possibly to a smaller extent β) depends on the nature of the solvent. We have now to consider what information, if any, can be obtained from viscosity measurements on polymers which are not necessarily either homogeneous or of linear structure.

Confining attention first to linear polymers, it is clear that since the viscosity method applies to homogeneous materials, it must give some sort of average molecular weight for a mixture. This average is not, however, the same as that given by the osmotic method, which is easily seen to conform to the natural definition of an average molecular weight as the total weight of material divided by the total number of molecules. The viscosity average molecular weight of $\sum_i N_i$ molecules of molecular weight M_i (where i takes all values) may be shown to be ¹¹

$$\bar{M}_{visc} = \left(\frac{\sum_i N_i M_i^{(1+\beta)}}{\sum_i N_i M_i} \right)^{1/\beta} \quad (15)$$

For $\beta = 1$ this reduces to a weight average.¹² For any value of $\beta > 0$ the viscosity average is greater than the osmotic average, and the ratio between them may be approximately 2 for an unfractionated polymer.* It is evident that if the distribution is unknown, the viscosity alone will give only an approximate molecular weight, though the order of magnitude will be correct unless the distribution is very unusual (e.g., a low molecular polymer with a proportion of very high molecular material). When both osmotic and viscosity molecular weights have been determined, a comparison of the two gives a rough idea of the homogeneity of the sample. The method is, however, extremely crude, and the approximate agreement of the two values is not inconsistent with a moderately broad distribution.

The viscosity method becomes of much less value when there is a possibility of the polymer being non-linear in structure. The intrinsic viscosity depends essentially on the length of the polymer molecules¹⁴ and, for a

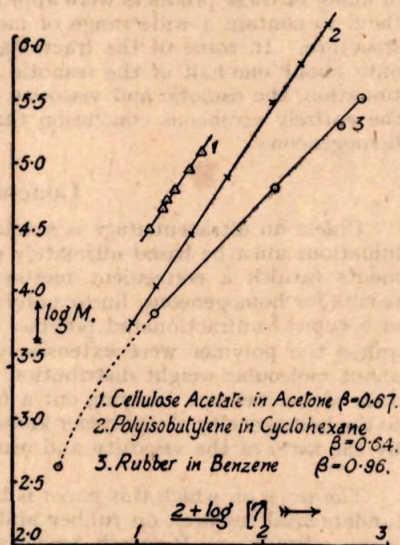


FIG. 2.—Dependence of Viscosity on Molecular Weight.

¹¹ Huggins, *Ind. Eng. Chem.*, 1943, **35**, 980.

¹² Lansing and Kraemer, *J. Physic. Chem.*, 1935, **39**, 153.

* The theoretical ratio for an unfractionated polyester is exactly 2 if $\beta = 1$.¹³

¹³ Flory, *J.A.C.S.*, 1936, **58**, 1877.

¹⁴ Staudinger and Fischer, *J. prakt. Chem.*, 1941, **157**, 19.

given molecular weight, should be less for a branched than for a linear structure. This expectation has been abundantly borne out by some work on the thermal degradation of rubber carried out in collaboration with Dr. Bolland.* Although the osmotic and viscosity molecular weights of many of these products were approximately equal, fractionation showed them to contain a wide range of molecular sizes, and to be of branched structure. In some of the fractions the viscosity molecular weight was only about one-half of the osmotic value. In the absence of any fractionation, the osmotic and viscosity molecular weights would have led to the entirely erroneous conclusion that the products were approximately homogeneous.

Conclusions.

Unless an ultracentrifuge is available, *absolute* molecular weight determinations must be based ultimately on osmotic data. Viscosity measurements furnish a convenient method of interpolation and give reliable results for homogeneous, linear polymers. The viscosity molecular weight of a typical unfractionated polymer would not be very seriously in error unless the polymer were extensively branched. No reliable conclusions about molecular weight distribution can be drawn from molecular weight data alone, without carrying out a fractionation, although a useful guide to the homogeneity of a polymer known to be of linear structure is furnished by the ratio of the viscosity and osmotic molecular weights.

The work on which this paper is based forms part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

48 Tewin Road,
Welwyn Garden City,
Hertfordshire.

* Details of this work will be published elsewhere.