

AN ULTRACENTRIFUGAL ANALYSIS OF FRACTIONATED POLYVINYLCHLORIDE—I

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Abstract—The sedimentation constants and intrinsic viscosities of fractionated PVC (Geon III) have been determined in tetrahydrofuran at 20 and 25° respectively. A comparison of the molecular weights as evaluated from the above constants is made. The M_w values derived from the intrinsic viscosity are low; the M_n values evaluated from sedimentation and viscometric data are rather high compared with those obtained for the whole polymer. This behaviour indicates the presence of long branched molecules in the polymer.

INTRODUCTION

THE VELOCITY ultracentrifugal method of determining molecular weights has been used mainly for naturally occurring polymers. For synthetic polymers, there is little published work although polystyrene and polymethylmethacrylate have received some attention.⁽¹⁻⁵⁾ Relatively little information is available on the ultracentrifugation of polyvinylchloride.⁽⁶⁾ Oth⁽⁷⁾ made use of the method to show the presence of aggregates due to association of the PVC molecules in solution. Further work by Hengatenburg *et al.*⁽⁸⁾ and by Danusso *et al.*⁽⁹⁾ on this problem has convincingly shown the difficulties this phenomenon can cause when measuring molecular weights.

EXPERIMENTAL

Materials

Polyvinylchloride (Geon III) was kindly supplied by British Geon Ltd. and was purified as follows. The polymer was shaken for 24 hr in peroxide-free tetrahydrofuran to give a 1 per cent solution, which was subsequently precipitated in a large excess of methanol with constant stirring, allowed to stand overnight, filtered and dried *in vacuo* at 47° for two days. This procedure was repeated.

Tetrahydrofuran (THF) supplied by Eastman Kodak Ltd. was refluxed over ferrous sulphate for 2 hr to remove peroxides, refluxed over calcium chloride and distilled before use.

Cyclohexanone, supplied by May and Baker Ltd., was distilled under reduced pressure before use.

Apparatus

The analytical ultracentrifuge used was a Spinco Model E manufactured by the Spinco Division of Beckman Instruments Ltd.

Procedure

Fractionation of polymer. Twelve grams of twice purified Geon III was dissolved in two litres of peroxide-free THF, shaken for 2 hr and allowed to stand overnight. The solution in a 3-l. 3-necked flask was kept under nitrogen at 25° in a thermostat bath. Methanol was run into this solution from a burette with constant stirring until the solution became cloudy. The flask was removed and placed in a thermostat bath at 40° for 2 hr, still under nitrogen; it was then returned to the bath at 25° and the precipitate allowed to settle. This procedure was followed to prevent polymer of molecular weight, other than that which was insoluble in the particular methanol/THF concentration, being entrapped by the precipitating polymer. The precipitated fraction was filtered through a weighed Gooch (porosity

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4) crucible and dried *in vacuo* at 40° for two days. This procedure was repeated until all the polymer was precipitated.

Preparation of polymer for ultracentrifugation

The solutions of PVC in THF were made up in sealed tubes, immersed in a thermostat at 60° for an hour with occasional shaking, removed, and shaken for a further 30 min. On opening, the solutions were centrifuged in a bench centrifuge for 1 hr. These solutions were used for viscometry and ultracentrifugation.

Molecular weight-intrinsic viscosity

The viscosity-weight average molecular weight relationship derived by Freeman and Manning⁽¹⁰⁾ was used to evaluate M_w :

$$[\eta]_{2.25}^{\text{THF}} = 1.63 \times 10^{-4} [M_w]^{0.766}. \quad (1)$$

Sedimentation constant evaluation

The sedimentation coefficients were determined using standard aluminium 4° sector 12 mm cells. The Schlieren photographs were taken at regular intervals (normally 16 min) on Kodak 0.250 Rapid Metallographic plates. Normal exposure times were between 15 and 20 sec. The plates were developed for 105 sec in Kodak D163 developer at 65°F, fixed in Kodafix for 10 min, washed in running water for 30 min and then dried. Measurements from the photographs were made using a cathetometer reading to ± 0.001 cm.

The values of the sedimentation coefficients were calculated using the integrated form of the sedimentation coefficient expression:

$$S_c' = \frac{2.303}{\omega^2 \cdot 60} \cdot \frac{\log X_{n+1} - \log X_n}{t_{n+1} - t_n} \quad (2)$$

where X_n and X_{n+1} are the distances moved by the peaks from the reference line at times t_n and t_{n+1} (in minutes) after reaching the operating speed, 59,780 r.p.m. Using the relationship⁽³⁾

$$1/S_c' = 1/S_c (1 + K_s C) \quad (3)$$

where S_c' , S_c , K_s and C are the sedimentation coefficient, sedimentation constant, constant and concentration in g.dl⁻¹ respectively. The reciprocal of the sedimentation coefficient was plotted against the concentration, the sedimentation constant being obtained from the intercept on the $1/S_c'$ axis at zero concentration.

MOLECULAR WEIGHT FROM SEDIMENTATION CONSTANT

Because of insufficient available data on the diffusion constant of polyvinylchloride in tetrahydrofuran solution, the method outlined by Wales⁽¹¹⁾ has been used to yield a constant from which can be obtained the Sedimentation-Viscosity Average Molecular Weight.

By combining the Mandelkern⁽¹²⁾ expression for the friction factor (F)

$$F = \eta_0 \cdot P \cdot \langle r^2 \rangle^{1/2} \quad (4)$$

with the Fox-Flory⁽¹³⁾ expression for the intrinsic viscosity ($[\eta]$)

$$[\eta] = \Phi \cdot \langle r^2 \rangle^{3/2} \cdot M^{-1} \quad (5)$$

we obtain the equation

$$F = \frac{M^{1/3} \cdot [\eta]^{1/3}}{\Phi^{1/3}} \cdot \eta_0 \cdot P \quad (6)$$

where η_0 is the viscosity of the solvent, Φ and P are constants, M and $\langle r^2 \rangle$ are the molecular weight and the mean square end-to-end length of the polymer molecules respectively.

Substituting for F in the Svedberg equation,⁽¹⁴⁾

$$S_c = M \cdot (1 - V\rho) \cdot F^{-1} \quad (7)$$

we obtain the equation:

$$S_c \cdot [\eta]^{1/3} / M^{2/3} = (1 - V\rho) \cdot \Phi / P \cdot \eta_0 \cdot N \quad (8)$$

(where V , ρ , and N are the partial molar volume of the polymer, the density of the polymer solution and the Avogadro Number respectively) from which the molecular weight of the polymer can be evaluated. This value for the molecular weight depends upon the $3/2$ power of the Sedimentation Constant and the half power of the intrinsic viscosity, and has been termed the Sedimentation-Viscosity Molecular Weight.

From sedimentation and viscosity measurements on bulk Geon III, values of 5.73 Svedbergs and 1.04 dl.g^{-1} were obtained for S_c and $[\eta]$ respectively. A value of 2.523×10^{-3} for the constant $S_c[\eta]^{1/3} \cdot M^{-2/3}$ was found using a value of $110,000$ for the weight average molecular weight of the polymer.⁽¹⁵⁾

RESULTS

The fractionation, sedimentation and viscosity results for Geon III are given in Table 1, and are presented as outlined on page 4 of Ref. 11. All values of $[\eta]$, S_c , K_s and b were calculated from lines obtained using the method of least squares.

Schlieren photographs of the sedimentation of a solution of fraction 3 (concentration 10.09 g l^{-1}) are shown in Fig. 1. The peaks obtained are symmetrical and their movement across the cell gave consistent values for the sedimentation coefficient. Similar results were obtained at four different concentrations for each of fractions 1–9.

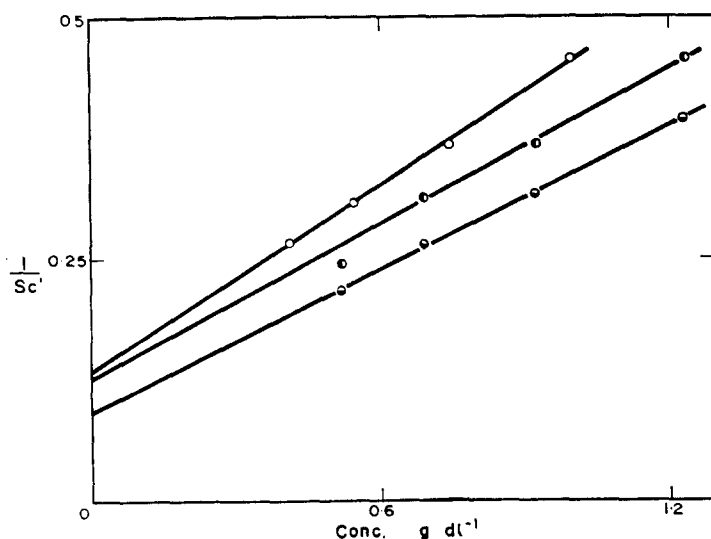


FIG. 2. Variation of the reciprocal of the sedimentation coefficients of fractions 1, 5 and 9 with polymer concentration.

To avoid superposition 0.05 and 0.1 have been subtracted from the reciprocal sedimentation coefficient values for fractions 5 and 9 respectively.

○ fraction 1; ● fraction 5; ◐ fraction 9.

TABLE 1. FRACTIONATION, SEDIMENTATION AND VISCOSITY RESULTS FOR UNDEGRADED FRACTIONATED GEON III

Fraction No.	Fraction (g)	Cumulative weight fraction	Corrected cumulative weight fraction	Intrinsic viscosity at 25° (dl.g ⁻¹)	Sedimentation constant at 20° (Sved.)	Weight average molecular weight (M _w)	Sedimentation viscosity average molecular weight M _η	K _s	K _s /[η]
1	0.671	1.0000	0.9708	1.08	7.69	97,250	175,000	2.47	2.29
2	0.916	0.9414	0.9017	1.05	6.51	93,910	134,500	2.04	1.93
3	0.921	0.8620	0.8217	1.04	5.67	92,600	108,800	1.53	1.47
4	1.365	0.7818	0.7222	1.03	5.52	91,310	103,900	1.43	1.38
5	2.005	0.6630	0.5755	1.01	5.53	89,620	103,500	1.44	1.41
6	1.098	0.4883	0.4404	1.00	5.40	87,680	99,130	1.44	1.44
7	0.597	0.3926	0.3666	0.98	5.10	85,000	89,130	1.23	1.27
8	1.680	0.3406	0.2674	1.17	5.33	107,800	105,100	1.17	1.14
9	1.034	0.1943	0.1492	1.15	5.32	105,300	103,700	1.32	1.14
10	0.369	0.1042	0.0882	0.76	—	61,420	—	—	—
11	0.828	0.0721	0.0361	0.44	—	30,210	—	—	—

Plots of the reciprocal of the sedimentation coefficients against the concentrations of the corresponding solutions are given in Fig. 2 for fractions 1, 5 and 9. To avoid superposition of the lines, 0.05 and 0.1 have been subtracted from the reciprocal sedimentation coefficient values for fractions 5 and 9 respectively. The plots are good straight lines as were those obtained for the other fractions. The sedimentation coefficients obtained by the least squares method are given in Table 1, column 6.

The intrinsic viscosities and sedimentation constants of fractions 8 and 9 are rather high in comparison with those of the other fractions. The intrinsic viscosity results were, however, quite reproducible, even after reprecipitation of the fraction. A time interval of 2 weeks had occurred between the precipitation of fractions 7 and 8, and so it seems possible that association of the polymer molecules might have occurred during this interval. There is a slight indication of association in the Schlieren photographs obtained during ultracentrifugation of some of the fractions.

Figure 3 shows the integral molecular weight distribution curve constructed using the composite molecular weight $M_{s\eta}$. The distribution curve shows a rather narrow molecular weight range though there are indications of a high molecular weight tail. Further fractionation of fractions 1 and 2 would have been necessary to confirm this. Figure 4 is the conventional Mark-Houwink⁽¹⁶⁾ plot of $\log [\eta]$ against $\log M$. From this, the relationship:

$$[\eta] = 0.022 [M_{s\eta}]^{0.33} \quad (9)$$

can be derived if we ignore the very high values obtained for fractions 8 and 9. There is a marked deviation from linearity for the higher molecular weight fractions.

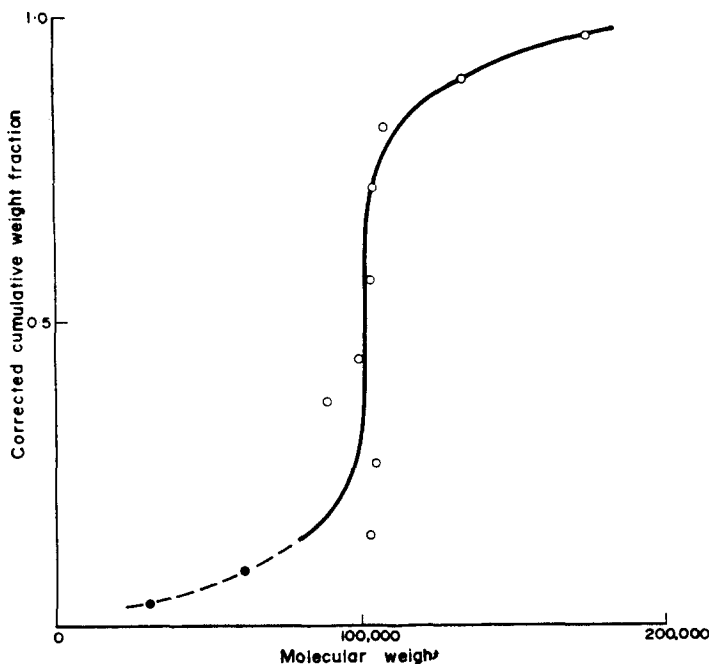


FIG. 3. Integral molecular weight distribution curve for Geon III. O, $M_{s\eta}$; ●, M_w .

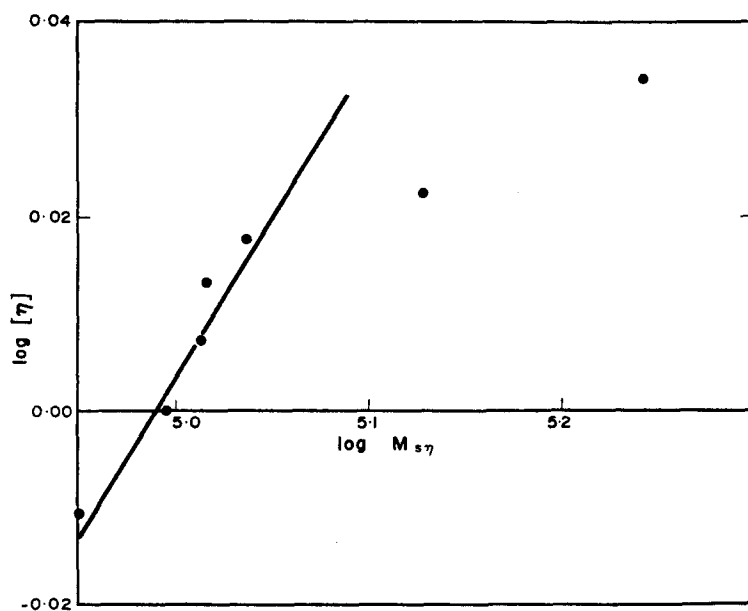


FIG. 4. Variation of intrinsic viscosity with molecular weight ($M_{s\eta}$) for fractionated Geon III.

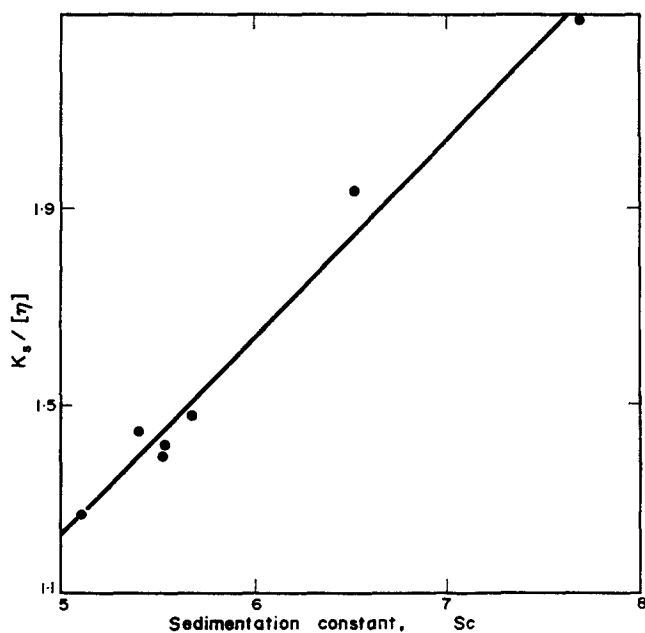


FIG. 5. Relationship between $K_s/[\eta]$ and the sedimentation constant for fractionated Geon III.

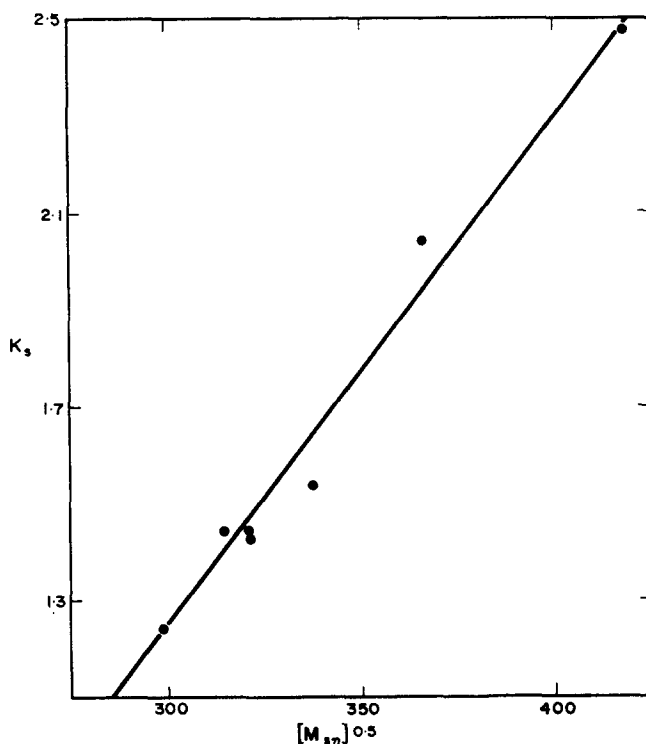


FIG. 6. Relationship between K_s and $M_{w,0.5}$ for fractionated Geon III.

The values of K_s were obtained by calculating the gradients of the $1/S_c$ against concentration plots using the method of least squares. A linear relationship between $K_s/[\eta]$ and the sedimentation constant was found (Fig. 5):

$$K_s/[\eta] = 0.4102 S_c - 0.825 \quad (10)$$

A plot of K_s against $M_{w,0.5}$ is shown in Fig. 6. This plot is linear, in agreement with the findings of Newman and Eirich.⁽¹⁾

DISCUSSION

Before discussing the results presented in this paper, the association phenomenon which occurs when PVC is in solution must be considered. Doty⁽¹⁷⁾ was the first to observe this effect, noting a drop in molecular weight on heating PVC samples in dioxan at 60°. The presence of molecular aggregates has been convincingly shown by the use of the ultracentrifugal method.^(7,8) Crugnola and Danusso⁽⁹⁾ studied solutions of PVC in different solvents and concluded that for vinyl chloride polymerized at low temperatures, it was not possible to disperse associated molecules in tetrahydrofuran; this was not the case for commercial suspension PVC. They concluded that this difference in behaviour was due to differences in the crystallinity of the polymers, the more crystalline polymer tending to associate more readily. In the present work, a commercial suspension PVC (Geon III) was used. All polymer solutions were heated at 60° for 1 hr. Ultracentrifugal and viscometric determinations were completed within 36 hr

of this treatment to avoid re-association. In a few of the sedimentation experiments, some very small diffuse peaks which sediment only slightly faster than the main peak were observed. These presumably provide evidence of a small degree of association of some of the polymer molecules in the solutions used in these particular experiments. Viscometric and sedimentation theory give rise to equations of the form

$$[\eta] = k'[M]^a \quad (11)$$

and
$$S_c = k''[M]^b \quad (12)$$

respectively. Combining equations (8) and (11) we get

$$b = (2 - a)/3. \quad (13)$$

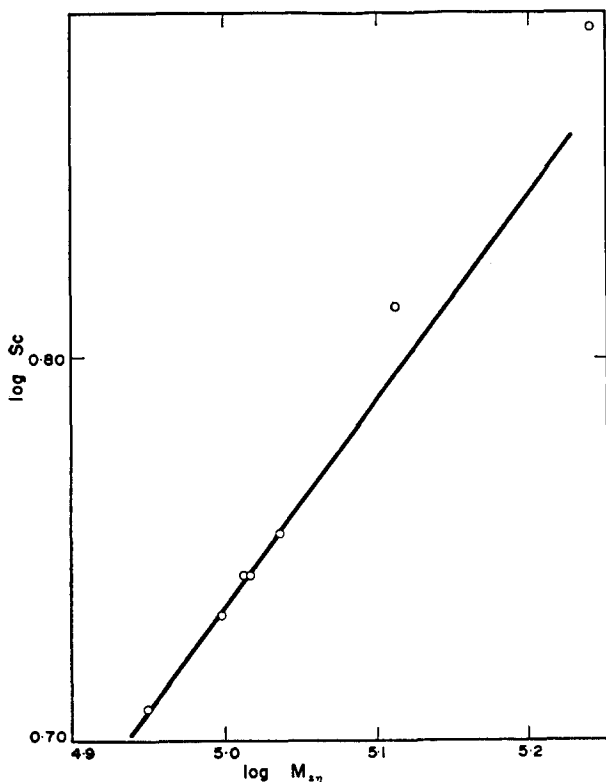


FIG. 7. Variation of S_c with $M_{s\eta}$ for fractionated Geon III.

From the plot of $\log S_c$ against $\log M_{s\eta}$ shown in Fig. 7 values of 1.054 for k'' and 0.54 for b are obtained. Substituting this value for b in equation (13), a value of 0.37 is obtained for a , which is a little lower than the theoretical limit of 0.5.

It is generally held that a low value of the exponent a is synonymous with long chain branching in the polymer. Association of polymer molecules would also tend to have the same effect. However, the ultracentrifuge experiments indicate that there is only little, if any, association in the polymer solutions used in these experiments.

One of the most striking features of the results shown in Table 1 is the relatively high values obtained for the Sedimentation Constant for the first two fractions compared with the remainder. Such values would be expected if these fractions are composed of polymer molecules which have long chain branched structures, since the structurally independent Sedimentation-Viscosity Average Molecular Weight $M_{s\eta}$ is quite high for these two fractions. Again the values of \bar{M}_w calculated using the equation of Freeman and Manning (e.g. 92,300 for the unfractionated polymer) are well below those expected⁽¹⁵⁾ for polymer with an actual overall \bar{M}_w of 110,000, as might be expected if there is a substantial amount of long chain branched molecules in the polymer.

Several authors⁽¹⁸⁻²⁰⁾ have made use of the lack of linearity of the $\log [\eta]$ against $\log M$ plot as evidence for long chain branching. Krasovec⁽²⁰⁾ used the number average molecular weight as the molecular weight parameter, whereas Zimm and co-workers⁽¹⁸⁾ used the weight average molecular weight. Both of these plots show deviation from linearity and it would not be surprising if the composite molecular weight average $M_{s\eta}$ were to show a similar effect when branched polymer molecules are present.

The effect of branching is to reduce the hydrodynamic volume of the polymer molecule and consequently to give a lower intrinsic viscosity than would be expected for a linear molecule of the same molecular weight. The Sedimentation Constant, however, will increase with extent of branching in the polymer.

In the Svedberg equation⁽¹⁴⁾ (7), as shown earlier (4), the friction factor F can be expressed in terms of the mean square end-to-end distance using the Fox-Mandelkern⁽¹²⁾ theory. This was developed for linear molecules; for a branched polymer of the same molecular weight, the value of $\langle r^2 \rangle$ is lower than for the linear molecule, consequently S_c is larger than would be expected for the molecular weight being measured.

The effect of conversion on polymer branching and consequently on these results has to be considered. Geon III is a commercial polymer taken to high conversion. Krasovec⁽²⁰⁾ investigated the differential molecular weight distribution curves of emulsion polymerized PVC samples taken to different conversions. He used the Bengough and Norrish⁽²¹⁾ postulate to explain the appearance of a second maximum in the distribution curve for a sample taken to 96 per cent conversion. This involves chain transfer to "dead" polymer giving rise to long chain branching at later stages of the polymerization reaction.

In evaluating the Sedimentation Constants at infinite dilution, equation (3) was used. This equation includes only the first term of a power series in concentration terms expressing the friction factor. For low concentrations of polymer ($< 0.7 \text{ g.dl}^{-1}$), this equation holds well but is thought to break down at higher concentrations. Signer and Egli⁽²²⁾ have postulated that the sedimentation velocity is no longer proportional to the molecular weight at higher concentrations. Despite this factor, good linearity in $1/S_c$ against concentration plots was obtained for concentrations up to 1.2 g.dl^{-1} (Fig. 2). If this effect were playing a significant part, linearity would hardly be achieved over the entire range of concentrations used.

Even with this linearity, the value of 1.6 for $K_s[\eta]$ which Wales and Van Holde⁽³⁾ obtained for a series of vinyl polymers (excluding PVC) was not found. As indicated in the results section, $K_s/[\eta]$ was found to vary with the Sedimentation Constant. Since

the expression for the friction factor involves K_s and C , it appears that K_s is dependent upon the degree of branching in the polymer molecules.

At first sight it is rather surprising that despite the variation in K_s , there is a linear relationship between K_s and $M_{s,\eta}^{0.5}$ as found by Newman and Eirich⁽¹⁾ for polystyrene with $K_s/[\eta] = 1.6$. The range of molecular weights they investigated was approximately 1,300,000–250,000 whereas the range in our work is 175,000–89,130. Again their samples were prepared in the laboratory and were presumably composed of linear molecules. Thus it seems possible that there is a fortuitous agreement over the narrow molecular weight range studied in this investigation.

Different methods of determining molecular weights are sensitive to different regions of the molecular weight distribution curve. This fact, together with the added complication of long branched molecules present in the higher molecular weight fractions, makes the use of values derived from whole polymer to calculate molecular weights of fractions somewhat doubtful.

Despite the drawbacks of the method, ultracentrifugation can be used to show the presence of long chain branching in polymers and provides a visual check on the presence of agglomerates which could affect the results.

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Résumé—Les constantes de sédimentation et les viscosités intrinsèques de PCV fractionné (Geon III) ont été déterminées dans le tétrahydrofurane à 20 et 25° respectivement. On compare les valeurs des masses moléculaires obtenues à partir de ces constantes. Les valeurs M_w obtenues à partir des viscosités intrinsèques sont faibles; les valeurs $M_{s,\eta}$ obtenues à partir des données de sédimentation et de viscosimétrie sont relativement élevées par rapport à celle obtenue pour le polymère global. Ce comportement indique la présence de molécules à longs branchements dans le polymère.

Sommario—Sono state determinate le costanti di sedimentazione e la viscosità intrinseca del PVC (Geon III) frazionato, in tetraidrofurano a 20 e 25° rispettivamente. Si fa un raffronto dei pesi molecolari determinati dalle costanti sopracritte. I valori M_w derivati dalla viscosità intrinseca sono

bassi; i valori M_{η} , determinati dai dati di sedimentazione e viscosimetrici sono piuttosto alti, se raffrontati con quelli ottenuti per l'intero polimero. Questo comportamento indica la presenza di molecole con lunghe catene laterali nel polimero.

Zusammenfassung—Die Sedimentationskonstanten und die Viskositätszahlen von fraktioniertem PVC. (Geon III) wurden in Tetrahydrofuran bei 20 bzw. 25° bestimmt. Die aus diesen Konstanten berechneten Molekulargewichte wurden verglichen. Die aus den Viskositätszahlen erhaltenen M_w Werte sind niedrig; die aus den Sedimentations- und Viskositätsdaten berechneten M_{η} Werte sind jedoch sehr hoch im Vergleich zu denjenigen, die für das unfractionierte Polymere erhalten wurden. Dies Verhalten läßt darauf schließen, daß in dem Polymeren lang verzweigte Moleküle vorliegen.