Large-Scale Fractionation of Poly(vinyl Chloride) and Characterization of the Fractions

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Synopsis

A large-scale fractionation of poly(vinyl chloride) (3000 g.) has been carried out by a fractional precipitation method. The molecular weight distribution of some fractions has been controlled by refractionation. The fractions have been also characterized by viscometry, osmometry, light-scattering, and glass transition temperature measurements. The data available in literature concerning the molecular weight characterization of poly(vinyl chloride) fractions have been critically reviewed. It has been shown that most of the viscometric and osmometric data are in good agreement when the molecular weights are below 10^5. Above 10^5 the literature discrepancies can be attributed to aggregation.

INTRODUCTION

The viscoelastic properties of polymers above the glass transition temperature T_g are strongly dependent upon the average molecular weight M and the molecular weight distribution MWD.

Also the properties of polymers below T_g are affected by the molecular weight, in particular when M is of the order of 10,000 or less.[1,2]

The studies of the effect of M and MWD on the properties of polymers are concerned mainly with the rheological behavior of polymers above T_g[1, 3–5] and they are usually carried out with polydisperse samples.

However, an essential step of similar studies should be the preparation of samples having different M but narrow MWD. Secondly, samples having the same average molecular weight M but different MWD could be obtained by mixing fractions or polydisperse polymers.

For some polymers, samples having narrow MWD can be obtained by anionic polymerization processes.[6] A widely used technique, in recent years, has been that of preparing fractions by large-scale preparative fractionations.[7]

This paper will describe the preparation and the characterization of samples of poly(vinyl chloride) (PVC) having relatively narrow MWD by a large-scale fractionation procedure.

Among the various techniques used for fractionating polymers, the fractional precipitation seems to be the simplest way to obtain the large amounts (e.g., 100 g.) of samples needed for physical testing.

In this work, the fractional precipitation method employed was that in which the stepwise addition of a precipitant to a polymer solution causes the progressive precipitation of fractions of decreasing molecular weight.

EXPERIMENTAL

Polymer

The poly(vinyl chloride) sample fractionated was a commercial polymer (Sicron 548). It was obtained by a suspension polymerization process at approximately 50°C. The sample was carefully washed with water for several hours at 95°C. and with methanol, at room temperature, for 2 hr., after which it was dried at 60°C. Its chlorine content, determined by combustion in oxygen and chlorine titration, was 56.0%. The intrinsic viscosity, measured in cyclohexanone at 25°C., was 105 ml./g.

The number-average molecular weight M_n, measured in cyclohexanone by osmometry, was 53,000, and the weight-average molecular weight M_w measured in tetrahydrofuran by light scattering, approximately 130,000.

Selection of the Fractionation Conditions

It is known that a satisfactory fractionation of PVC can be achieved using the following solvent–precipitant mixtures: (a) tetrahydrofuran–water, (b) cyclohexanone–ethylene glycol. Aggregation of the PVC molecules always occurs with mixtures such as cyclohexanone–alcohols or tetrahydrofuran–alcohols[8] so that the efficiency of the fractionation is very low.[9] In a preceding paper[10] it was shown that the resolving power of the cyclohexanone–ethylene glycol pair, in the fractionation of a sample of PVC very similar to the polymer here studied, was exactly the same of the tetrahydrofuran–water system. The latter was used for carrying out the large-scale fractionation described in this work.

The polymer concentration was chosen by carrying out three preliminary fractions, with the usual procedure,[11] at the initial concentrations of 0.3, 1.0, and 2.4 g. PVC for 100 ml. of tetrahydrofuran. The results, expressed as "integral weight distribution function W_x," of every fraction, are plotted in Figure 1 vs. the corresponding value of the intrinsic viscosity $[\eta]$. It is clearly seen that the resolving power of the fractionation at the higher concentration is rather low. The fractionation is satisfactory at the lower concentration, but still acceptable at the concentration of 1 g. PVC/100 ml. solvent. Taking into account the large quantities of solvent required, the latter was chosen for the large-scale fractionation.
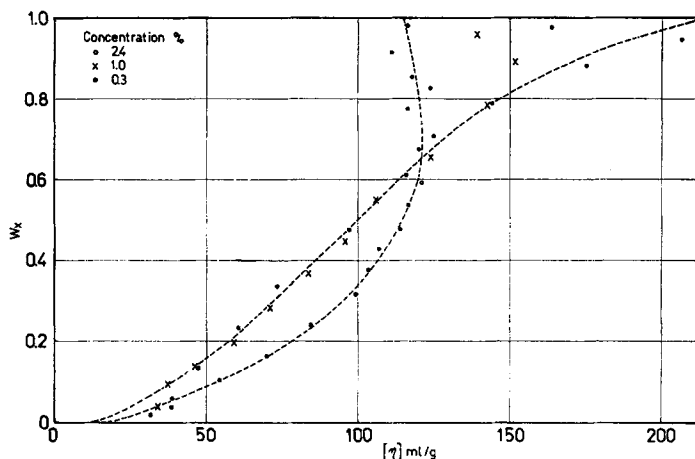
Fig. 1. Integral weight distribution curves obtained at different polymer concentration in the pilot fractionations.

Fractionation Equipment and Procedure

The fractional precipitation has been carried out in a metallic vessel of large capacity thermally isolated by a thick glass-wool jacket. Its bottom was of conical shape and terminated in a 10-mm. bore metallic stopcock. A glass window permitted visual inspection of the inferior part of the vessel. Stirring was provided by a large propeller-type stirrer turning at 45 rpm.

The basic fractionation temperature was 30 ± 2°C., and when necessary the whole vessel could be heated at 42 ± 2°C., by means of steam circulating within a copper serpentine immersed in the solution. Exposure of the solution to the air and solvent evaporation were avoided.

A 3000 g. sample of polymer was initially dissolved in 270 kg. of reagent grade tetrahydrofuran. Water was added under agitation until the solution became turbid due to the beginning of phase separation. When the turbidity was sufficient, the whole solution was heated at 42°C. until homogenity was reached again. The solution was allowed to cool slowly (10 hr.) to the fractionation temperature of 30°C., at which stirring was stopped. The solution was kept at 30°C. for 24 hr., after which the settled precipitate was withdrawn and its density measured. Successive fractions were precipitated from the remaining solution in the same way.

The succession of the fractionation can be seen in Table I, where for each successive fractionation step, the following data are collected: (1) the fractional volume of water in the solution γ_1; (2) the volume of the coacervate V; (3) the density of the coacervate at 30°C.; (4) the polymer content of the coacervate w_2 (%); and (5) the product of w_2 and $[\eta]$, intrinsic viscosity of the polymer recovered from the coacervate.

TABLE I
Characterization of the Coacervates Precipitated in the
Course of the Fractionation

Fraction	Fractional volume of water γ_1	Volume of coacervate, ml.	Density at 30°C., g./ml.	Polymer conc. (weight fraction) w_2	Product $[\eta]w_2$
1	0.121	1,715	0.944	0.081	11.6
2	0.123	1,472	0.940	0.082	12.6
3	0.137	4,500	0.940	0.093	14.0
4	0.1398	3,960	0.940	0.085	12.7
5	0.1418	2,210	0.942	0.094	12.1
6	0.1419	2,850	0.932	0.107	13.4
7	0.1441	2,940	0.933	0.108	12.1
8	0.1472	2,000	0.936	0.115	11.5
9	0.1555	2,680	0.946	0.145	12.2
10	0.1735	1,980	0.970	0.187	12.2
11	0.2435	860	0.994	0.256	11.5

It can be observed that the polymer content of the coacervates increases from 8 to 25% as the fractionation proceeds,[12] while its $[\eta]$ decreases accordingly, so that the product $[\eta]w_2$ remains approximately constant.

In order to isolate the polymer from the coacervates, the latter have been diluted in cyclohexanone at a final concentration of approximately 2% and precipitated in methanol. The polymers have been washed and dried in a vacuum oven at 50°C. overnight.

Characterization of the Fractions

The fractions so obtained have been characterized by chlorine content and dilute solution techniques (viscometry, light-scattering, and osmometry). The results are collected in Table II.

TABLE II
Characterization of the Fractions Obtained by the Large-Scale Fractionation

Fraction	$[\eta]$, ml./g.	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Chlorine content, %	$T_g°$, °C.	Branching index (CH$_3$/100 C)
1	143	88	>470	>5.3	—	—	1.50
2	154	93	>330	>3.5	55.2	80	—
3	151	90	161	1.80	55.5	79	1.65
4	149	98	179	1.82	55.6	77	—
5	129	91	159	1.75	55.4	78	—
6	125	87	155	1.78	55.4	78	—
7	112	78	137	1.76	55.4	77	1.70
8	100	71	121	1.70	56.4	76	—
9	84	54	95	1.75	55.5	75	—
10	65	40	80	2.00	56.2	75	1.70
11	45	25	48	1.92	55.7	73	—

The glass transition temperature of the fractions has been measured by means of a Perkin-Elmer differential scanning calorimeter (DSC-1). The branching index of some fractions has been determined, and three fractions have also been refractionated.

Viscometry. The intrinsic viscosity $[\eta]$ has been evaluated by carrying out measurements in cyclohexanone solutions at $25.0 \pm 0.1°C.$ with a Desreux-Bischoff viscometer.[13] The correction for kinetic energy was of the order of 0.4% for the solvent, and it was therefore never applied. The equation of Huggins was used for extrapolating $[\eta]$ from the viscometric data.

Complete dissolution of the polymer was achieved by heating the cyclohexanone solutions at 80°C. for approximately 30 min.

Osmometry. The osmotic pressure measurements were performed with Hellfritz glass osmometers of the single-chamber type. The osmotic membranes used were of the "Fein" type, produced by Membranfilter. For the conditioning the membranes were transferred from water to acetone, and from acetone to cyclohexanone. The measurements have been carried out at 55°C., controlling the temperature within 0.01°C. Diffusion of polymer through the membranes could not be proved by precipitation with methanol. In a single case, with the polydisperse polymer, it was found that the number-average molecular weight M_n was independent of the temperature of test, between 7 and 78°C., within approximately $\pm 5\%$, which can be considered the best possible accuracy of osmotic measurements.
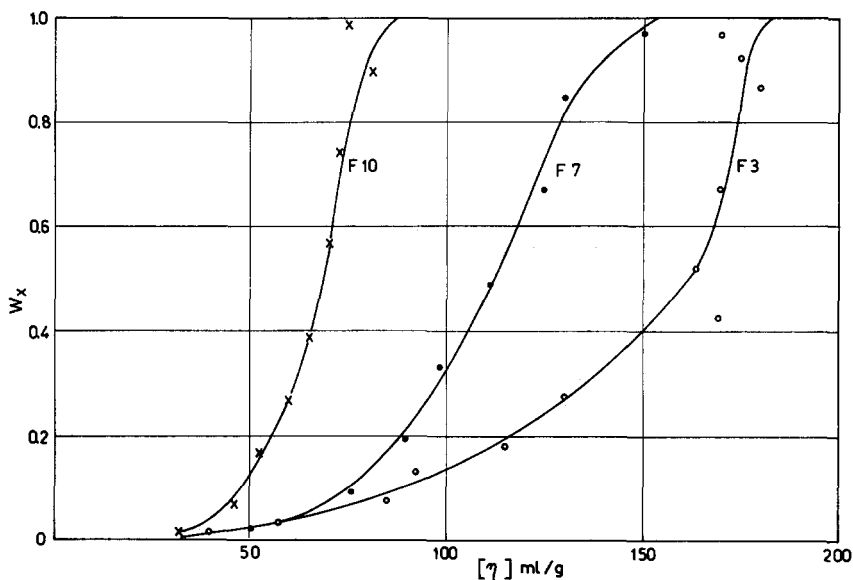

Fig. 2. Refractionation of fractions 3, 7, and 10. Integral weight distribution curves.

Light Scattering. The measurements were carried out in tetrahydrofuran solution, at room temperature, with a Brice-Phoenix photometer. The dissolution of the polymer was carried out at room temperature, since heating of these solutions can result in aggregation of the polymer molecules.[14] The clarification was reached by filtration through G5 sintered glass filters, under slight pressure.

The first two fractions have high weight-average molecular weight due probably to incomplete dissolution in tetrahydrofuran at room temperature. The presence of aggregates in dilute solutions of PVC has been often noticed.[15−17]

Refractionation of Fractions. The fractions Nos. 3, 7, and 10 have been refractionated, in the system cyclohexanone–ethylene glycol, at the initial concentration of 0.30, 0.45, and 0.67 g. PVC for 100 ml. of cyclohexanone, respectively. The results are seen in Figure 2 and Table III.

TABLE III
Refractionation of Fractions F10, F7 and F3

Fraction	$[\eta]$, ml./g.	$M_n \times 10^{-3}$	$M_w \times 10^{-4}$	M_w/M_n
F10–1	75	44	>180	>4
10–2	81	60	100	1.66
10–3	75	45	68	1.51
10–4	70	42	64.5	1.53
10–5	65	38	58	1.52
10–6	60	34	47	1.38
10–7	52	32	40	1.25
10–8	46	25	37.5	1.50
10–9	33	22	30.5	1.38
F7–1	152	163		
7–2	130	115		
7–3	125	105		
7–4	112	89		
7–5	97	72		
7–6	88	59		
7–7	76	49		
7–8	50	30		
F3–1	167	136		
3–2	175	111		
3–3	180	138		
3–4	170	171		
3–5	164	166		
3–6	169	151		
3–7	130	122		
3–8	115	103		
3–9	92	77		
3–10	85	52		
3–11	57	35		
3–12	40	24		

Most of the subfractions obtained have been characterized by viscometry and osmometry, and those obtained from fraction 10 have been studied also

by light-scattering measurements. The differential weight distribution curves obtained from Figure 2 are compared in Figure 3 with the distribution curve of the original polymer.
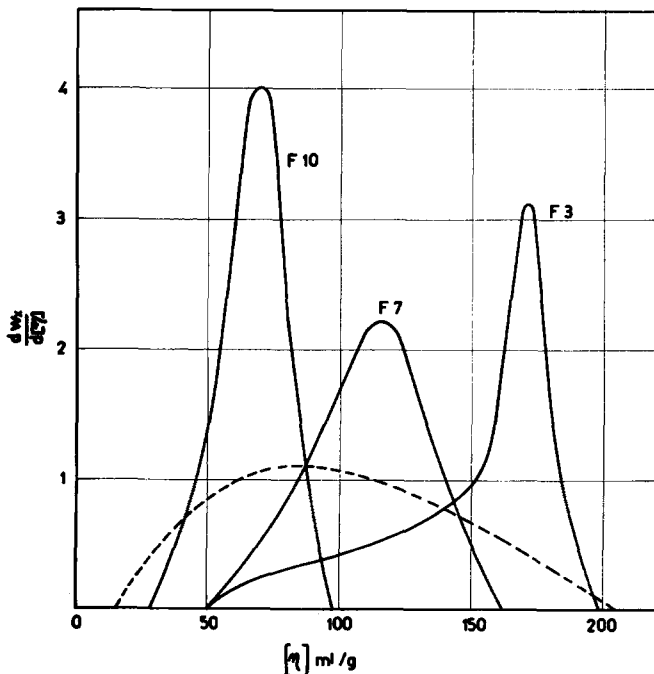

Fig. 3. Differential weight distribution curves obtained from Figures 1 and 2 by graphical differentiation.

Branching Index. The branching index of several fractions has been determined[18] by the well-known infrared method after reduction of the samples with lithium aluminum hydride.[19,20]

The results shown in Table II indicate that the fractions are all branched at the same extent, irrespective of their molecular weight.

Glass Transition Temperature. The glass transition temperature of the fractions changes only slightly with the molecular weight, in the range of molecular weight investigated (M_n larger than 25,000).

A large decrease of T_g is usually found, for linear polymers, only when M_n is of the order of 10,000 or less.[1,2]

RESULTS AND DISCUSSION

Fractionation

From Figure 1 it is seen that the polymer concentration influences strongly the efficiency of the fractionation. At 2.4% concentration almost 60% of the polymer is precipitated without appreciable fractionation,

while at 0.3% concentration only the first fraction is precipitated anomalously. At 1% concentration the efficiency is still good, as seen from Figure 1.

The integral distribution curve obtained in the large-scale fractionation, not shown in Figure 1, is less satisfactory than the corresponding curve at 1% concentration obtained in the pilot fractionation. The molecular weight of the fractions, as measured by their $[\eta]$, lies in the same range (from $[\eta] = 40$ to $[\eta] = 150$ ml./g.) but the curve as a whole is slightly displaced, due to a smaller separation efficiency. This may be caused by the difficulty of scaling up the precipitation procedure and the temperature control of the laboratory fractionation.

The first one or two fractions isolated show the phenomenon of "reverse precipitation," reported also by other authors.[10,21-23] This phenomenon is particularly severe when the fractionation is carried out at high concentration, or with solvent–precipitant pairs not correctly chosen,[8] or with crystalline PVC,[23] and can be attributed to aggregation of the polymer molecules during precipitation.

The molecular weight distribution of the fractions is narrower than that of the original polymer, as can be argued from Figure 3, but the heterogeneity index M_w/M_n is still relatively high, being of the order of 1.8. It is surprising that even the subfractions obtained from fraction 10 have a high M_w/M_n ratio (approximately 1.4, see Table III).

The data of several authors[23-26] show that the PVC fractions are always rather polydisperse, as found in the present work. This may be partly due to errors made in the measurements of M_w by light scattering (incomplete clarification of the solutions and polymer aggregation[16,27]) and of M_n by osmometry, but it must of remembered that even for poly(methyl methacrylate) fractions one can find in literature average heterogeneity ratios as high as 1.4 and 1.5.[28]

Molecular Weights

The results of Tables II and III can be used to establish the relation between the molecular weight and the intrinsic viscosity of PVC fractions, as expressed by the Mark-Houwink equation

$$[\eta] = KM^\alpha \tag{1}$$

For monodisperse fractions, it would be immaterial to use the number-average molecular weight M_n or the weight-average molecular weight M_w.

The data of Table II and III indicate however that the fractions are rather polydisperse, and two different sets of the constants K and α of eq. (1) are obtained for M_w and M_n.

For the weight-average molecular weight M_w the resultant equation, obtained from a large number of fractions,[27] is:

$$[\eta] = 6 \times 10^{-3} M_w^{0.84} \text{ ml./g.} \tag{2}$$

For the number-average molecular weight M_n the $[\eta]/M_n$ data are plotted in Figure 4, where several results obtained on PVC fractions not shown in Table III have been added.

A set of data obtained recently by Bohdanecky and co-workers[29] on carefully fractionated PVC samples is also shown in Figure 4.

Within the range of molecular weight from 10,000 to 100,000 the points of the log $[\eta]$ − log M_n plot define a fair straight line, described by the equation

$$[\eta] = 9 \times 10^{-3} M_n^{0.84} \text{ ml./g.} \tag{3}$$

which can be compared with similar equations obtained by other authors on PVC fractions.

In Table IV are listed data from 12 different sources.[15,25,26,30−38] Although the viscosities have been measured in two solvents and between 20 and 25°C., these data should be comparable, because $[\eta]$ varies only slightly with temperature, and the intrinsic viscosities measured in tetrahydrofuran differ at most by 8% from those measured in cyclohexa-
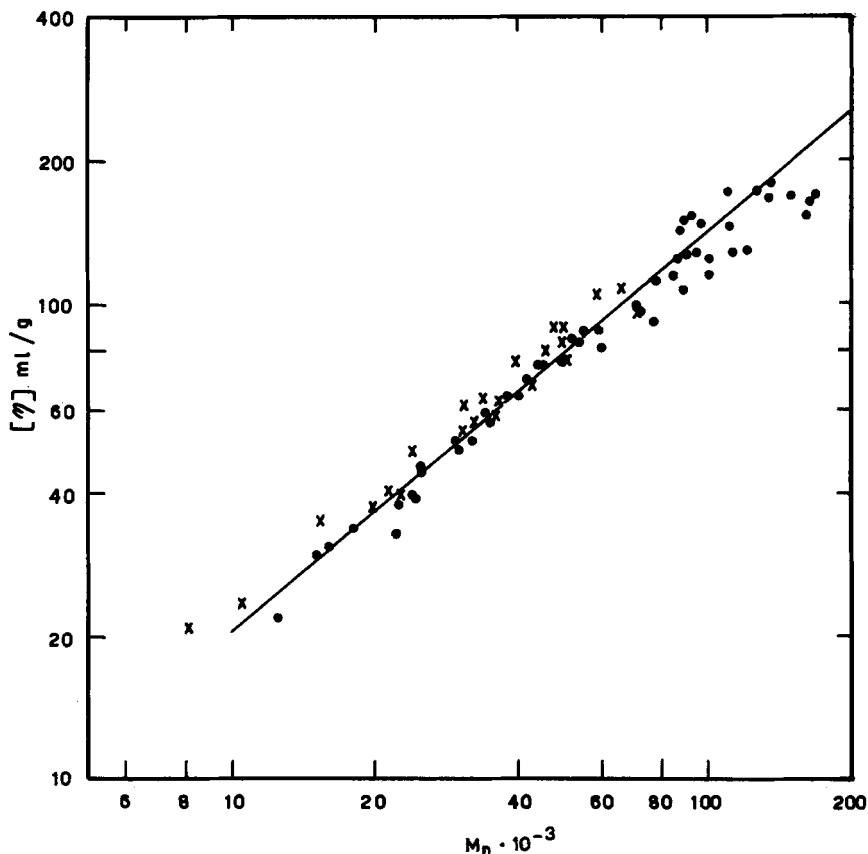

Fig. 4. The $[\eta]$–M_n dependence for PVC fractions: (●) this work; (×) ref. 29.

TABLE IV
Parameters of the Mark-Houwink Equation for PVC Fractions

Authors[a]	Ref.	α	$K \times 10^3$	Number of frac-tions	Solvent[b] $[\eta]$	Solvent M_n
Mead-Fuoss	30	1.0	1.12	4	CX (25°C.)	—
Fournier-Thiesse	31	0.76	15.6	12	CX (20°C.)	—
Staudinger-Haeberle	32	1.0	1.6	10	CX (20°C.)	THF (27°C.)
		0.76	21.5	8	CX (20°C.)	THF (27°C.)
Oth	15	0.85	10	3	THF (25°C.)	THF (25°C.)
Mencik	33	0.56	204	32	CX (25°C.)	THF (25°C.)
Bier-Kraemer	34	1.0	1.4	24	CX (20°C.)	THF (25°C.)
		0.63	113	8	"	"
Krasovec	35	0.84	8.3	19	THF (20°C.)	THF (20°C)
Batzer-Nisch	36	0.92	3.6	62	THF (20°C.)	THF (27°C.)
Guyot-Benevise	37	0.79	15.3	6	THF (25°C.)	THF (25°C.)
Endo	38	0.72-1.08	30-0.5	—	CX (30°C.)	CX (30°C).
Moore-Hutchinson	25	0.56	208	6	CX (25°C.)	CX (25°C.)
Freeman-Manning	26	0.76	—	7	THF (25°C.)	THF (—)

[a] Fractionations carried out always by successive precipitation in the system tetra-hydrofuran–water with the exception of refs. 30 and 37, where fractional extractions have been used.

[b] CX, cyclohexanone; THF, tetrahydrofuran.

none.[15,27,32] Moreover, almost all the fractionations have been carried out with the same procedure, and the molecular weights of the fractions are always restricted in the range 20,000–200,000.

Nevertheless, there are very large differences among the values of K and α determined by various authors.

It is seen that some authors obtain exponents α as low as 0.56, which should correspond to solutions close to the θ-conditions (i.e., to bad solvents) while most authors find values of α between 0.8 and 1.0, which correspond to polymer solutions in good solvents. Since it is well established that tetrahydrofuran and cyclohexanone are good solvents for PVC, the discrepancies of Table IV have to be ascribed to experimental errors or to structural differences of the PVC macromolecules.

The sets of M_n and $[\eta]$ data relative to the authors listed in Table IV intersect and overlap over the entire M_n range, as can be seen in Figure 5. Large deviations are observed for the data of Fournier and Thiesse,[31] obtained in 1946, for the data of Mencik,[33] and for all the PVC fractions having $[\eta]$ larger than 130 ml./g. (M_n larger than 10^5).

It has been shown that the PVC molecules of high molecular weight can associate both in tetrahydrofuran[14,23,27] and in cyclohexanone,[15,39,40] so that the discrepancies of Figure 5 above $[\eta]$ = 130 ml./g. could be attributed to molecular association.

However, several authors are of the opinion that the anomalous behavior of the high molecular weight PVC fractions can be explained by
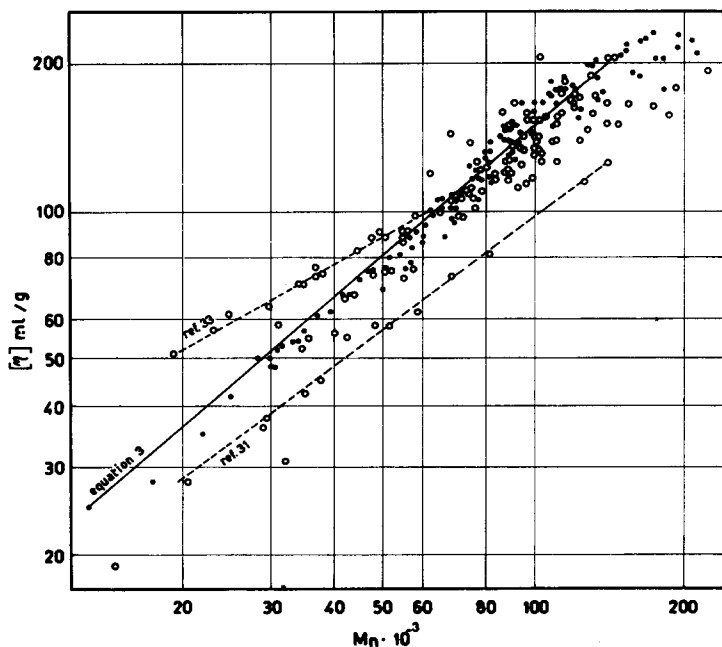
Fig. 5. The $[\eta]-M_n$ dependence for PVC fractions according to the authors listed in Table IV: (●) refs. 32, 35, and 36; (○) other authors.

structural differences, i.e., by chain branching.[26,34,35] The determination of the branching index of several fractions, carried out in the course of this work, shows however that the fractions are practically branched at the same extent (1.6–1.7 methyl groups per hundred carbon atoms) so that in the authors opinion the anomalies of high molecular weight PVC solutions are attributable only to aggregation. It is known that high polydispersity ratios M_w/M_n are found also for polyacrylonitrile in solution, due to the polymer molecules association.[41]

It remains to be explained why different values for K and α have been found for PVC by different investigators in the range of M_n below 80,000, where the association should be negligible.

Several equations reported in Table IV have been obtained from very few experimental points (see refs. 15, 25, 30, 34, 37, 38) and their reliability should not therefore be considered very high.

The large sets of data obtained by the authors of refs. 32, 35, and 36, when plotted all together, give an equation identical to eq. (3).[42] Therefore, only the results of few authors[31,33] differ appreciably from the data presented in this work. At present, it is difficult to make any reasonable assumption which can explain the low exponent obtained by Mencik,[33] and the high molecular weights measured, at relatively low values of $[\eta]$, by Fournier-Thiesse.[31]

The eq. (3) can be considered equivalent to the eq. (2), obtained from light-scattering measurements if it is assumed that the polydispersity ratio of the fractions is constant and approximately equal to 1.5, as indicated by the results of Tables II and III.

It is interesting to note that the literature values of K and α listed in Table IV are not independent, but show a distinct regression.

Van Krevelen and Hoftyzer[43] found empirically that for a number of polymer–solvent systems the K and α values were related by the equation:

$$\log K = 0.58 - 3.0\alpha \qquad (4)$$

which they claimed to be of general validity and which was used to obtain a general form of the Mark-Houwink eq. (1).[43] For PVC, the plot of log K vs. α, shown in Figure 6, gives the following regression:

$$\log K = 2.3 - 5.1\alpha \qquad (5)$$

The eq. (5) differs considerably from eq. (4), whose general applicability can therefore be considered only a rough approximation.
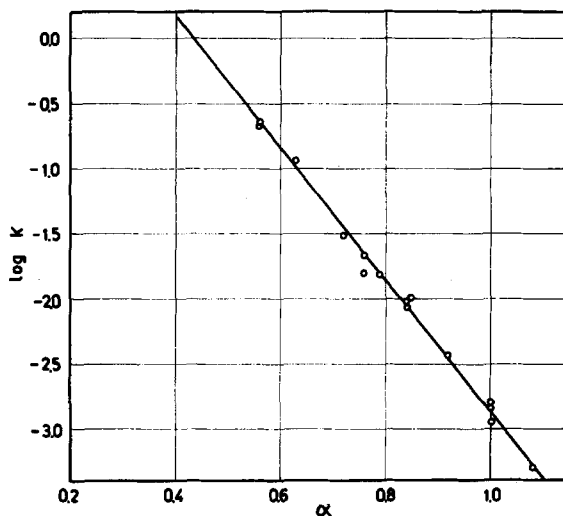

Fig. 6. Literature values of log K and α (Table IV) plotted according to ref. 43; straight line given by eq. (5).

References

1. O. Fuchs, in *Kunststoffe*, K. A. Wolf, Ed., Springer-Verlag, Berlin, 1962, Vol. I.

2. M. J. Kohan, in *Engineering Design for Plastics*, E. Baer, Ed., Reinhold, New York, 1964.

3. A. V. Tobolsky, R. Schaffhauser, and R. Böhme, *J. Polymer Sci. B*, **2**, 103 (1964); A. V. Tobolsky and K. Murakami, *J. Polymer Sci.*, **47**, 55 (1960).

4. K. Ninomiya and J. D. Ferry, *J. Phys. Chem.*, **67**, 2292 (1963); *ibid.*, **67**, 2297 (1963).

5. V. R. Allen and T. G Fox, *J. Chem. Phys.*, **41**, 337 (1964); T. G Fox and V. R. Allen, *J. Chem. Phys.*, **41**, 344 (1964).

6. H. W. McCormick, F. M. Brower, and L. Kin, *J. Polymer Sci.*, **39**, 87 (1959).

7. G. R. Williamson, B. Wright, and R. N. Haward, "Congress on Advances in Polymer Science and Technology," London, May 1963; A. S. Kenyon, I. O. Salyer, J. E. Kurz, and D. R. Brown, Am. Chem. Soc. Meeting, Chicago, September 1964; J. E. Guillet, R. L. Combs, D. F. Slonaker, D. A. Weemes, and H. W. Coover, *J. Polymer Sci. A*, **1**, 2869 (1963).

8. Z. Menick, *Chem. Zvesti*, **9**, 165 (1955); *J. Polymer Sci.*, **17**, 147 (1955).

9. P. Doty, H. Wagner, and S. Singer, *J. Phys. Colloid Chem.*, **51**, 32 (1947); A. Peterlin, Simposio Intern. Chim. Macromol., Milan–Turin, 1954.

10. G. Garbuglio, G. Pezzin, and G. Badoni, *Chim. Ind. (Milan)*, **46**, 797 (1964).

11. G. Pezzin, G. Talamini, and G. Vidotto, *Makromol. Chem.*, **43**, 12 (1961).

12. F. Patat and J. Klein, *Makromol. Chem.*, **93**, 230 (1966).

13. V. Desreux and J. Bischoff, *Bull. Soc. Chim. Belges*, **59**, 93 (1950).

14. R. Gautron and G. Wippler, *J. Chim. Phys.*, **58**, 754 (1961).

15. A. Oth, 27 Congr. Inter. Chimie Industrielle, Bruxelles, 1954.

16. J. Hengstenberg and E. Schuch, *Makromol. Chem.*, **74**, 55 (1964).

17. P. Kratochvil, *Collection Czech. Chem. Commun.*, **29**, 2767 (1964).

18. G. Boccato, A. Rigo, G. Talamini, and F. Zilio-Grandi, personal communication.

19. J. D. Cotman, *Ann. N. Y. Acad. Sci.*, **57**, 417 (1953).

20. A. Nakajima H. Hamada, and S. Hayashi, *Makromal. Chem.*, **95**, 40 (1966).

21. G. Garbuglio, A. Mula, and L. Chinellato, in *Macromolecular Chemistry, Prague 1965 (J. Polymer Sci. C*, **16**), O. Wichterle and B. Sedláček, Chairmen, Interscience, New York, 1967, p. 1529.

22. M. Hlousek and J. Lanikova, *Chem. Průmysl*, **16**, 160 (1966).

23. T. Kobayashi, *Bull. Chem. Soc. Japan*, **35**, 726 (1962).

24. O. Oth and V. Desreux, *Bull. Soc. Chim. Belges.*, **63**, 261 (1954).

25. W. R. Moore and R. J. Hutchinson, *Nature*, **200**, 1095 (1963).

26. M. Freeman and P. P. Manning, *J. Polymer Sci. A*, **2**, 2017 (1964).

27. G. Pezzin, G. Talamini, and N. Gligo, *Chim. Ind. (Milan)*, **46**, 648 (1964).

28. T. G Fox, J. B. Kinsinger, H. F. Mason, and E. M. Schuele, *Polymer*, **3**, 71 (1962); S. Krause and E. Cohn-Ginsberg, *ibid.*, **3**, 565 (1962).

29. M. Bohdanecky, K. Solc, P. Kratochvil, M. Kolisky, M. Ryska, and D. Lim, *J. Polymer Sci.*, in press.

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

31. M. Fournier and X. Thiesse, *C. R. Hebd. Seances Acad. Sci.*, **222**, 1437 (1946).

32. H. Staudinger, and M. Haeberle, *Makromol. Chem.*, **9**, 35 (1952).

33. Z. Mencik, *Chem. Listy*, **49**, 1598 (1955).

34. G. Bier and H. Kraemer, *Makromol. Chem.*, **18/19**, 151 (1956).

35. F. Krasovec, *J. Stefan Institute (Ljublijana)*, **3**, 202 (1956).

36. H. Batzer and A. Nisch, *Makromol. Chem.*, **22**, 131 (1957).

37. A. Guyot and J. P. Benevise, *Ind. Plast. Mod.*, **13**, 37 (June 1961).

38. R. Endo, *Chem. High Polymers, Japan*, **18**, 143 (1961).

39. P. Kratochvil, V. Petrus, P. Munk, M. Bohdanecky, and K. Solc, in *Macromolecular Chemistry, Prague 1965 (J. Polymer Sci. C*, **16**), O. Wichterle and B. Sedláček, Chairmen, Interscience, New York, 1967, p. 1257.

40. M. Kolinsky, M. Ryska, M. Bohdanecky, P. Kratochvil, and K. Solc, paper presented at IUPAC Symposium on Macromolecular Chemistry, Prague, Sept. 1965.

41. R. Chiang and T. C. Stauffer, *J. Polymer Sci.*, in press.

42. G. Talamini and G. Vidotto, *Chim. Ind. (Milan)*, **46**, 16 (1964).

43. D. W. Van Krevelen and P. J. Hoftyzer, *J. Appl. Polymer Sci.*, **10**, 1331 (1966).

Résumé

On a effectué un fractionement par precipitation de 3,000 g. de PVC. La distribution des poids molecularies de quelques fractions a été determinée par refractionement. Les fractions ont été étudiées par des mesures viscosimetriques, osmometriques, de diffusion de la lumière et de transition vitreuse. On a fait une analyse critique des résul-

tats trouvés dans la bibliographie sur la characterisation des poids molecularies des fractions de PVC.   On a trouvé que les données viscosimetriques et osmometriques sont en bon accord au dessous de $M = 10^5$, et que à poids molecularies superieurs les differences peuvent etre attribueés à l'aggregation des macromolecules.

Zusammenfassung

Eine Fraktionierung von Polyvinylchlorid in grossem Masstab (3,000 g.) wurde nach der Methode der fraktionierten Fällung auseführt.   Die Molekulargewichtsverteilung einiger Fraktionen wurde durch Refraktionierung bstimmt.   Die Fraktionen wurden auch durch Viskosimetrie, Osmometrie, Lichtstreuung und Messung der Glasumwandlungstemperatur charakterisiert.   Ein kritischer Überblick über die Literaturdaten bezüglich der Molekulargewichts-charakterisierung von Polyvinylchloridfraktionen wurde gegeben.   Bei Molekulargewichten unterhalb 10^5 stimmen die meisten viskosimetrischen und osmotischen Daten gut überein.   Die Literatur-diskrepanzen oberhalb 10^5 können auf Aggregationserscheinungen zurückgeführt werden.