

An Improved Block Osmometer Used to Determine the Molecular Weight Distribution of Commercial Poly(vinyl Chloride)

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Synopsis

Commercial PVC was fractionated into five fractions by the incremental addition of a nonsolvent to the polymer solution. The number-average molecular weights of the original sample and fractions were determined by osmometry. The weight-average molecular weights of the sample and fractions were also determined by means of viscosity measurements and by the application of a Mark-Houwink type of equation. From a knowledge of the polydispersity of each fraction and the assumption that the number distribution of molecular weights was Gaussian, the molecular weight distribution for the composite sample was determined. The block osmometer used incorporated most of the features found useful in earlier work to facilitate rapid and reliable osmotic pressure measurements. In addition, microvolume-regulating valves were utilized in the capillary tube lines to permit an independent precise positioning of the interface level in either capillary.

INTRODUCTION

The complete characterization of a polymeric material includes a knowledge of its molecular weight distribution. The molecular weight distribution frequently gives some insight into the kinetics of polymerization, the adequacy of the control of the process, and, in general, the polymer properties. Although gel permeation chromatography (GPC) has opened a valuable new approach to the characterization of polymers, it has not entirely supplanted osmometry in measuring number-average molecular weights of many polymers, such as, for example, vinyl chloride polymers. Monodisperse PVC has not been available for the direct calibration of GPC instruments in the same way that monodisperse polystyrene samples have, and, as a result, osmometry still has a role to play in the calibration of GPC instruments if not for the complete determination of the molecular weight distributions.

A procedure for obtaining a complete molecular weight distribution using osmometry can involve the following steps: (1) design and construction of osmometer; (2) fractionation of polymer sample; (3) determination

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of number-average molecular weights for fractions; (4) determination of weight-average molecular weights for the fractions; and (5) reconstitution of molecular weight distribution for original polymer sample from information for the fractions. Improvements in reliability or speed of any of these operations would necessarily facilitate the overall process of obtaining an accurate molecular weight distribution.

A considerable amount of research has already been directed toward improving the design of block osmometers.¹⁻³ We have chosen a number of desirable features of different osmometers that were reported to perform satisfactorily and have incorporated them into one design. In addition, we have used readily available components and relatively simple construction methods in an attempt to make the block osmometer a more frequently used laboratory tool.

Ideally, fractionation of a polymer sample produces a large number of essentially monodisperse fractions. If this were achieved, the task of producing a molecular weight distribution would be considerably simplified. Most commonly, even with considerable care and time, only a few fractions are recovered, of different weights, usually with less than 100% recovery of polymer, far from being monodisperse but instead having a considerable degree of overlapping between them. In fact, then, fractionation usually produces fractions which are small in number, unequal in mass, overlapping in molecular weights, and unequal in polydispersity. It is therefore useful to know not only the weight of polymer and number average of each fraction, but also some other average (preferably the weight average) molecular weight from which the degree of polydispersity for each fraction can be estimated.

Although a light-scattering photometer or other such device would be useful in obtaining the weight-average molecular weight, an indirect route is often available. Intrinsic viscosity-weight average correlations are available for a number of polymers; and hence for these, providing that there was reason to assume that the polymer structure was similar, viscosity measurements could be used to estimate the weight-average molecular weight.

The conventional way to treating data for fractionated polymers consists of plotting the cumulative number of molecules (moles) or cumulative weights in the fractions versus the molecular weights, as discussed by Blackley.⁴ The graphic differentiation of the curve would be expected to yield the number or weight distribution. Such a procedure has the disadvantages that it requires a considerable number of fractions (at least ten) to locate with accuracy the inflection points, and any inaccuracies in the measurements are greatly amplified on taking slopes from the cumulative number or weight diagrams.

By using another procedure, it is possible to determine a molecular weight distribution with as few as five fractions. In this procedure the assumption is made that, within a particular fraction, the numbers of molecules are normally distributed regardless of the extent of overlapping

with other fractions. Further, the width of the normal distribution can be determined if both the number- and weight-average molecular weights for the fraction are known.⁵ The standard deviation can be obtained from:

$$\sigma_{n_j}^2 = (\bar{M}_{n_j})^2 \left(\frac{\bar{M}_{w_j}}{\bar{M}_{n_j}} - 1 \right) \quad (1)$$

A separate distribution curve can be constructed for each fraction, making the area under the curve (and the ordinates) proportional to the mole fraction of polymer in the particular fraction. Then the sum of the areas under the curves for all fractions would be normalized, or equal to 1 gram-mole. The number of moles and mole fraction can be readily calculated:

$$N_j = \frac{W_j}{\bar{M}_{n_j}} \quad (2)$$

$$n_j = \frac{N_j}{\sum N_j} \quad (3)$$

A cumulative number distribution for the original polymer sample can be constructed by summing the contributions from all the fractions corresponding to particular molecular weights. It is also possible to construct a weight distribution of molecular weights by multiplying the value of the number distribution function by the molecular weight to which it corresponds.

When the number- and weight-average molecular weights for the unfractionated sample have also been measured, it is possible to check the consistency of all the measurements. The number and weight averages for the sample can be compared with those calculated from the information for the fractions:

$$\bar{M}_{ns} = \frac{\sum W_j}{\sum N_j} = \frac{W_s}{\sum W_j / \bar{M}_{n_j}} \quad (4)$$

$$\bar{M}_{ws} = \frac{\sum W_j \bar{M}_{w_j}}{\sum W_j} \quad (5)$$

The weight-average molecular weights for each fraction should be associated with the mass of each fraction.⁶

We have fractionated a sample of commercial suspension-polymerized PVC into five fractions, and have measured the mass and the number- and weight-average molecular weights for each fraction. The same measurements were also performed for the original composite sample. The results for the fractions were developed to show the distribution of molecular weight for the original sample. Although the number of fractions was insufficient to accurately define secondary peaks in the molecular weight distribution, the distribution obtained indicates the general utility of the method proposed.

EXPERIMENTAL

The Osmometer

The basic considerations in the design of osmometers have been discussed by Hookway⁷ and include, for the purpose of rapid attainment of equilibrium; a small cell volume, a large membrane area, and a small cross-sectional area of capillary tubes. Block osmometers have been found to be reliable, rugged, and highly serviceable.¹⁻³

The osmometer used in our work was designed to use Schleicher and Schuell type 08, large (65 mm) membranes which were recommended for organic solvents and for minimum molecular weights of 20,000. The Schleicher and Schuell type B-18, B-19, and B-20 membranes, although specified for aqueous solutions, have been found suitable for certain organic solvents.⁸

Figure 1 shows details of the osmometer construction. The membrane support faces were machined from two circular stainless steel blocks with matching concentric grooves, semicircular in cross section and of $1/16$ -in.

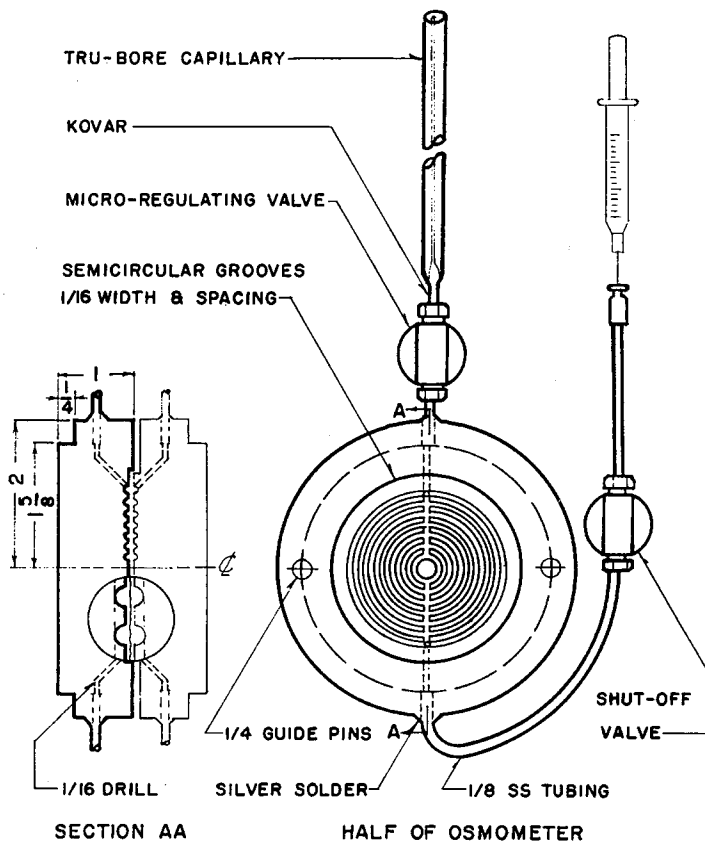


Fig. 1. Osmometer details.

widths. Thus the maximum span of membrane was short, while nearly 50% of the membrane area was exposed to the solvent. The rear portions of the blocks were initially machined so that the blocks could be accurately fitted (repeatedly as required) into the chuck of a lathe for refinishing the membrane support areas. No compelling reasons were found for immersing the complete osmometer in a solvent jar, involving additional construction difficulties, so that the osmometer was constructed with two identical chambers. For good temperature control, the osmometer was immersed directly in a constant temperature bath ($\pm 0.01^\circ\text{C}$). The edge of the membrane and the two osmometer block faces formed a seal between the two chambers of the osmometer and the water in the bath. An original version of the osmometer included a large O-ring for installation between the blocks to keep any water from touching the membrane edge. The use of an O-ring was subsequently found entirely unnecessary. The two faces were clamped together with an stainless steel C-clamp so that the compressive force was centrally exerted, and guide pins were utilized to ensure alignment. A similar method was utilized by Freeman and Manning.⁹ The use of bolts for applying a uniform pressure on the membrane was found to require considerable care and sometimes to cause the membrane to tear if too much pressure was applied at one spot.

Two pieces of high-pressure stainless steel tubing, $1/8$ -in. OD, were silver soldered into each block to serve as filling and hydraulic head measuring lines. After the lines were fixed in the blocks, the faces required refinishing because of thermal distortion. Microneedle shut-off valves (available from Whitey Manufacturing Company) were connected to the inlet lines at the bottom of the osmometer by means of regular compression fittings. One of the very useful additions to the design of the osmometer was the installation in the capillary lines of two microneedle valves requiring 14 turns from the completely open position to the completely closed position, to serve as solvent or solution volume regulators. By means of these valves, containing at most 0.5 ml of liquid, the position of the meniscus in either capillary could be easily and independently adjusted over a wide range of positions.

The capillaries used for hydraulic head measurements were of a uniform 0.5-mm bore purchased from the Wilmad Glass Company. Although smaller-bore capillaries were available, the 0.5-mm bore was found most satisfactory, minimizing movements resulting from minor temperature fluctuations, yet highly sensitive to small transfers of solvent through the membrane. The capillaries were joined to the volume-regulating valves by means of $1/8$ -in. OD Kovar glass connectors. Contrary to previous experience of pitting with Kovar,² no significant corrosion of the Kovar was observed. The use of Kovar connectors permitted easy replacement of the capillaries if accidentally broken.

Each chamber of the osmometer could be separately filled by means of a syringe and septum stopper while the osmometer was immersed in the bath. An osmometer support was used to hold the osmometer in a vertical

position. A bench-top cathetometer reading to 0.01 mm and an electric timer were the only other auxiliary devices required in conjunction with the osmometer.

Fractionation

A commercial sample of PVC, Esso PVC grade 373, produced by a suspension polymerization process was obtained from Imperial Oil Enterprises, Sarnia. The sample was of relatively high molecular weight and therefore relatively difficult to dissolve in any solvent. The solution process has been described by Allen¹⁰ as consisting of two steps, the initial one involving a slow swelling of the polymer the rate of which cannot be enhanced by agitation, and the second involving the disintegration and actual disappearance of the solid polymer to form a true solution. It appears probable that the initial process of solution is diffusion controlled; that is, the rate of polymer swelling is largely determined by the rate of solvent diffusion through the partially swollen polymer. In this event, a solvent which would diffuse more rapidly would swell the polymer more quickly even if it were not the best available solvent in terms of its capacity for dissolving polymer. Then it should be possible to use one solvent with a high diffusivity to increase the rate of swelling and a second solvent in which the polymer solubility is high to reduce the overall time required for solution.

Moore and Hutchinson¹¹ have reported that cyclohexanone is the best among several common solvents for PVC. However, especially while attempting to make up fairly concentrated solutions, it was found that even after several days, the polymer sample did not dissolve in cyclohexanone. When the sample was first soaked in acetone for a period of about one day, subsequent solution in added cyclohexanone was facilitated. Although the role of the initial soaking step is not clear, the use of the two solvents definitely increased the rate of solution.

Polymer fractions were precipitated by the addition of a miscible nonsolvent solution. As with the solution process itself, we did not restrict the choice of nonsolvents to pure liquids. Distilled water alone as a precipitant resulted in the complete precipitation of the sample in the form of a very fine suspension, colloidal in some instances, with the addition of only a very small amount of water. A mixed nonsolvent solution consisting of water, ethanol, and acetone in volumetric proportions of 40, 40 and 20% produced a fine precipitate which could be centrifuged and hence separated from the polymer solution. The ethanol in the precipitant solution produced much less colloidal precipitate that was difficult to separate, while the acetone served merely as a diluent increasing the total volume of precipitant required. Once separated from the supernatant liquid, each fraction was redissolved in acetone and cyclohexanone, and reprecipitated. The reprecipitated fractions were filtered and dried to constant weight.

Viscosity Measurements

The fractions and sample were dissolved in THF for viscosity and osmotic pressure measurements. The two highest molecular weight fractions took particularly long to dissolve (about five days) and only dilute solutions (less than 2 g/liter) were prepared. Less difficulty was encountered in dissolving the lower molecular weight fractions, so that these were prepared in higher concentrations. Aliquot portions of the solutions were further diluted with THF to prepare the lower polymer solution concentrations.

Viscosities of the solvent and polymer solutions were measured by means of a calibrated Canon-Fenske viscometer (purchased from the Fisher Scientific Company) immersed in a constant temperature bath ($\pm 0.02^\circ\text{C}$). The capillary tube of the viscometer was of such a diameter that all the efflux times exceeded the minimum 100 seconds required for good viscosity measurements.

Plots of reduced viscosity and solution concentration were linear. Least-mean-square lines were fitted to the data and used to determine the best intrinsic viscosities by extrapolation to zero concentration. The intrinsic viscosities were used to calculate the corresponding weight-average molecular weights by means of the Mark-Houwink equation obtained by Freeman and Manning⁹:

$$[\eta]_{\text{THF}}^{25^\circ\text{C}} = 1.63 \times 10^{-4} (\bar{M}_w)^{0.766} \text{ (in dl/g)} \quad (6)$$

Freeman and Manning obtained weight-average molecular weights of fractionated polymers by means of light-scattering measurements. Somewhat different constants for the Mark-Houwink equation were obtained by Bohdanecky et al.¹² for narrow molecular weight fractions after correction for branching in the polymer. Because the fractions we obtained were not narrow in range of molecular weights, we used the former constants which we considered more representative of our particular fractions.

Osmotic Pressure Measurements

The cellulose-derivative Schliecher and Schuell type 08 membranes which were received in a 20% aqueous alcohol solution were first conditioned to pure ethanol in a series of solution baths. The membranes were conditioned to THF after installation in the osmometer. A wet membrane was carefully laid on one of the osmometer faces, the matching half of the osmometer was positioned directly on top with the aid of the guide pins, and the two halves were clamped together. While supported vertically in the bath, both chambers of the osmometer were filled with ethanol by means of a syringe. The conditioning was performed in the standard method of using solvent solutions of increasing THF concentration on both sides of the membrane. Initial attempts to condition the unsupported membrane were unsuccessful because of the tendency of the membranes to shrink.

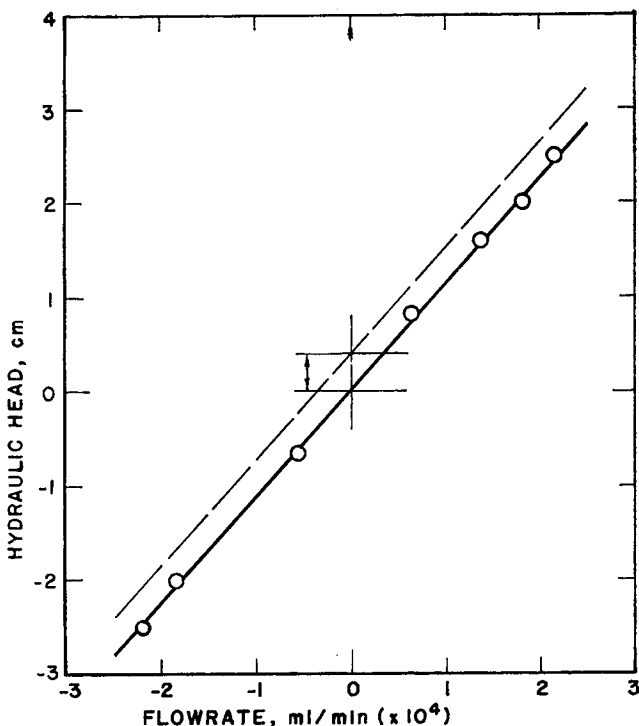


Fig. 2. Flow rate-hydraulic head interpolation for membrane asymmetry with THF solvent.

It was relatively easy to detect leakage or entrapped air bubbles in the osmometer. When liquid was flushed through each chamber, any bubbles which were present were usually dislodged and flushed out. If any remained, the interface levels could not be adjusted to remain at the same elevation in both capillaries because the density of the liquid in the capillary system containing the bubble was effectively reduced. By observing a continued net movement of liquid levels in both capillaries, it was apparent that leakage was occurring.

The osmometer was filled with polymer solution after it had been placed in the constant temperature bath and had attained thermal equilibrium. The procedure usually consisted of simply displacing the solvent with the solution by using a syringe and subsequently flushing the solution through the osmometer to ensure that the solution in the osmometer was undiluted. When the amount of solution available was insufficient for repeated flushing, the solvent was initially withdrawn by means of the syringe prior to filling, and the chamber was filled and flushed only once with about 5 ml of solution.

Prior to the measurement of osmotic pressure, it was necessary to test the membrane for possible asymmetry. If it is considered that neither the extent of solvent-membrane interaction nor the membrane structure itself

changes with time, nor the solvent flow rate or the imposed hydraulic difference, then the rate of solvent flow through the membrane becomes a problem in hydrodynamics. If the flow is considered to be laminar because of the small size of the pores, then the Poiseuille law should apply; the flow should be directly proportional to the imposed pressure difference. One can then speak of a pore size (length and diameter) equivalent to the actual tortuous path through the membrane. It would be expected that for a membrane of uniform porosity and properties, and for pure solvent on both sides of the membrane, the flow through the membrane would be directly proportional to the imposed pressure difference, regardless of the direction of flow. This hydraulic consideration permits a simple test for membrane asymmetry. For an initial hypothesis that the membrane is symmetrical in all respects, a plot of flow rate versus imposed pressure difference should not only be linear but also should pass through the point of zero flow through the membrane corresponding to a zero imposed pressure differential. Such a plot is shown in Figure 2. If the line does not pass through the point of zero flow corresponding to a zero pressure differential (dotted line), then the extent of membrane asymmetry (or other extraneous effects) is readily apparent. It can be mentioned that the micro-volume-regulating valves installed in the osmometer greatly facilitated the measurement of flow rate–pressure difference relationships.

The same hydrodynamic principles are equally applicable to the measurement of osmotic pressure and form the basis of the “dynamic methods.” Osmotic pressure can be considered to be a constant pressure exerted through the membrane by the solvent which, if there is no superimposed pressure difference, causes flow through the membrane. The superimposed pressure difference just necessary to stop the flow through the membrane establishes a hydraulic equilibrium with the osmotic pressure and is exactly related to it. It is possible to wait until a sufficient amount of solvent passes through the membrane to cause an equilibrium pressure differential opposing the osmotic pressure, as done in the “static method.” It is less time consuming to use a dynamic method in which the flowrate through the membrane is measured for different superimposed pressure differences. A plot of the flow rate and pressure difference will be linear as long as the simple hydrodynamic considerations apply. The pressure difference corresponding to no flow through the membrane, the hydraulic equivalent to the osmotic pressure, can then be linearly interpolated. Such a plot is shown in Figure 3 and was used in a slightly different form by Bruss and Stross.^{13,14} Those workers apparently did not consider the flow rate–pressure difference relation to be continuous for the whole range of flow rates from one direction to the opposite direction. One advantage of this method of plotting is that, if the solute permeates into the membrane to any appreciable extent, the line will be discontinuous at the point corresponding to zero flow. Another advantage is that, if the plot is made while the experiment is in progress, it is possible to recheck points that appear to deviate widely from expected behavior.

The flow rates and imposed pressure differences were measured by initially positioning the interface levels widely apart (about 4–8 cm), then observing the time for the levels to be reduced by about 2 mm. From a knowledge of the capillary bore size, it was possible to calculate an actual volumetric flow rate corresponding to an (arithmetic) average pressure difference for the particular time interval. The interface levels were then positioned closer together, and the flow rate corresponding to the reduced

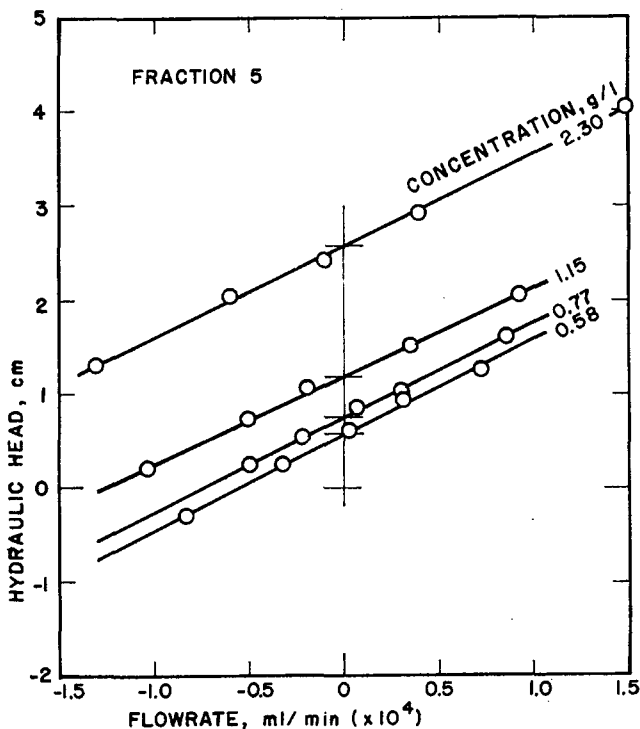


Fig. 3. Flow rate-hydraulic head relationship for obtaining osmotic pressure of PVC in THF at indicated concentrations.

pressure difference was measured. At hydraulic heads close to equilibrium, the full precision of the cathetometer (± 0.01 mm) was required for good accuracy in flow rate measurement. In the next series of measurements, the interface levels were again positioned far apart to cause a solvent flow in the reverse direction. Several pairs of flow rates and hydraulic differences were obtained. The pairs of values were plotted at the time they were measured to observe possible gross deviations in results. Apparently reliable data were subsequently fitted by a best straight line by means of least mean squares using a computer. The equilibrium hydraulic head equivalent to the osmotic pressure and the osmotic pressure itself were calculated from the linear relation.

TABLE I
 Characterization Data for Fractions and Composite PVC Sample

Fraction	$[\eta]$, dl/g	Mass, g	No. of gram- moles $\times 10^6$	$\bar{M}_{n_j} \times 10^{-3}$	$\bar{M}_{w_j} \times 10^{-3}$	$(\bar{M}_{w_j})/(\bar{M}_{n_j})$	$\sigma_{n_j} \times 10^{-3}$ [eq. (1)]	n_j [eq. (3)]
1	1.466	0.2978	2.38	125.0	146.0	1.168	51.2	0.039
2	1.410	0.3825	3.46	110.8	136.0	1.229	52.8	0.056
3	1.335	2.4265	26.30	92.3	128.0	1.384	57.1	0.429
4	1.039	1.2754	20.40	62.6	95.4	1.521	45.2	0.332
5	0.548	0.2689	8.85	30.4	40.2	1.322	17.3	0.144
Sample	1.174	4.6511	61.39	79.8	112.0	1.405	50.7	1.00
Sample			75.8 ^a		115.8 ^a			

^a Calculated using eqs. (4) and (5).

RESULTS AND DISCUSSION

Several features of the osmometer greatly facilitated its use. The capability of conditioning the membranes while installed in the osmometer, the provision for flushing sample solution and solvent through their respective chambers by using a syringe, the possibility for replacing capillaries if broken, and especially the provision of microvolume-regulating valves for rapid, precise positioning of the interfaces were all found to speed up and simplify the measurement of osmotic pressure. Osmotic pressure data for one concentration of polymer solution could usually be obtained within a time interval of between 1 and 2 hours. Hence it was possible to obtain the data for the number-average molecular weight of one sample or fraction within one day.

The results of the viscosity and osmotic pressure measurements, including the calculated number- and weight-average molecular weights for the fractions and original PVC sample, are shown in Table I. Also shown in Table I are the mass of each fraction, the calculated number of moles, as well as the standard deviation of the normal (molar) distribution and polydispersity for each fraction. The number and weight averages for the original sample were calculated using eqs. (5) and (6), based on data for the fractions, and were compared with measured values. The calculated number and weight averages of 75,800 and 115,800, respectively, compare favorably with those measured of 79,800 and 112,000, respectively. It is apparent that the measurements are self-consistent.

Table II shows in detail the method for obtaining the normal distribution corresponding to a particular fraction 1. The number average, or mean, of distribution, the standard deviation calculated from eq. (1), and the number of gram-moles in the fraction were available for each fraction. To maintain the conventional basis for a distribution function, a basis of 1 gram-mole was chosen for the total composite sample. The area under the distribution curve for each fraction was made equal to the mole fraction in each polymer fraction. This was accomplished by multiplying all the ordinates of the distribution by the mole fraction in the particular fraction.

TABLE II
Normal Distribution for Fraction^a

Z	$Z\sigma_{n_j}$ $\times 10^{-3}$	\bar{M}_{n_j} $-Z\sigma_{n_j}$ $\times 10^{-3}$	\bar{M}_{n_j} $+Z\sigma_{n_j}$ $\times 10^{-3}$	Y	Y/σ_{n_j} $\times 10^6$	$\theta_n = (n_j Y)/$ (σ_{n_j}) $\times 10^7$
0	0	125.0	125.0	0.399	7.79	3.04
0.5	25.6	99.4	150.6	0.3521	6.87	2.68
1.0	51.2	73.8	176.2	0.2420	4.72	1.84
1.5	76.8	48.2	201.8	0.1295	2.53	0.986
2.0	102.4	22.6	227.4	0.0540	1.05	0.410
2.5	128.0	-3.0	253.0	0.0175	0.34	0.133

^a Z and Y obtained from normal probability distribution tables; $n_j = 0.039$; $\sigma_{n_j} = 51.2 \times 10^3$; $\bar{M}_{n_j} = 125 \times 10^3$.

The sum of the areas under the distribution curves for all the fractions was thus equal to 1 (gram-mole). The resulting distributions are shown in Figure 4. The cumulative distributions are the graphical summation of the ordinates for the distributions of the fractions corresponding to the particular molecular weight. It would have been possible to obtain the sum of the normal distributions analytically by means of a computer; however, such a procedure appeared to be justifiable only for a large number of fractions.

It can be observed from Figure 4 that, because of the broad "tails" of the normal distributions for the fractions, a certain amount of material is indicated to have a negative molecular weight. This of course is impossible; in fact, even polymer molecules of molecular weights less than about 20,000

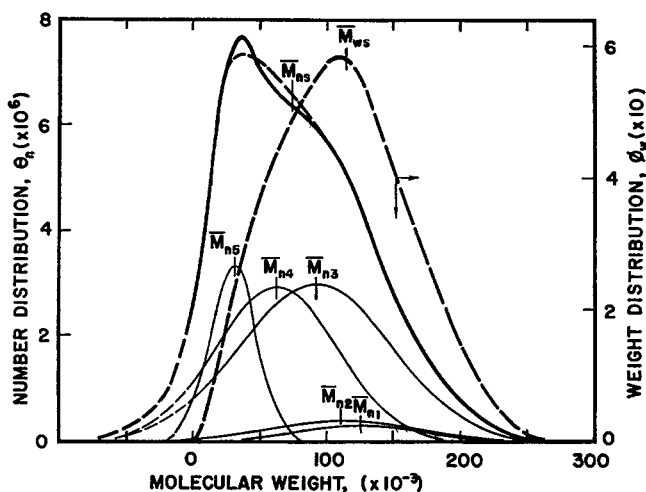


Fig. 4. Molecular weight distributions for a PVC sample obtained by a summation method from the number and weight averages for the fractions.

were not detectable with the osmometer membrane used. Hence the relatively small number of molecules shown below the molecular weight of about 20,000 should be qualitatively added to the material of molecular weight above 20,000. The general shape of the cumulative distribution curve would not be significantly altered, however.

A sharp peak in the molar distribution curve can be observed corresponding to a molecular weight of about 30,000, which resulted because a relatively narrow low molecular weight fraction was obtained. With only five fractions, it did not appear justifiable to define secondary peaks in the molar distribution curve. The dotted portion of the curve was considered to be closer to the actual distribution.

From an observation of the cumulative molar or number distribution, it could be expected that the shape of the corresponding weight distribution would be more nearly like a normal distribution. The cumulative weight

distribution was calculated from the molar distribution still on the basis of 1 gram-mole of polymer. The resulting distribution is a somewhat skewed normal distribution.

The PVC sample characterized showed a relatively narrow range of molecular weights and appeared to be relatively free of a high molecular weight "tail" corresponding to gel-like, branched, or crosslinked polymer. Such would be the essential characteristics of a commercial polymer that was produced under stringently controlled conditions for good processing properties. Material polymerized to high conversion might be expected to yield a greater amount of high molecular weight polymer with a higher polydispersity ratio.

The summation method for obtaining a molecular weight distribution can be applied with other types of distribution functions. The log-normal distribution would appear to be particularly useful for extremely polydisperse samples. The general shapes of both the gamma or the Poisson distributions could be adequately approximated by the summation of a series of normal distributions. It would appear to be possible to construct the molecular weight distribution curve for a polymer of any polydispersity, provided that the polymer could be fractionated and both the number and weight averages for the fractions could be obtained.

Nomenclature

\bar{M}_{nj}	= number-average molecular weight for fraction j
\bar{M}_{wj}	= weight-average molecular weight for fraction j
$\bar{M}_{ns}, \bar{M}_{ws}$	= number- and weight-average molecular weights for composite sample
n_j	= mole fraction of fraction j in total sample
N_j	= number of gram-moles in fraction j
W_j, W_s	= weight of fraction j , and sample, in grams
θ_n	= molar distribution function, per gram-mole of polymer = $n_j / [(\sigma_{nj} \sqrt{2\pi})] \exp\{- (M - \bar{M}_{nj})^2 / 2\sigma_{nj}^2\}$
σ_{nj}	= standard deviation of a normal number distribution about the number-average molecular weight for fraction j
ϕ_w	= weight distribution function, per gram-mole of polymer = $M\theta_n$
$[\eta]$	= intrinsic viscosity

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