

Molecular Weight Distribution in a Poly(vinyl Chloride-vinyl Acetate) Copolymer

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Synopsis

The molecular weight distribution of a vinyl chloride-vinyl acetate copolymer has been studied by three methods: (a) solution fractionation; (b) osmometry and light scattering; (c) gel permeation chromatography. In (a), the fractions were precipitated from a tetrahydrofuran solution by water, then characterized. The data yielded models for the intrinsic viscosity and the molecular weight distribution, in terms of the copolymer molecular weight. In (b), the unfractionated copolymer was characterized by osmometry and light scattering, using in the latter case the two currently accepted theories for the determination of the true weight-average molecular weight. Conflicting data suggest caution in the use of these theories. In (c), the original fractions served to establish a calibration curve which yielded exceptionally low results when applied to the analysis of the unfractionated VC-VAc copolymer. Further investigations using proposed universal calibration theories bring to light serious discrepancies.

INTRODUCTION

It is clearly recognized that the processability of synthetic macromolecular materials and their properties thereafter are by far the most important qualities that need to be controlled in the polymer industry. The predominant factor determining these qualities is the molecular weight distribution (MWD). Much of the work in this laboratory has been centered on the preparation of copolymers^{1,2} establishing a need for an accurate method of MWD characterization. Various methods have been developed to establish the MWD, but numerous problems arise when these are applied to copolymers. Several approaches have been made in an attempt to find the one which yields the most accurate results.

A vinyl chloride-vinyl acetate copolymer provided by the Shawinigan Chemicals Division of the Gulf Oil Co., was used in this work. The product, designated as VS-814, was synthesized by suspension polymerization and contained 15 wt-% vinyl acetate. This material, purified by total precipitation from a tetrahydrofuran solution with distilled water, then dried at 60°C under vacuum, was utilized throughout all of this work.

EXPERIMENTAL AND RESULTS

Copolymer Characterization Through Solution Fractionation

For the purpose of fractional precipitation, a 1 wt-% solution was prepared by dissolving the copolymer in tetrahydrofuran. Each fraction was precipitated in a pear-shaped separatory funnel by adding small amounts of distilled water to the well-agitated solution. Before drawing off, each precipitate was allowed to settle in the funnel for at least 24 hr to favor equilibrium between the solution and the precipitate. The precipitation process was performed in a laboratory where the temperature was maintained at $25^\circ \pm 0.5^\circ\text{C}$.

Each fraction was examined by gel permeation chromatography that relative comparisons might be made with chromatograms obtained using

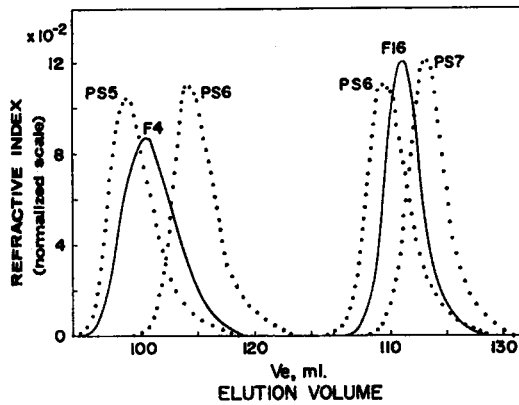


Fig. 1. GPC chromatograms of polystyrene standards (PS) and copolymer fractions (F). PS5: $\overline{M}_n = 164,000$, $\overline{M}_w/\overline{M}_n \leq 1.06$; PS6: $\overline{M}_n = 49,000$, $\overline{M}_w/\overline{M}_n \leq 1.06$; PS7: $\overline{M}_n = 19,600$, $\overline{M}_w/\overline{M}_n \leq 1.06$; F4: $\overline{M}_n = 60,500$; F16: $\overline{M}_n = 15,400$.

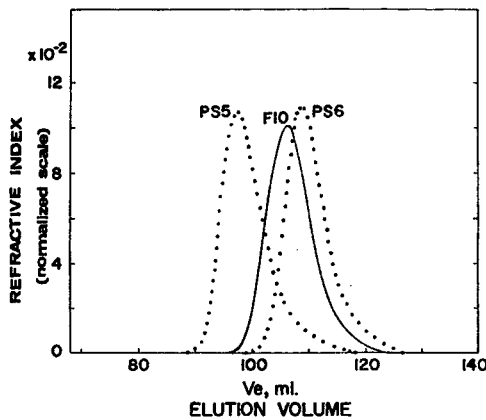


Fig. 2. GPC chromatograms of polystyrene standards (PS) and copolymer fraction (F). PS5: $\overline{M}_n = 164,000$, $\overline{M}_w/\overline{M}_n \leq 1.06$; PS6: $\overline{M}_n \leq 49,000$, $\overline{M}_w/\overline{M}_n = 1.06$; F10: $\overline{M}_n = 34,000$.

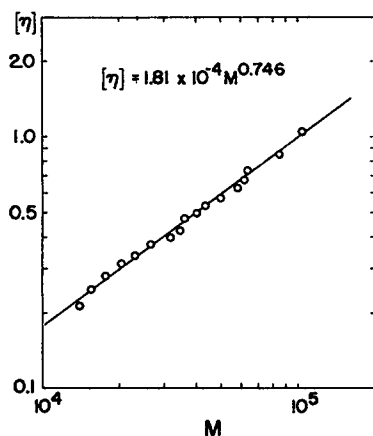


Fig. 3. Intrinsic viscosity $[\eta]$ vs. molecular weight M for the vinyl chloride-vinyl acetate copolymer.

standard polystyrene samples having polydispersity indices ranging from 1.06 to 1.20. The comparisons (cf. Figs. 1 and 2) revealed that the hydrodynamic volume distribution of each copolymer fraction was very nearly identical to that of polystyrene standards eluting in the same region. For this reason, the fractions were assumed to be quasi-monodisperse.

TABLE I
Results Obtained from Fractionation, Osmometry, Viscosity, and GPC

Fraction no.	Fraction weight, g	$\bar{M}_n \times 10^{-3}$	$[\eta]$, dl/g	Elution volume V_e , ml
1	0.57	102.0	1.05	97.5
2	0.58	82	0.85	99
3	0.55	63	0.72	100.5
4	0.68	61	0.67	101
5	0.42	58	0.63	102
6	0.47	50	0.57	103
7	0.75	42.4	0.53	104
8	0.69	39.7	0.51	105
9	0.48	35.5	0.47	105.5
10	0.34	34	0.42	106
11	0.62	31.8	0.41	107
12	0.71	26.2	0.37	108
13	0.57	22.7	0.34	109
14	0.40	20	0.32	110.5
15	0.30	17.5	0.28	111.5
16	0.31	15.4	0.25	112.5
17	0.31	14.1	0.22	113.5
18	0.23	8.5 ^a	—	114.5
19	0.14	6.2 ^a	—	120
Unfractionated sample	—	28.0	0.51	—

^aBy vapor pressure osmometry.

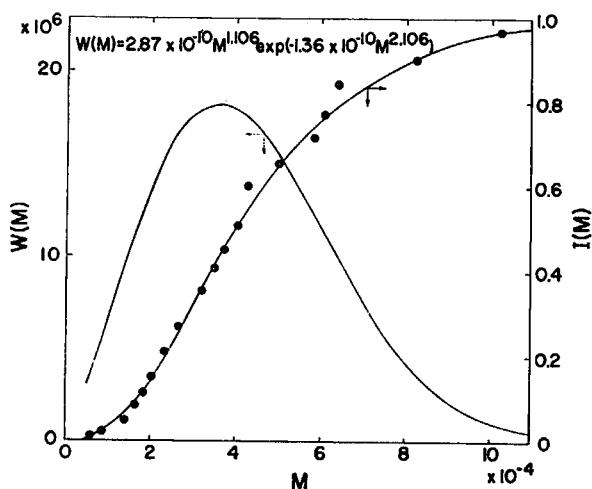


Fig. 4. Molecular weight distributions of the copolymer. $I(M)$: integral distribution; $W(M)$: differential distribution.

The number-average molecular weight, \bar{M}_n , of each fraction was then determined at 25°C with a Model 503 Hewlett-Packard high-speed membrane osmometer, using as solvent tetrahydrofuran which had been degassed at 45°C. The osmometer membrane, Schleicher & Schuell Type 0-8, originally supplied in an aqueous isopropanol solution, had to be conditioned for tetrahydrofuran operation by several successive steps. These steps involved soaking the membrane for 5-hr periods (minimum) in the following solvents: water/isopropanol mixtures, isopropanol, isopropanol/toluene mixtures, toluene, toluene/tetrahydrofuran mixtures, and, lastly, pure tetrahydrofuran. The hydrostatic solvent head in the osmometer at equilibrium was measured to the nearest 0.01 cm.

The intrinsic viscosity for each fraction was then determined at 25°C in tetrahydrofuran, using an Ubbelohde suspending level viscometer. The size of the viscometer capillary was so chosen that the effluent time for the solvent was more than 120 sec, thus eliminating the effect of shearing rate. A Hewlett-Packard automatic viscometer system facilitated the measurements, effluent times, accurate to 0.01 sec, being measured by pairs of photocells.

The fractionation, osmometry, and viscometry results are summarized in Table I. From the curve shown in Figure 3, the following relationship between the intrinsic viscosity $[\eta]$ and the molecular weight M was obtained for the above-mentioned vinyl chloride-vinyl acetate copolymer:

$$[\eta] = 1.87 \times 10^{-4} M^{0.746}. \quad (1)$$

Using 0.51, the $[\eta]$ value for the unfractionated copolymer, the viscosity-average molecular weight \bar{M}_v , calculated with eq. (1), was equal to 4.22×10^4 . When plotting the integral molecular weight distribution $I(M)$ as a function of molecular weight, an S-shaped curve was obtained (see Fig. 4).

The functional relationship between $I(M)$ and M for this curve is expressed³ by an equation of the form

$$I(M) = 1 - \exp(-\alpha M^\beta) \quad (2)$$

where α and β are parameters which can be determined by plotting on log-log paper $\log 1/(1 - I(M))$ against M . The slope of the plot is equal to β , and the intercept, to $\log \alpha$. The values of α and β obtained in this work were 1.36×10^{-10} and 2.106, respectively.

Differentiating eq. (2) yields the following differential molecular weight distribution function, $W(M)$:

$$W(M) = \alpha\beta M^{\beta-1} \exp(-\alpha M^\beta). \quad (3)$$

From the well-known definitions of the various molecular weight averages,

$$\begin{aligned} \bar{M}_w &= \frac{\int W(M)M dM}{\int W(M)dM}, \quad \bar{M}_n = \frac{\int \frac{W(M)}{M} M dM}{\int \frac{W(M)}{M} dM}, \quad \text{and} \quad \bar{M}_v \\ &= \left[\frac{\int W(M)M^a dM}{\int W(M)dM} \right]^{1/a}, \end{aligned}$$

and using $W(M)$ from eq. (3) and letting, $\int W(M)dM = 1$, one obtains

$$\bar{M}_w = \alpha^{-1/\beta} \Gamma(1 + 1/\beta) \quad (4-1)$$

$$\bar{M}_n = 1/[\alpha^{1/\beta} \Gamma(1 - 1/\beta)] \quad (4-2)$$

$$\bar{M}_v = [\alpha^{-a/\beta} \Gamma(1 + a/\beta)]^{1/a} \quad (4-3)$$

where Γ is the gamma function and a , in the expression for \bar{M}_v , is the exponent value in eq. (1).

Inserting the numerical values of a , α , and β in eqs. (3) and (4) leads to the following expression for $W(M)$:

$$W(M) = 2.87 \times 10^{-10} M^{1.106} \exp(-1.36 \times 10^{-10} M^{2.106}) \quad (5)$$

and values for the various molecular weights:

$$\bar{M}_w = 4.26 \times 10^4, \quad \bar{M}_n = 2.86 \times 10^4, \quad \text{and} \quad \bar{M}_v = 4.11 \times 10^4.$$

For \bar{M}_n and \bar{M}_v , the calculated values are identical to the experimental results obtained by osmometry and by viscometry when using eq. (1). The polydispersity index of the copolymer, defined as the ratio \bar{M}_w/\bar{M}_n , has a value of 1.50.

Copolymer Characterization Through Osmometry and Light Scattering

One of the most commonly used methods to characterize a polymer sample is to establish its polydispersity index. This is done by determining the value of \bar{M}_n by osmometry and that of \bar{M}_w by light scattering. The \bar{M}_n value of the unfractionated copolymer sample used in this study was found

to be 2.8×10^4 (see Table I). The \bar{M}_w value for the same sample was determined with a Model 2000 Brice-Phoenix light-scattering photometer. The apparatus, usually calibrated with a standard opal glass diffuser provided by the manufacturer, was checked by measuring the Rayleigh ratio of benzene (experimental value $46.8 \times 10^{-6} \text{ cm}^{-1}$) with an incident light of 4360 Å. The specific refractive index increment of the polymer solution, d_n/d_c , was measured with a Brice differential refractometer calibrated with an aqueous solution of KCl.

It is generally known that the intensity of light scattered from a dilute copolymer solution is a function not only of molecular weight but also of composition of the copolymer. The molecular weight derived from a Zimm plot, by extrapolation to zero-angle intensity and to zero concentration, yields but an apparent weight-average value, M_{app} . Based on the assumption that dn/dc is a linear function of the copolymer composition, an expression has been established relating M_{app} to the true weight-average molecular weight, \bar{M}_w , for a copolymer system consisting of components A and B:⁴

$$M_{\text{app}} = \bar{M}_w + 2P \frac{m_A - m_B}{m} + Q \left(\frac{m_A - m_B}{m} \right)^2 \quad (6)$$

where $P = \sum w_i \bar{M}_i (\Delta x_i)$, $Q = \sum w_i \bar{M}_i (\Delta x_i)^2$, and m , m_A , and m_B are, respectively, the dn/dc values of the copolymer and of the pure components A and B. In the expressions for P and Q , $\Delta x = x_i - x$ where x is the overall average weight fraction of component A and x_i is the composition of the i th copolymer segment which has a molecular weight \bar{M}_i and a weight fraction w_i . P and Q are related to the composition heterogeneity of the copolymer.

More recently, an expression similar to eq. (6) has been proposed:⁵

$$M_{\text{app}} = \bar{M}_w \frac{m_A m_B}{m^2} + M_A \frac{m_A (m_A - m_B)}{m^2} x + M_B \frac{m_B (m_B - m_A)}{m^2} (1 - x) \quad (7)$$

where M_A and M_B are defined as the weight-average molecular weights of the A and B parts of the copolymer, respectively.

Both eqs. (6) and (7) include the true weight-average molecular weight, \bar{M}_w . One can therefore use, in principle at least, either one or the other of these equations to evaluate \bar{M}_w with experimental data on the apparent molecular weights and the refractive index increments obtained with three different solvents. It is then necessary to solve a set of three linear simultaneous equations, in order to obtain a numerical value of \bar{M}_w , as well as values for P and Q in eq. (6) and M_A and M_B in eq. (7).

Tetrahydrofuran, propylene oxide, and ethylene chloride were the three solvents used in this work. The copolymer solutions were clarified by filtration through a 5- μ Millipore Teflon filter, then by centrifugation at 20,000 g for 45 min. The experimental values obtained for m , m_A , and m_B with the above three solvents and the corresponding apparent weight-average molecular weights, M_{app} , obtained from Zimm plots, are sum-

TABLE II
Light Scattering Data

Solvent	m	m_A	m_B	$M_{app} \times 10^{-4}$
Tetrahydrofuran	0.1055	0.115	0.0638	5.67
Propylene oxide	0.140	0.150	0.0938	4.93
Ethylene chloride	0.0702	0.0796	0.0224	11.0

marized in Table II. Solving eqs. (6) and (7) with these data gave the following results:

$$\bar{M}_w = 4.85 \times 10^4, P = -3.48 \times 10^4, \text{ and } Q = 17.8 \times 10^4 \text{ by eq. (6)}$$

$$\bar{M}_w = 5.10 \times 10^4, M_A = 18.4 \times 10^4, \text{ and } M_B = 137 \times 10^4 \text{ by eq. (7)}$$

where A stands for the poly(vinyl chloride) (PVC) segments and B for the poly(vinyl acetate) segments (PVAc) in the copolymer.

As can be seen, the \bar{M}_w values obtained by eqs. (6) and (7) are in excellent agreement. However, the M_A and M_B values are not acceptable, for how can the parts of a copolymer have a molecular weight greater than that of the whole? Further investigation has brought to light the fact that the use of eqs. (6) and (7) results too often in ill-conditioned systems. It was found, for such systems, that small changes in the coefficients give rise to unduly large changes in the results being sought. Measurements made in light scattering are not exempt from experimental error; therefore, in practice, erroneous results for molecular weights can too easily be obtained by solving these sets of three linear simultaneous equations. The existence of such ill-conditioned systems was disclosed when attempts were made to recalculate the unknown parameters in eqs. (6) and (7) using the data reported by Bushuk and Benoit.⁵ The authors are of the opinion that equally valid results could be obtained if one determines the values of M_{app} in several solvents and one retains preferably the lowest value obtained or the lowest value which is common to the greatest number of solvents. In this study, the lowest value of M_{app} , 4.93×10^4 with propylene oxide, was taken to approximate the true value of \bar{M}_w . Using this value, the polydispersity index of the copolymer sample was calculated and found to be 1.76.

Copolymer Characterization Through Gel Permeation Chromatography

The recent popularity of gel permeation chromatography (GPC) arises from the fact that information on molecular weight or size distributions can be obtained very rapidly. One of the major problems hampering the quantitative use of this method, however, is the need for a proper calibration of the instrument. Much work has been done with homopolymers on this problem, but relatively little with copolymers. One of the prime reasons for this is the fact that one must take into account not only the overall average composition but also heterogeneities in composition and in chain segments of the copolymer. Owens⁶ first mentioned the difficulties of obtaining good quantitative data on the distributions of size in copolymers.

Cantow⁷ and Runyon,⁸ more recently, suggested using dual detectors (an ultraviolet spectrometer in series with a differential refractometer) to determine simultaneously the distributions of composition and size. In the present study, an attempt has been made to better understand the problems that arise from the use of GPC by making appropriate comparisons with data obtained by other methods.

The unfractionated copolymer and its fractions were analyzed with a Model 200 Waters gel permeation chromatograph installed in an air-conditioned room where the temperature was kept constant at $25^\circ \pm 0.5^\circ\text{C}$. The column arrangement consisted of three columns in series, each 4 ft long. These were packed with crosslinked polystyrene gel having nominal permeabilities (Waters) of 1×10^6 , 1.5×10^5 , and 3×10^3 Å, respectively.

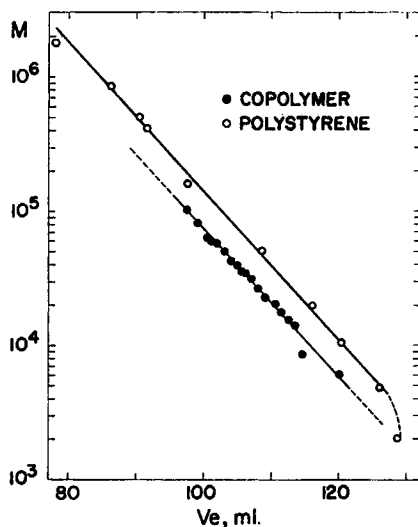


Fig. 5. GPC calibration curves.

Flow rate of the solvent, tetrahydrofuran degassed with dry nitrogen, was controlled at 1 ml/min. Concentrations of all sample solutions were adjusted to 0.125 wt-% to render concentration effects on the peak position of the chromatogram negligible. The data reported in Table I on the various copolymer fractions were used to plot a GPC calibration curve ($\log M$ versus elution volume V_e , shown in Fig. 5). A similar curve prepared with polystyrene standards is also shown in the same figure for comparison purposes. The peak position of the GPC chromatogram for each of the copolymer fractions was assigned the corresponding number-average molecular weight by osmometry. Though, in practice, the peak position is usually assigned a weight-average molecular weight, it was believed in this work that little error would be introduced by using \bar{M}_n instead of \bar{M}_w values. This was based on the assumption that the polydispersity of the fractions was quite low.

In order to correct for axial diffusion of the copolymers in the columns, the method proposed by Smith⁹ was applied to the chromatogram of the unfractionated copolymer sample, after which the average molecular weights of the unfractionated sample were evaluated using the calibration curve given in Figure 5. The results obtained for \overline{M}_w and \overline{M}_n were, respectively, 28,000 and 12,000, from which the polydispersity index was found to be 2.47.

DISCUSSION

The agreement between the results obtained by the classical methods and those calculated from the function obtained with the fractionation data is good and well within the limits of the experimental errors. It is not possible, however, to say the same thing about the results obtained by GPC. The polydispersity index resulting from this method is the highest of the three, while the molecular weight averages are the lowest. In an attempt to explain these differences, the GPC chromatogram (curve B in Fig. 6) of the unfractionated copolymer was plotted on the same coordinates as the envelope (curve A in Fig. 6) resulting from the superposition of the GPC curves of each fraction (keeping in mind the individual weight percentage of each). Both curves have been normalized to give unit area. It is obvious that a given species i within the unfractionated sample has a longer residence time in the GPC columns than the same species within any of the narrow distributed fractions. Therefore, it may be erroneous to seek a precise interpretation of the copolymer GPC chromatogram by means of a calibration line established from fractions obtained by the precipitation method, since this method may introduce a different solution history between the whole polymer and its fractions.

Pushing the investigation further, $\log [\eta]M$ versus V_e was plotted for both the copolymer fractions and the polystyrene standards (see Fig. 7). As suspected, two very distinct straight lines were obtained. For any given elution volume, the value of $[\eta]M$ for polystyrene is approximately

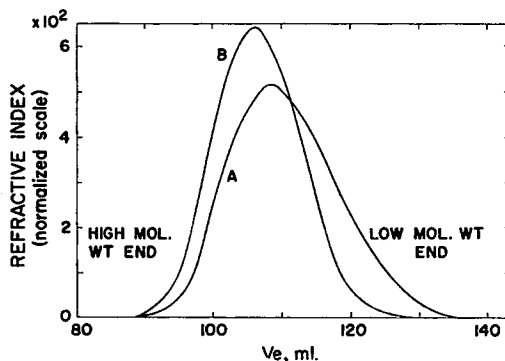


Fig. 6. Comparison of GPC chromatograms: (A) envelope of the unfractionated copolymer; (B) envelope resulting from the superposition of fractions.

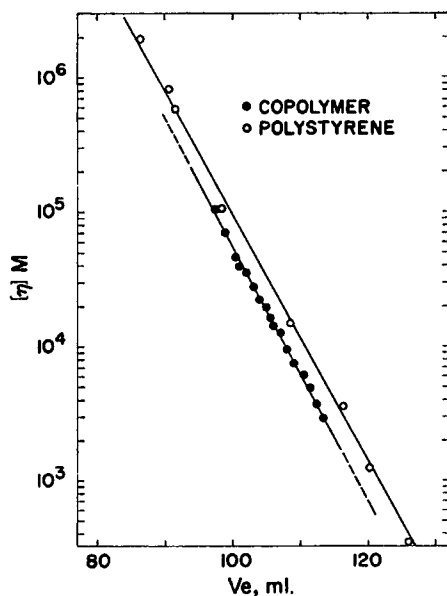


Fig. 7. Plot of $\log [\eta]M$ vs. elution volume for polystyrene standards and copolymer fractions.

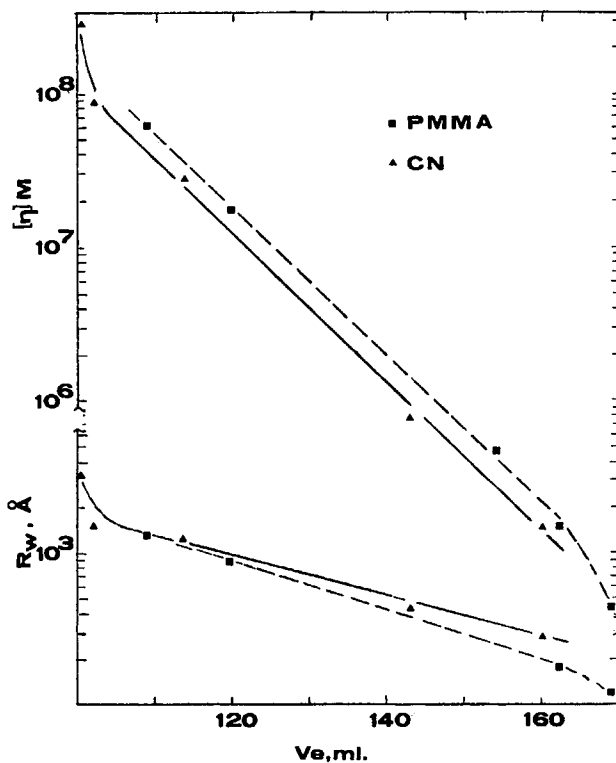


Fig. 8. Plot of $\log [\eta]M$ and \log radius of gyration R_g vs. elution volume for poly(methyl methacrylate) (PMMA) and cellulose nitrate (CN) in acetone.¹¹

80% higher than that of the copolymer. This is very much greater than the error possibly introduced by the use of \overline{M}_n instead of \overline{M}_w values for the copolymer fractions. It implies that the universal calibration method¹⁰ is not valid for all polymeric materials. Recently, Meyerhoff¹¹ has reported GPC results made with cellulose nitrate and poly(methyl methacrylate) in acetone. As shown in Figure 8, he points out that the universal calibration curve resulting from the combination of $[\eta]$ and M proves inadequate. A better GPC correlation line can be obtained, in his work, by plotting the log of the radii of gyration, as determined directly by light scattering, as a function of the corresponding elution volumes. He mentions further that two separate $\log [\eta]M$ -versus- V_e lines were found in his laboratories for polystyrene and poly(methyl methacrylate) in tetrahydrofuran. This contrasts with the result obtained by other authors¹⁰ who established a single, universal calibration curve for the same two polymers in the same solvent.

It is not possible, at the present time, to explain the observed discrepancy. The effects of other parameters which determine the retention time of solute particles in the GPC columns will have to be better understood. Work in this area is being continued, and further results will be reported later.

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