

## Characterization of Nylon 66 by Gel Permeation Chromatography

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### Synopsis

The quantitative characterization of nylon 66 of various polydispersities has been carried out by gel permeation chromatography (GPC), using *m*-cresol solvent at 130°C. A *Q*-factor value of 13.9 for nylon 66 has been validated, by limiting viscosity-number determinations for the particular solvent/temperature combination described above. Using this value together with a simple correction technique for viscous fingering and unsymmetrical dispersion, the practical quantitative characterization of linear nylon 66 has been achieved. Construction of a universal calibration curve, based on hydrodynamic volume, gave a straight-line relationship for polystyrene fractions and nylon 66 samples covering a broad range of polydispersity values.

### INTRODUCTION

Before undertaking this study to develop a simple method for obtaining quantitative molecular weight values for linear nylon 66, the suitability of two polyamide solvents for continuous operation in the gel permeation chromatograph (GPC) was examined. The solvents were trifluoroethanol and *m*-cresol. The former was selected because of the high polymer/solvent refractive index ratios that could be achieved in the GPC at the low operating temperature of 30°C, and the latter because of its relatively low cost. Trifluoroethanol had to be abandoned after approximately two weeks to a month of operation, since it affected the crosslinked polystyrene packing in the chromatograph columns causing the production of binodal chromatograms. However, *m*-cresol was found to be an almost ideal solvent, providing that suitable precautions are taken with regard to handling and data interpretation. Use of this solvent system combined with the development of simple correction techniques, to account for the viscous fingering and unsymmetrical axial dispersion encountered, enabled the quantitative characterization of linear nylon 66 on a regular practical basis.

A universal calibration curve has been constructed to allow characterization of branched polyamides.

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## EXPERIMENTAL

### Materials

The *m*-cresol solvent was commercial grade. It was distilled under a reduced pressure of nitrogen at 140°C before use in the GPC. Solvent recycling was not carried out because of the tendency of the *m*-cresol to degrade in the chromatograph.

The characterized polystyrene fractions used were those supplied with the GPC instrument, by Waters Associates.

The nylon 66 samples were autoclave-produced plant polymers of various relative viscosity (RV) values, ranging in molecular weight from 30 to 65 RV. The nylon 66 fractions were prepared in the laboratory as described below.

### Operating Conditions of the GPC

All of the GPC characterizations were performed on a Waters Associates instrument, Model 200, to which two modifications were made. These were the removal of some 8 to 10 ft of tubing to reduce the volume of flow between the injection loop and the first column,<sup>1</sup> and the insertion of a vapor feedback arrangement into the syphon block assembly.<sup>2</sup> This device eliminated errors due to solvent evaporation and degradation, which would have been significant at the 130°C operating temperature.

It was also found that baseline stability was improved by thermally insulating the refractometer detector housing. A typical chromatogram of nylon 66 autoclave polymer produced under these conditions is shown in Figure 1. The small negative peak after 155 ml eluted volume is caused by moisture in the nylon sample, and the large peak at 165 ml is due to dissolved gases. The operating conditions of the instrument are outlined in Table I.

TABLE I  
Operating Conditions of the GPC

Parameter	Material or condition
Solvent	<i>m</i> -cresol (distilled)
Columns	10 <sup>5</sup> , 10 <sup>4</sup> , 10 <sup>3</sup> , and 250 Å (in series)
Sample concentration	0.5% (w/v)
Injection time	2 min
Sample size	10 mg
Flow rate	1 ml/min
Oven temperature	130°C
Refractometer temperature	130°C
Syphon temperature	130°C
Injection port temperature	130°C
Degasser temperature	160°C
Plate count	1037 plates/ft
Resolution index	0.46

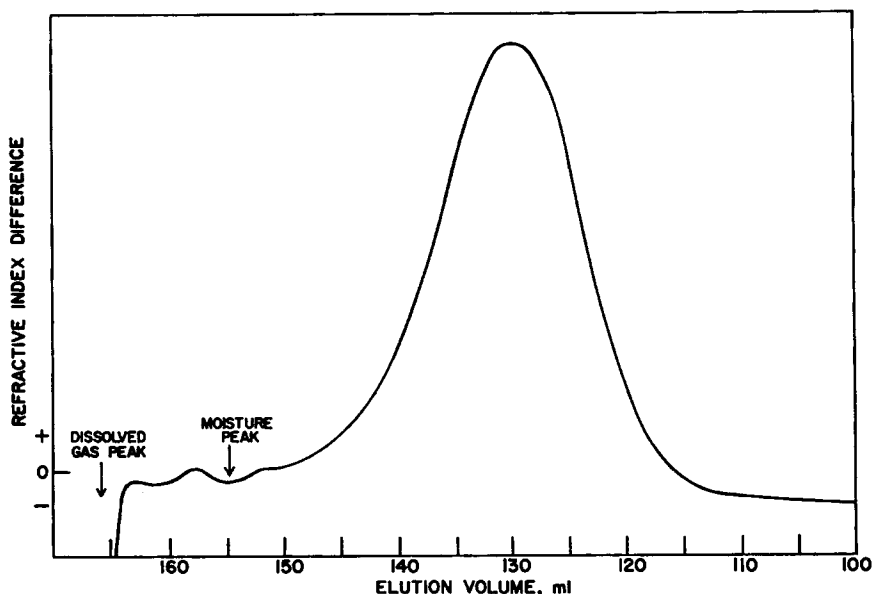


Fig. 1. Typical GPC chromatogram of nylon 66 polymer.

The plate count was determined using the equation

$$\text{plates/ft} = \frac{16}{f} \left[ \frac{V_e}{W} \right]$$

where  $f$  = column length in feet;  $V_e$  = peak elution volume; and  $W$  = peak base width.

The resolution index was calculated as

$$R = \frac{M_1}{M_2}$$

where  $M_1$  and  $M_2$  = molecular weight at half-peak height for the low and high molecular weight sides of the peak, respectively.

### Polymer Fractionation

Fractionation was carried out on two nylon polymers of different molecular weights using the phenol/water fractional precipitation technique described by Taylor.<sup>3</sup> To prevent phenol degradation, two modifications were made to the method. A nitrogen blanket was used over the polymer solution during settling; and after precipitation of the polymer in boiling water, the water was rapidly cooled to room temperature before filtration. The rewash precipitate was then vacuum dried at 60°C, to constant weight, before characterization.

### Determination of Number-Average Molecular Weight

The number-average molecular weights,  $\bar{M}_n$ , of the laboratory-prepared nylon fractions and plant polymers were obtained using a Shell-Stabin-type

membrane osmometer, manufactured by Hallikainen Instruments. The solvent used was distilled *m*-cresol, the operating temperature, 105°C, and the membranes were gel cellophane, grade no. 600.

Osmotic height determinations were carried out at four polymer concentrations. No polyelectrolyte effect was experienced, thus the need for the addition of a salt was obviated. Regression analysis was used to determine the osmotic pressure over concentration,  $\pi/C$ , extrapolated value, at  $C = 0$ .

### Determination of Limiting Viscosity Number

Limiting viscosities in *m*-cresol at 130°C were determined for both the polystyrene and nylon fractions and also for the production nylon polymers. Measurements were made using a Cannon-Ubbelohde dilution viscometer in an oil bath at 130°C. Initial solutions were prepared by the direct addition of weighed quantities of polymer and solvent to the viscometer. To prevent oxidation of the *m*-cresol solvent, a heated inert gas blanket was maintained over the viscometer, and all in-viscometer solution mixing was done using the heated gas.

To prevent the effects of solvent evaporation and nylon 66 depolymerization from becoming significant, it was necessary to have elution times of the order of 40–50 sec. Despite this short time, there were no significant differences between replicate determinations. Regression analyses were used to determine the limiting viscosity numbers.

## RESULTS AND DISCUSSION

### Quantitative Characterization of Linear Nylon 66 Polymer

In their earlier work, Moore and Hendrickson<sup>4</sup> indicated that the extended chain length might be universally related to appearance volume. This calibration parameter, designated *Q*-factor, is the ratio of the molecular weight of a monomer unit to its extended chain length, derived from bond lengths and valence angles. (The value for nylon 66 was determined as 13.9 using a Dreiding Stereo model.) Comparison of molecular weight averages determined from GPC chromatograms using the *Q*-factor and absolute methods have shown large differences, and the approach has been discarded for purposes of deriving a universal calibration parameter.<sup>5</sup> However, the *Q*-factor can be of use for characterizing linear polymers by GPC, providing the solvent used is near "ideal" at the operating conditions chosen and instrument parameters such as viscous fingering and dispersion are taken into account.

The "ideality" of the solvent may be assessed from the value of  $\alpha$  in the Mark-Houwink relationship:

$$[\eta] = KM^\alpha$$

where  $[\eta]$  is the limiting viscosity number,  $M$  is the molecular weight of the

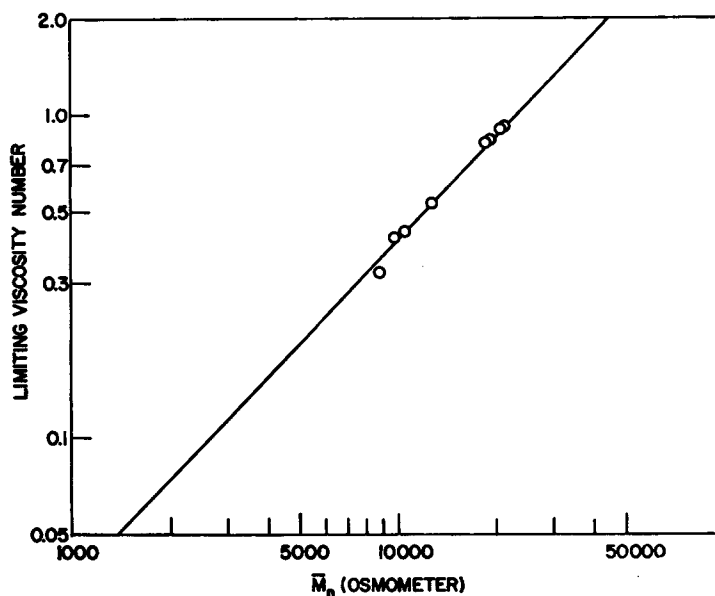


Fig. 2. Relation of  $\ln [\eta]$  to  $\ln \bar{M}_n$  determined by osmometry for fractionated nylon 66.

polymer  $\equiv \bar{M}_n$  from osmotic determinations,  $K$  is an error factor constant, and  $\alpha$  is the polymer/solvent interaction constant.

For a "nonideal" solvent where the polymer chain is presumed to exist in a coil-like configuration,  $\alpha = 1/2$ ; for an ideal solvent where an extended chain polymer configuration tends to exist,  $\alpha$  approaches unity.

Figure 2 shows a plot of  $\ln [\eta]$  against  $\ln \bar{M}_n$  for the fractionated nylon samples, the values of which are tabulated in Table II.

A regression analysis carried out on the above values resulted in the following equation:

$$[\eta]_{m\text{-cresol}}^{130^\circ\text{C}} = 4.008 \times 10^{-5} (\bar{M}_n)^{1.00}.$$

Thus, at  $130^\circ\text{C}$  in *m*-cresol, nylon 66 has an  $\alpha$ -value of 1.0, indicating that the molecules assume an extended chain configuration. Since the value of

TABLE II  
 $[\eta]$  and  $\bar{M}_n$  Values for Nylon Fractions

Fraction	Number-average molecular weight $\bar{M}_n$	Limiting viscosity number $[\eta]$
3	24,440	0.90
$2/2$	22,850	0.93
$4/5$	19,510	0.83
6	18,600	0.81
8	12,860	0.53
$3/1$	10,770	0.44
$3/3$	9,790	0.42
$3/4$	8,830	0.32

the  $Q$ -factor is determined assuming an extended chain configuration, the  $\alpha$ -value of unity supports the assumption that the factor so obtained may rightly be used in the determination of nylon 66 molecular weights from GPC chromatograms.

All the uncorrected calculations of  $\bar{M}_w$  and  $\bar{M}_n$  of the nylon fractions, from the GPC chromatograms, were based on those from the Waters Associates Instruction Manual. The molecular size-versus-elution volume calibration curve was obtained using the supplied polystyrene fractions, and the equation of this curve was derived by regression analysis. This equation, in combination with those for  $\bar{M}_w$  and  $\bar{M}_n$  outlined in the Waters' Manual, and a chromatogram curve area normalization procedure were formulated into a computer program to give values of  $\bar{M}_w$  and  $\bar{M}_n$  from input data of chromatogram height and corresponding elution volume. These values are not absolute, since they are uncorrected for viscous fingering and dispersion, both of which occur with nylon in the *m*-cresol solvent system.

### Correction for Viscous Fingering

The phenomenon of viscous fingering occurs whenever an injected polymer solution has a significantly higher viscosity than the solvent stream in the chromatograph. Such is the case with polyamides in *m*-cresol, where, upon injection, the solvent stream tends to channel round the sample "plug," causing the sample to take longer to reach the first column than flow/volume calculations would predict. Reduction of this phenomenon by using a 0.25% w/v solution resulted in a reduced size chromatogram, making height measurements difficult at the ends of the chromatogram and consequently introducing significant error in the molecular weight values obtained.

Therefore, to correct for viscous fingering mathematically, the  $\bar{M}_n$  values for the nylon fractions obtained from GPC and osmometry were plotted one against the other (Fig. 3) and subjected to linear function relationship analyses. This produced the following equation, which was found to apply to all the linear polyamide samples that were characterized by both techniques:

$$\bar{M}_{n(\text{osmometry})} = 2617 + 1.002 \bar{M}_{n(\text{GPC})}.$$

The closeness of the slope to 1 indicates that viscous fingering is the main factor affecting the  $\bar{M}_n$  values determined by GPC.

### Correction for Unsymmetrical Dispersion

Due to axial dispersion occurring within the columns, the chromatograms of the essentially monodisperse polystyrene fractions appeared Gaussian. Attempts were therefore made to first correct for symmetrical dispersion using one of the simpler mathematical solutions, namely that of Aldhouse and Stanford.<sup>6</sup>

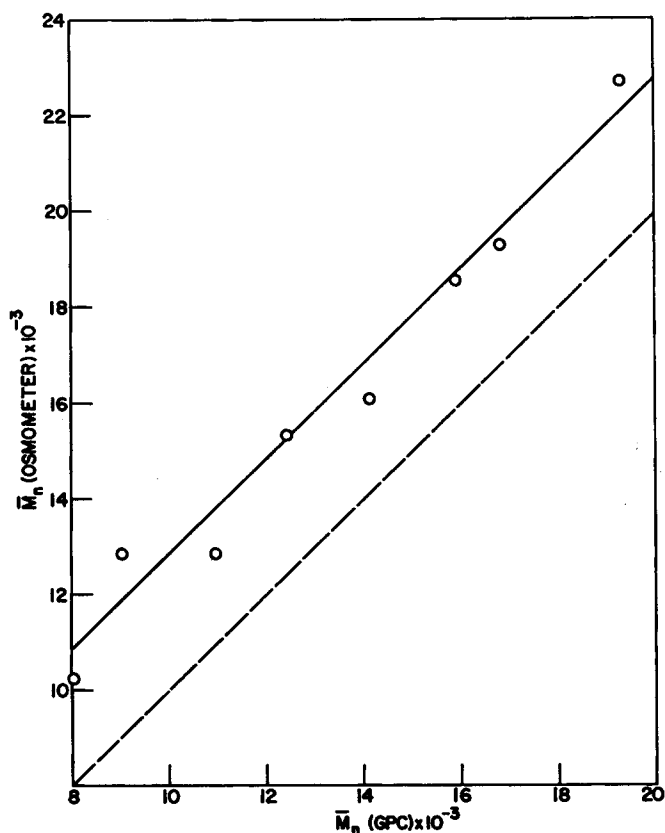


Fig. 3. Correlation of  $\bar{M}_n$  determined by GPC with  $\bar{M}_n$  from osmometry for nylon 66 polymers.

Table III presents the given polydispersity values for the polystyrene fractions along with those calculated from uncorrected, and the Aldhouse and Stanford corrected, chromatogram heights. This table shows that, while the mathematical correction produced some improvement in the right direction, the magnitude was not sufficient to bring the polydispersities in line with the absolute values. The explanation for this is found in Figure 4, a plot of " $\sigma$ -dispersion" against elution volume;  $\sigma$ -dispersion is a measure of the axial dispersion caused by the gel permeation chromatograph. Using this particular solution for symmetrical dispersion,  $\sigma$ -dispersion should remain constant. However, its value varies with elution volume, indicating unsymmetrical axial dispersion.

Several attempts have been made to account for unsymmetrical dispersion.<sup>7-11</sup> Three of the treatments have been reviewed<sup>10</sup> and were found to be lacking in stability and magnitude of correction, or were extremely difficult to carry out because of ill-conditioned algebraic equations. One promising technique is an analytical solution proposed by Balke and

TABLE III  
Comparison of Given Polydispersity with Mathematically Corrected Values

Sample	Given polydispersity	Uncorrected GPC polydispersity	Corrected polydispersity
PS-244	1.06	1.17	1.15
PS-1220	1.04	1.12	1.09
PS-2360	1.02	1.12	1.10
PS-4160	1.05	1.16	1.14
PS-9800	1.05	1.23	1.19
PS-20200	1.12	1.35	1.30

Hamielec.<sup>10</sup> However, their result required a prior knowledge of resolution factors or a "skew factor." Without this knowledge, two polymer samples of the same peak elution volume but different polydispersity values are needed. Neither of these two conditions could be satisfied in this study, and therefore an original, if somewhat empirical, approach to the solution was pursued.

The assumption is made that the degree of dispersion occurring at a given elution volume is shown by the spread of a monodisperse material (e.g., a polystyrene fraction) having a molecular weight equivalent to that particular elution volume. Since for GPC chromatograms the molecular weight at the peak,  $M_p$ , has a value such that  $\bar{M}_n < M_p < \bar{M}_w$ ,<sup>12</sup> one may expect the ratio of the GPC  $\bar{M}_w/\bar{M}_n$  to the absolute polydispersity will

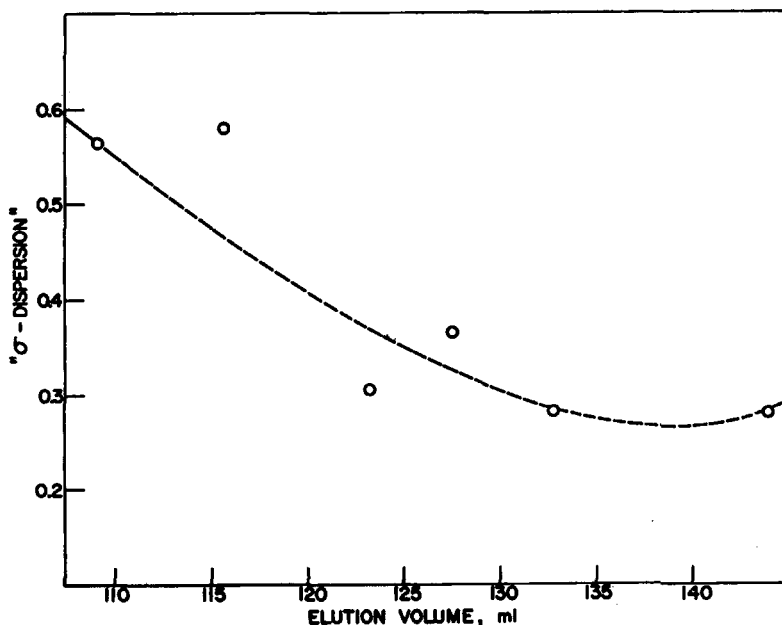


Fig. 4. Variations of  $\sigma$ -dispersion with peak elution volume for monodisperse polystyrene samples.



give a good representation of the dispersion occurring at  $M_p$ , providing that  $\bar{M}_w - \bar{M}_n$  is small.

Figure 5 shows a plot of the ratio of polydispersities obtained from the GPC to the given absolute values against elution volume for the polystyrene fractions. The similarity of this curve to that of Figure 4 supports the above reasoning. An horizontal line in Figure 5 would have indicated that only symmetrical dispersion was occurring in the columns. However, since the curve is not linear, the dispersion must have been unsymmetrical. For the correction curve to be suitable for use with other polymers, it was necessary to correlate the polydispersity ratio with extended chain length. Regression analysis of the values yielded the following equation:

$$P_{D(\text{GPC})} : P_{D(\text{ABS})} = 1.56 - 0.1446 \ln A + 0.011 (\ln A)^2$$

where  $P_D$  = polydispersity and  $A$  = molecular size in angstroms, determined from the polystyrene calibration curve.

The logic of this approach to dispersion corrections was confirmed by using this equation to correct the polydispersity values obtained for the nylon fractions by GPC and predicting the absolute  $\bar{M}_w$  values by multiplication of the corrected polydispersity values with the  $\bar{M}_n$  values obtained by osmometry.

The  $\bar{M}_w$  values of five of the nylon fractions were determined by 90° light scattering in 95% formic acid, with 0.02 moles of sodium formate,

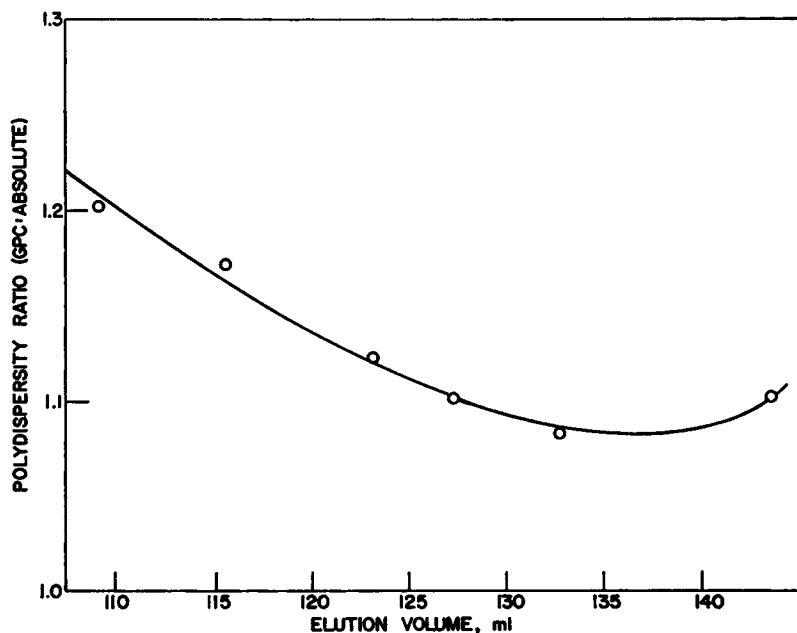


Fig. 5. Variation of polydispersity ratio (GPC: absolute) with peak elution volume for the polystyrene samples.

TABLE IV  
Comparison of  $\bar{M}_w$  Predicted with  $\bar{M}_w$  Absolute for Nylon Samples

Fraction	Predicted $\bar{M}_w$	Light scattering $\bar{M}_w$
$2/2$	41,350	42,800
3	40,500	51,000
6	28,800	25,800
8	18,000	18,800
$2/1$	15,900	14,000

using both green and blue illumination.<sup>13</sup> These values are compared with the predicted values of  $\bar{M}_w$  in Table IV. With the exception of the discrepancy of fraction 3, the predicted and absolute  $\bar{M}_w$  values agree within the precision of absolute  $\bar{M}_w$  determinations.

Thus, through the use of the polystyrene calibration curve, the  $Q$ -factor, the viscous fingering, and the dispersion correction equations, quantitative characterization of linear nylon 66 on a regular practical basis was made possible. During subsequent operation of the GPC using different column configurations, the general forms of the correction equations remained applicable.

#### Construction of a Universal Calibration Curve

The foregoing corrections have been applied to GPC molecular weights calculated using a  $Q$ -factor for the shape of the molecule in solution. While this has been shown to be sufficient for linear nylon 66, it has little meaning when applied to branched polymers. Thus, for purposes of work to be carried out on branched nylon polymer, it was necessary to establish a universal calibration curve.

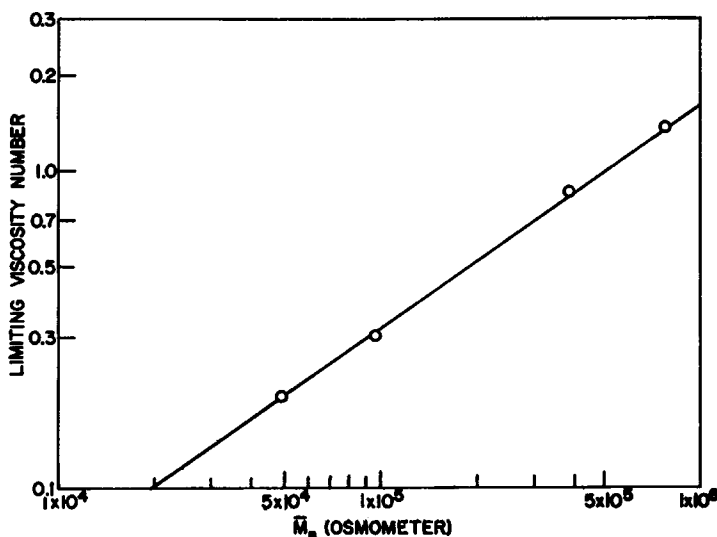


Fig. 6. Relation of  $\ln [\eta]$  to  $\ln \bar{M}_n$  for four characterized polystyrene polymers.

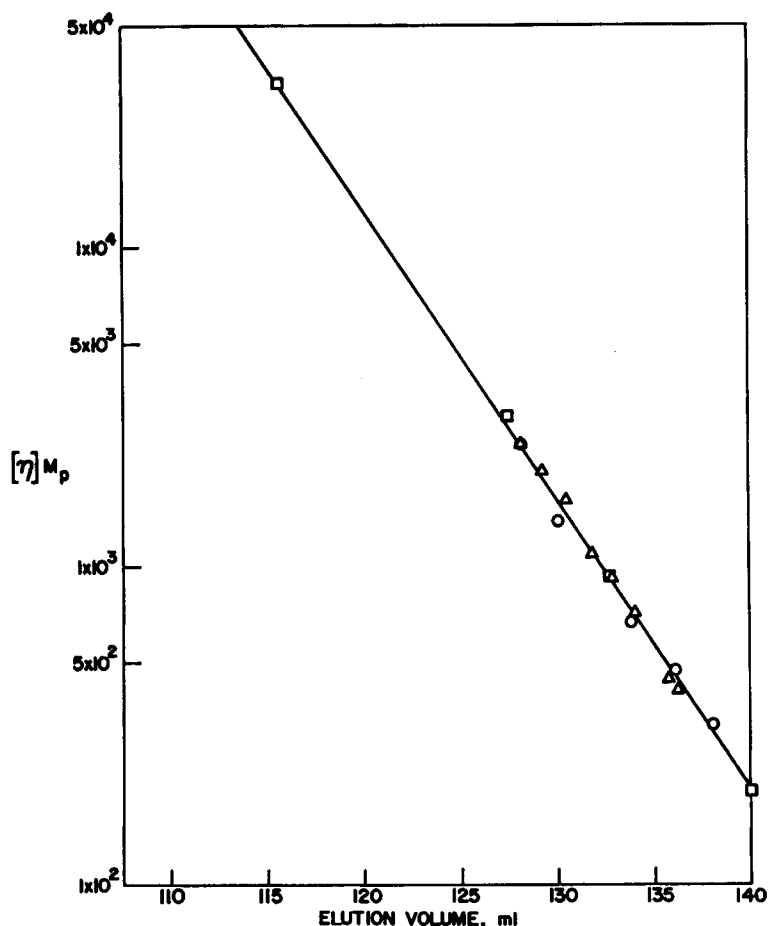


Fig. 7. A universal calibration curve for (□) monodisperse polystyrene; (○) fractionated nylon 66; (△) polydisperse nylon 66.

The use of hydrodynamic volume as a calibration parameter was first proposed by Benoit et al.<sup>14</sup> through their work with branched polystyrenes. They suggested this parameter on the basis of the Einstein viscosity law,

$$[\eta] = k \left( \frac{V}{M} \right)$$

where  $V$  is the hydrodynamic volume of the particles,  $M$  is the molecular weight, and  $k$  is a constant. This equation shows  $[\eta]M$  to be a direct measure of the hydrodynamic volume. In order to obtain values of this volume parameter for the polystyrene standards, solution viscosities were measured at 130°C in the same apparatus used for the nylon viscosity determinations. A plot of  $\ln [\eta]$  against  $\ln \bar{M}_n$ , shown in Figure 6, gave the following equation by regression analysis:

$$\text{polystyrene } [\eta]_{m\text{-cresol}}^{130^\circ\text{C}} = 8.465 \times 10^{-5} (\bar{M}_n)^{0.715}.$$

A universal calibration plot of the product of limiting viscosity number and molecular weight at the chromatogram peak apex against elution volume at maximum peak height for the polystyrene standards, nylon fractions, and regular polydisperse plant polymer was constructed and is shown in Figure 7. The good correlation obtained for the two polymer types and the different polyamide dispersities further substantiates the results of other workers<sup>5,14</sup> on the universal nature of hydrodynamic volume as a calibration parameter.

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