An Extrapolation Method for Eliminating Overload Effects from Gel Permeation Chromatograms†

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For high polymers eluted through a gel permeation chromatograph by tetrahydrofuran at 50°C and by Tetralin at 130° to 145°C the level of distortion of a chromatogram decreases as the weight of polymer injected into the gel permeation chromatograph decreases. The effect is present down to injected weights of 44 microgrammes. Comparing single chromatograms of polymers of different molecular weight by injecting constant weight may be misleading because the level of distortion of the chromatogram also decreases as the molecular weight of the polymer decreases. A method to eliminate distortion due to finite injected weight by extrapolating data to zero injected weight has been developed for polystyrenes eluted by tetrahydrofuran. This method gives viscosity average molecular weights which agree with intrinsic viscosity measurements. The systematic and random errors in the calculation of average molecular weights from a single chromatogram and hence the errors in the extrapolation method are examined. The major random error stems from uncertainty in the chromatograph baseline. The size of this error first depends on the level of instrumental noise and drift and secondly depends strongly on the shape of the distribution.

MOORE[1] recognized in the earliest paper on gel permeation chromatography that the chromatogram of a high polymer is distorted by overload. Moore and Hendrickson[2] later described overload as being due to large or concentrated or very viscous injected solutions. Several methods have since been described for removing the effects of overload. There are two types. First there are methods[3-5] which correct for overload by, briefly, taking the elution curve of a monodisperse sample to be, say, Gaussian, then finding the value of the dispersion coefficient as a function of molecular weight and finally using these data to calculate the undistorted chromatogram from a single experimental chromatogram of a polydisperse polymer. The other methods[6,7] consider that overload distortion is avoided by extrapolating data to zero injected weight of polymer. Details of one of these are presented here.

EXPERIMENTAL

The instrument used was a Waters Associates Inc. MK 100 gel permeation chromatograph (GPC)[8]. During work with tetrahydrofuran (THF) at 50°C it was used in a constant temperature room at $23{\cdot}5 \pm 0{\cdot}5$°C. During work at 130° to 145°C with Tetralin (tetrahydronaphthalene) in the constant temperature room a Hallikainen temperature controller was fitted to the refractometer heat exchanger and power supplied to the whole instrument from a constant voltage transformer. Solvent flow rate was 1 ml/min

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nominal. Solution concentrations were 1% wt/vol or less. The instrument's performance at high temperatures was improved by replacing the original single pump split-stream solvent supply by two pumps to provide independent sample and reference streams.

The THF was analytical reagent grade. The Tetralin was technical grade dried to < 2 p.p.m. water by crude distillation and contained 0·2% wt/vol Ionol (2,6-di-*tert*-butyl-4-methyl phenol) as antioxidant. The Tetralin was purged in the GPC with dry, oxygen-free nitrogen. Polyolefin solutions in Tetralin containing antioxidant were made by dissolving polymer at the GPC oven temperature under a nitrogen blanket. The solutions were filtered through a Walters filter unit at 5 deg. C lower temperature using 80 lbf/in^2 nitrogen pressure and were reheated to the oven temperature under nitrogen before injection. Despite the precautions to prevent degradation of the polymer prior to and during elution there was slight thermal degradation of polypropylene. Polystyrenes easily dissolved in THF or Tetralin at 45°C. Three column sets were used:

A = 4×10^5, 10^5, 10^3 and 45 Å

B = 7×10^5, 3×10^4, 3×10^3, 8×10^2 Å

C = 10^6, 4×10^5, 2×10^4 and 10^4 Å.

Table 1 shows the calibration standards used.

Table 1. Details of calibration standards

GPC peak mol. wt	$\overline{M}_w/\overline{M}_n$	*Source*	*Column sets calibrated*
Polystyrene			
3 140 000	1·24[1]	S 114 ex Dow (See Note)	ABC
860 000	<1·15	Pressure Chemical Co. Batch 6a	BC
411 000	<1·06	Pressure Chemical Co. Batch 3a	BC
257 000	1·08[1]	Waters Associates Inc.	A
168 000	1·06[1]	Waters Associates Inc.	A
160 000	<1·06	Pressure Chemical Co. Batch 1a	BC
122 000	—	Waters Associates Inc.	ABC
97 200	<1·06	Pressure Chemical Co. Batch 4a	BC
51 000	<1·06	Pressure Chemical Co. Batch 7a	BC
19 800	<1·06	Pressure Chemical Co. Batch 2a	BC
10 300	<1·06	Pressure Chemical Co. Batch 8a	BC
4 000	<1·10	Pressure Chemical Co. Batch 11a	BC
2 000	<1·10	Pressure Chemical Co. Batch 12a	BC
Polypropylene Glycols			
3 900		Waters Associates Inc.	AB
2 000		Waters Associates Inc.	AB
1 250		Waters Associates Inc.	B
790		Waters Associates Inc.	AB

NOTE: M_{peak} calculated as $\overline{M}_w \{\overline{M}_n/\overline{M}_w\}^{\frac{1}{2}}$ using $\overline{M}_w = 3{\cdot}5 \times 10^6$.

RESULTS AND DISCUSSION

Overload effects on peak elution volume of fractions and polydisperse polymers

Figures 1 and *2* show the effect of the injection procedure on the peak

elution volume of a narrow molecular weight distribution polymer eluted by THF at 50°C through column set A. *Figure 1* shows how the peak elution volume of the 257 000 molecular weight polystyrene standard varies with the concentration and injection time of the injected solution. Note that the injection time is fairly closely related to the injected volume of solution. In *Figure 2* the same data are plotted as peak elution volume against injected weight of polystyrene and clearly the elution volume decreases smoothly with decreasing injected weight. The same smooth decrease is shown in many other instances in *Figure 3*. *Figure 3* shows two sets of data, first plots of peak elution volume against injected weight for polystyrene and polypropylene glycol standards eluted by THF at 50°C and, secondly, similar plots using the same column set, A, but eluted by Tetralin at 130°C. *Figure 4* shows the same smooth decrease for polystyrene only eluted with Tetralin at 145°C through column set C. *Figure 5* presents data of Seward[9] which shows again the smooth decrease of peak elution volume with decrease of injected weight for a polybutadiene fraction eluted by benzene at 65°C.

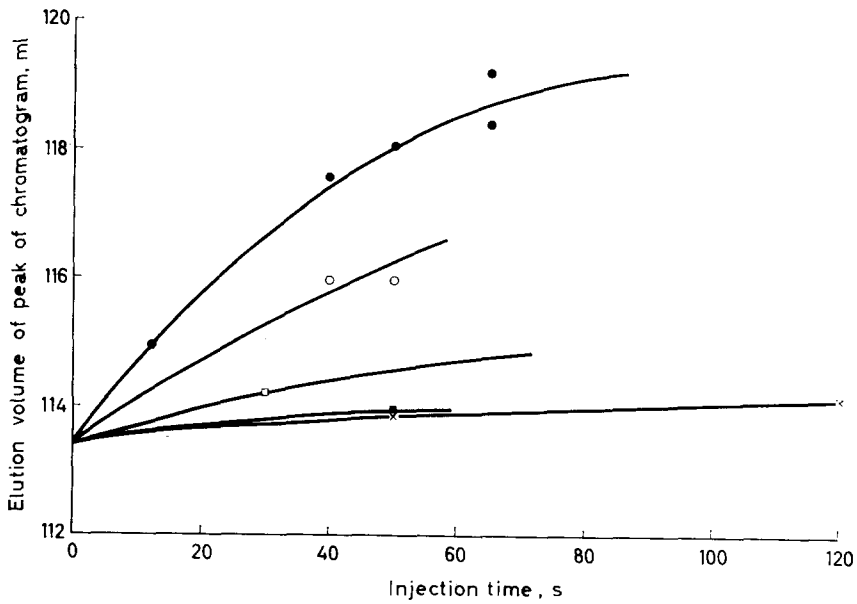


Figure 1—Effect of overload on peak elution volume of 257 000 molecular weight polystyrene standard for column set A in THF at 50°C. ● 1% ○ ½% □ ¼% ■ ⅛% × 1/16% wt/vol

For polydisperse polymers there is a similar decrease of peak elution volume with decrease of injected weight. This is illustrated in *Figure 6* which shows a polystyrene eluted by THF at 50°C and two results with Tetralin, one for low density polyethylene at 130°C and one for polypropylene at 145°C.

This decrease of peak elution volume with decrease of injected weight has been found in other polymer–solvent systems. These include *cis*-poly-

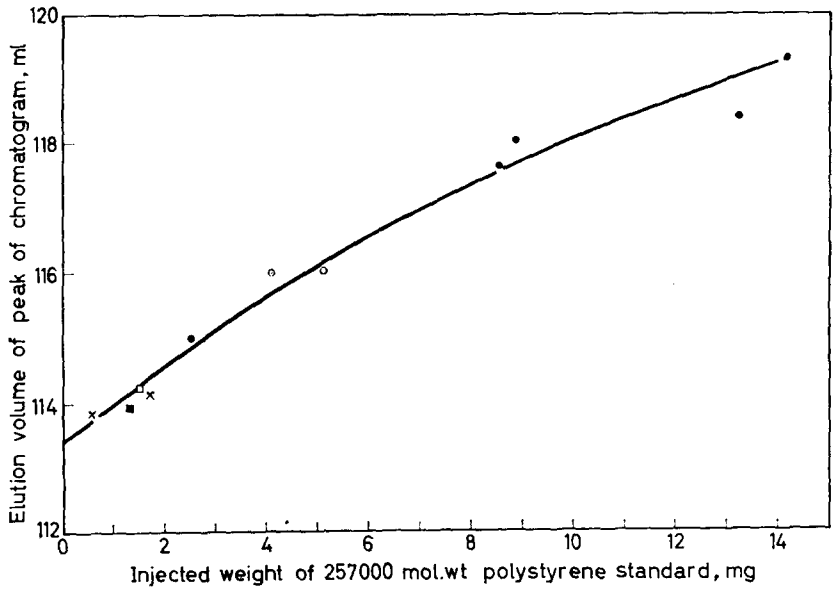


Figure 2—Effect of injected weight on peak elution volume of 257 000 molecular weight polystyrene standard for column set A in THF at 50°C. ● 1% ○ ½% □ ¼% ■ ⅛% × 1/16% wt/vol

butadienes with THF[10], polystyrenes with trichlorobenzene at 130°C[11], polystyrenes with toluene at 65°C[9] and polyisobutenes with trichlorobenzene at 150°C[7]. It is clear that this overload effect is common to all high polymer work. Down to 500 μg of injected polymer the results obtained at Carrington Plastics Laboratory show no evidence of a critical injected weight below which there is no longer a decrease in elution volume with decreasing injected weight. Seward[9] finds no evidence of a critical injected weight down to 55 μg polybutadiene eluted by benzene at 65°C and 44 μg polystyrene eluted by toluene at 65°C. Boni *et al.*[11] find no evidence down to *ca.* 50 μg polystyrene eluted by trichlorobenzene at 130°C.

Overload effects on shape of chromatograms of polydisperse polymers

Change in the injected weight not only alters the elution volume of the peak of the chromatogram but it also changes the shape of the chromatogram generally. This is illustrated in *Figure 7* for Carinex HRM nibs, a polystyrene of weight to number average molecular weight ratio 2·85, eluted by THF at 50°C through column set A. The areas under the chromatograms are drawn equal to make comparison easier. The dotted curve shows the zero injected weight curve deduced from 14 chromatograms of different weights by extrapolating the height at each elution volume to zero injected weight. The change of shape of the chromatogram is mainly at the high molecular weight end. At elution volumes above 107 ml the trace is moved bodily to higher elution volumes as the injected weight is increased. Below 107 ml the high molecular weight end of the trace is truly distorted.

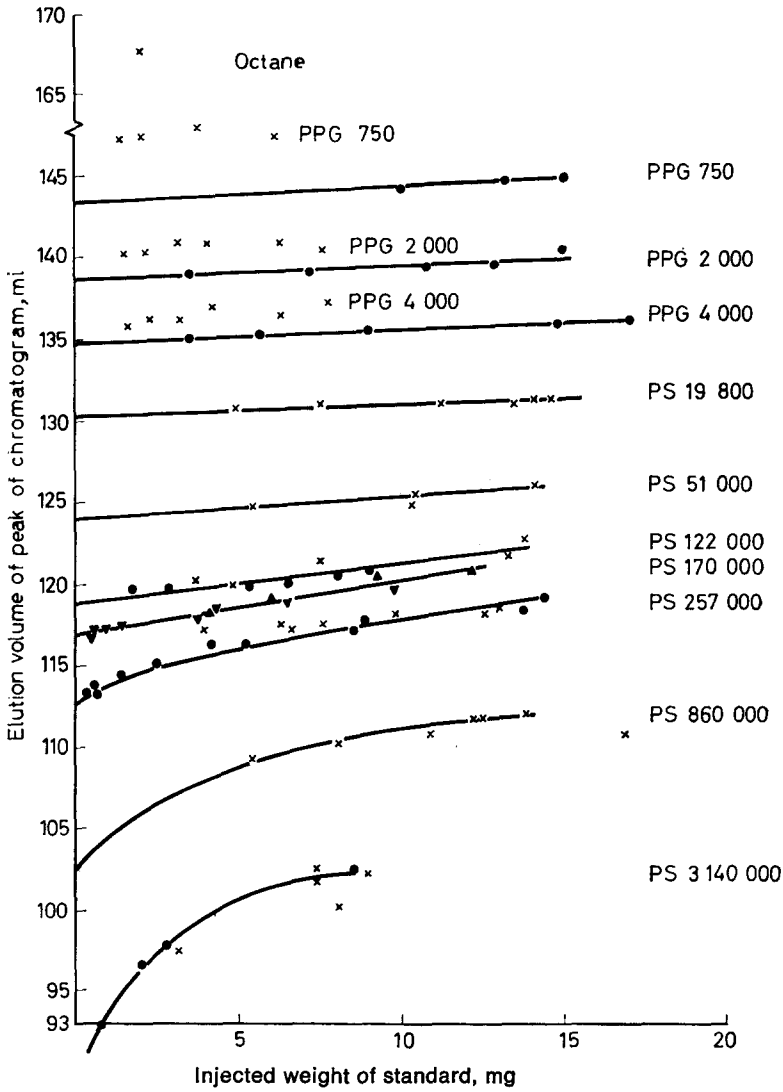


Figure 3—Effect of injected weight on peak elution volume of polystyrene and polypropylene glycol standards for column set A: ● and ▼, THF at 50°C; × and ▲, Tetralin at 130°C

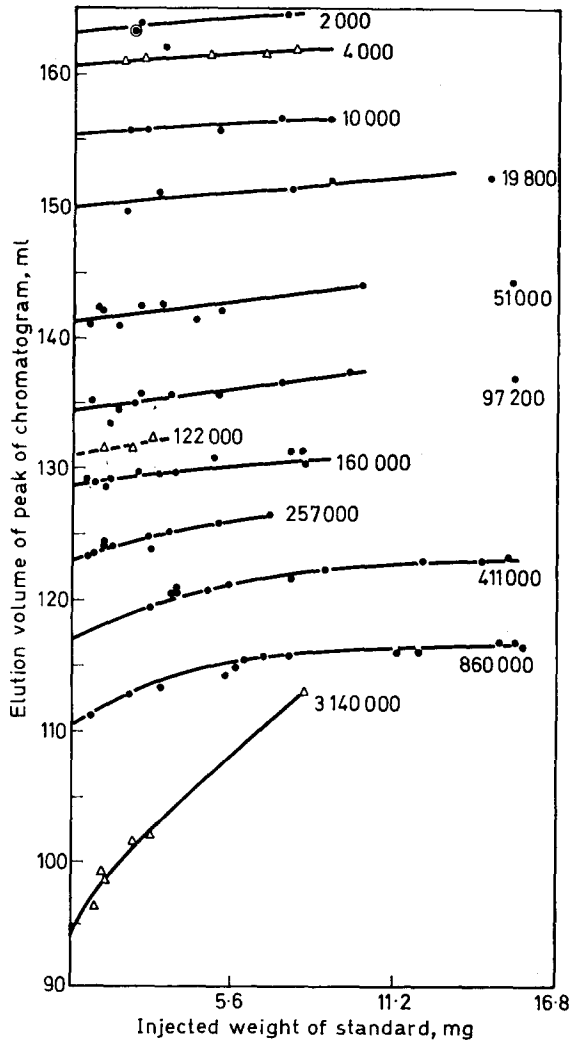


Figure 4—Effect of injected weight on peak elution volume of polystyrene standards for column set C in Tetralin at 145°C

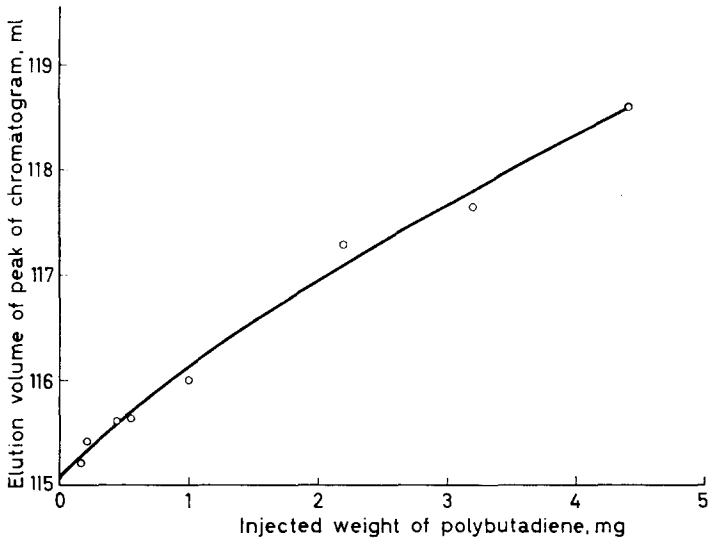


Figure 5—Effect of injected weight on peak elution volume of polybutadiene fraction (Seward's data). Benzene at 65°C; Columns: 6×10^5, 10^4, 10^2, 10^2; Flowrate: 1 ml/min; Null glass thickness: 0·008 in.; Number average molecular weight 66 000; $\bar{M}_w/\bar{M}_n$ about 1·5

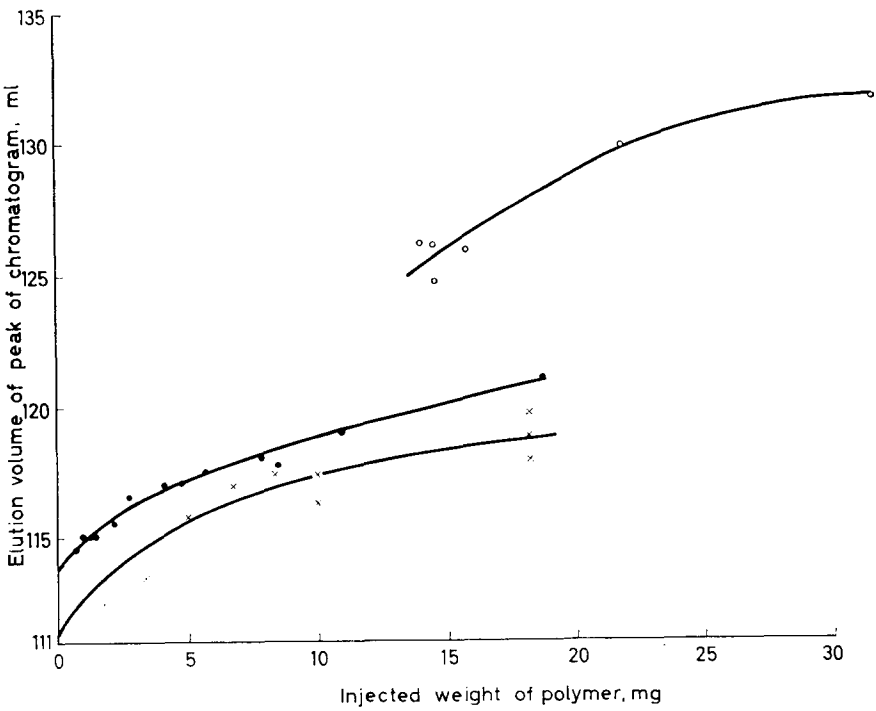


Figure 6—Effect of injected weight on peak elution volume of polydisperse polymers. ○ low density polyethylene; ● polystyrene (Carinex HRM nibs); × polypropylene

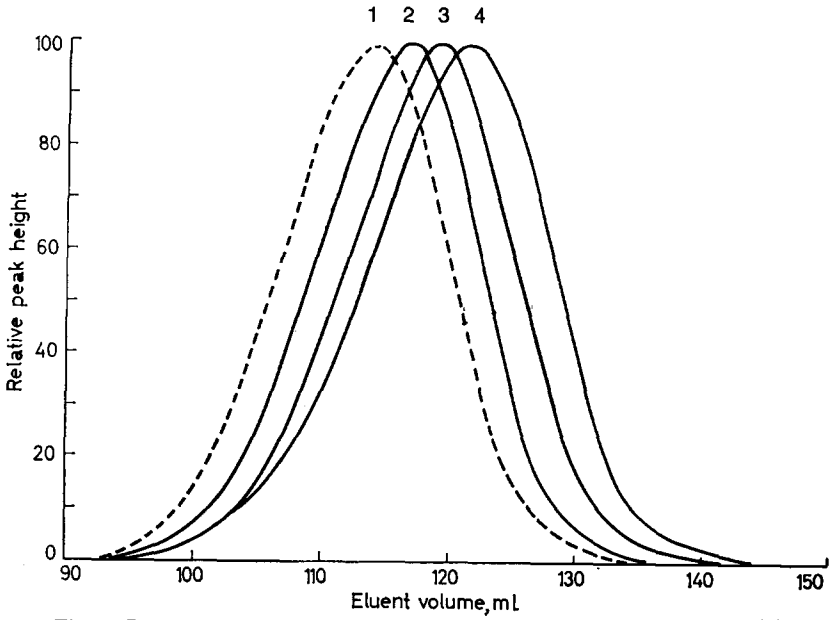


Figure 7—Effect of injected weight on chromatogram shape. (1) 0, (2) 5·68, (3) 10·9, (4) 18·6 mg injected weight of Carinex HRM nibs

Variation of overload effects with molecular weight

Figures 3 and *4* show that the initial rate of change of peak elution volume with change in injected weight decreases as the molecular weight of the polymer decreases. This explains why overload is not normally encountered in work on small molecules. Values of the initial rate of change are shown in *Figure 8* for polystyrene standards eluted by THF through the two column sets A and C. Above 10 000 molecular weight there is a linear relation between the logarithm of the rate of change and the logarithm of molecular weight. Boni *et al.*[11] found a similar result over a narrower molecular weight range for polystyrene standards eluted by trichlorobenzene at 130°C.

Calibration standards and calibration curves

For column set A the elution volume of standards eluted by THF at 50°C was measured by taking the syphon volume as 5 ml (nominal). While eluting with Tetralin at a higher temperature a combination of thermal expansion, different solvent–gel or solvent–polymer interaction slightly changed the elution volume of a standard. Using 4·942 ml as the syphon volume during elution by Tetralin permits the peak elution volumes of the polystyrene standards eluted by the two solvents through the one column set A to be superimposed very well. This is shown in *Figure 3*, from which calibration curves have been constructed. According to Harmon[12] the elution volume of polypropylene glycols and polystyrenes of the same molecular length are equal when eluted by THF. Therefore, from *Figure 3*, polypropylene gycol molecules must become relatively smaller than polystyrene molecules of the same length when eluted by Tetralin at 130°C.

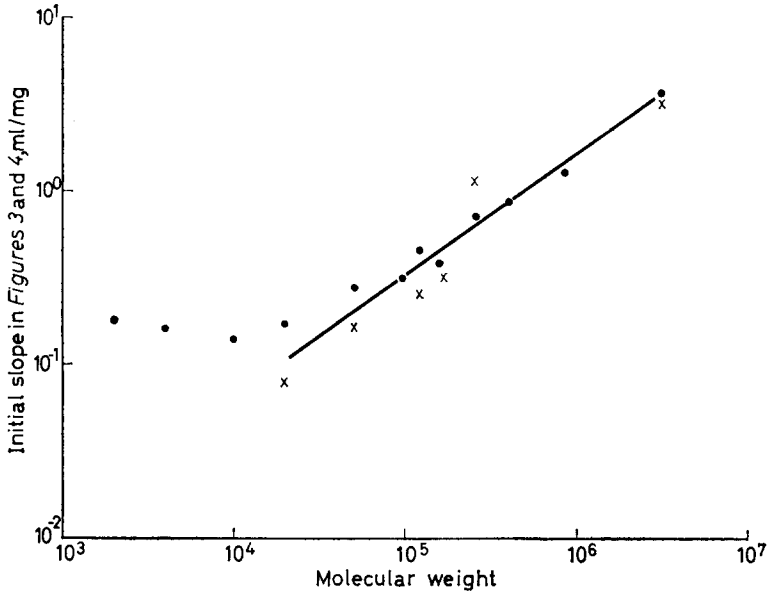


Figure 8—Variation of overload with molecular weight of polystyrene standards. × THF at 50°C and Tetralin at 130°C in column set A; ● Tetralin at 145°C in column set C

The elimination of overload effects by extrapolation

The effects of overload are present at all finite weights, so they ought to be eliminated by extrapolating data to zero injected weight. In order to calculate the undistorted average molecular weights it is thus necessary to have a chromatogram for the polymer and a calibration curve for the set of columns, both extrapolated to zero injected weight. The extrapolation of the peak elution volume of the calibration standards to give zero injected weight calibration curves has been illustrated in *Figures 3* and *4*.

It is convenient to extrapolate the chromatogram of the polymer to zero injected weight indirectly as follows. Each average molecular weight is calculated using the zero injected weight calibration curve with each of a series of finite weight chromatograms. The series of values are then extrapolated to zero injected weight of polymer.

This extrapolation method has been applied to six commercial grades of polystyrene eluted by THF at 50°C through column set A. The extrapolation for viscosity average molecular weight is shown in *Figure 9*. The diagonal line through each point represents the estimated maximum random error it can have. The derivation of this estimate is explained later.

The calculation of viscosity average molecular weight from a distribution involves α from Houwink's[13] equation $(\eta)=K\overline{M}_v^{\alpha}$. Since α changes with solvent and temperature the calculated $\overline{M}_v$ must be referred to one solvent and temperature, in this case toluene at 25°C using $(\eta)=1{\cdot}443 \times 10^{-4}\,\overline{M}_v^{0{\cdot}704}$. These values of K and α were determined by fitting the best straight line to a combination of six sets of data[14–19].

Table 2. Average molecular weights calculated from finite injected weight chromatograms

Polymer	*Injected weight (mg)*	$\bar{M}_n \times 10^{-3}$	$\bar{M}_v \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$S = \frac{\bar{M}_n \bar{M}_z}{(\bar{M}_w)^2}$
'Carinex' HRM	10·16	83	154	205	0·910
	7·50	93	215	245	0·844
	4·39	108	274	285	0·785
	4·10	120	254	300	0·852
'Carinex' MW	5·76	97	242	278	0·778
	4·66	105	252	289	0·829
'Carinex' HR	6·37	79	180	206	0·819
	6·02	80	185	209	0·830
	5·06	86	190	218	0·881
	4·77	83	196	225	0·833
	4·14	92	195	219	0·851
'Carinex' GP	3·11	83	192	217	0·757
	1·30	106	209	229	0·585
'Carinex' QP	4·38	82	188	214	0·818
	4·14	90	190	214	0·819
	4·04	79	190	213	0·675
	1·80	97	205	229	0·780
'Lustrex' HF 55	11·6	35	124	147	0·593
	8·75	38	132	156	0·581
	5·04	44	146	170	0·570
	3·98	47	169	(199)	0·570
	3·45	45	159	181	0·543

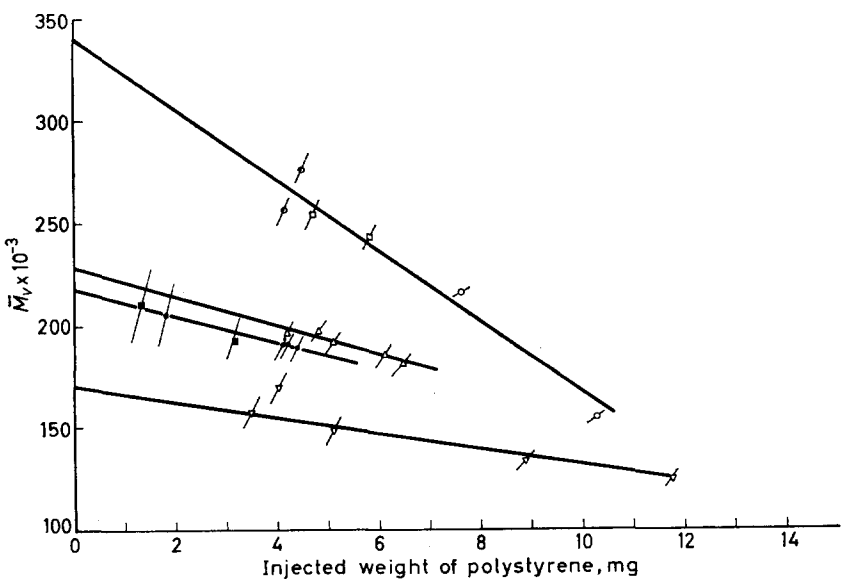


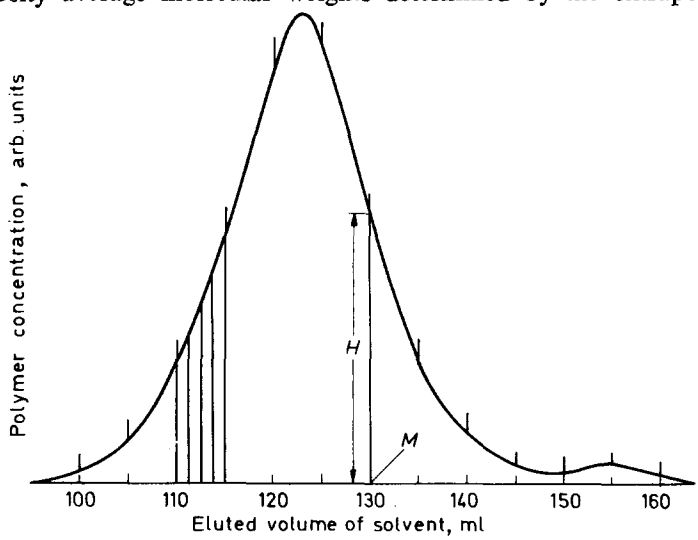
Figure 9—Extrapolation of finite weight $\bar{M}_v$ values to zero injected weight. ○ HRM nibs; □ MW nibs; △ HR nibs; ■ GP nibs; ● QP nibs; ▽ HF 55 nibs

The positions of the lines in *Figure 9* are not judged just from data on individual polymers. Because Carinex HRM and MW and Carinex QP and GP have almost identical molecular weights and distributions it is acceptable to couple the data for each pair. This does not predetermine the GPC results. Values of the average molecular weights calculated from finite

Table 3. Average molecular weights extrapolated to zero injected weight

Polymer	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\frac{\overline{M}_w}{\overline{M}_n}$	*S*	$\overline{M}_v$ *from i.v.* $\times 10^{-3}$
'Carinex' HRM	125±8	337±10	356±11	2·85±0·14	0·83±0·1	322
MW	125±8	337±10	356±11	2·85±0·14	0·83±0·1	324
HR	106±6	226±10	261± 9	2·46±0·13	0·83±0·1	225
GP	97±15	216±10	241±10	2·49±0·30	0·83±0·1	214
QP	97±15	216±10	241±10	2·49±0·30	0·83±0·1	214
'Lustrex' HF55	51± 3	172±10	194±10	3·80±0·36	0·55±0·15	201

injected weight chromatograms are given in *Table 2* and the results of the extrapolations to zero injected weight are given in *Table 3*. The errors in *Table 3* are the maximum random error any value can have. In *Table 3* the viscosity average molecular weights determined by the extrapolation



$$\overline{M}_n = \Sigma H / \Sigma (H/M)$$

$$\overline{M}_v = \left[\Sigma (HM^{\alpha}) / \Sigma H\right]^{1/\alpha} \text{ where } \alpha \text{ is given by } \overline{M}_v^{\alpha} = k[\eta]$$

$$\overline{M}_w = \Sigma (HM) / \Sigma H \quad \overline{M}_z = \Sigma (HM^2) / \Sigma (HM)$$

Figure 10—Chromatogram of Monsanto 'Lustrex' HF 55 showing use of strip method

method generally agree very well with those found from intrinsic viscosity measurements in toluene at 25°C. The $\overline{M}_w/\overline{M}_n$ ratio by GPC for the Carinex grades are as expected for suspension polymers and the ratio for the Monsanto grade is as expected from a bulk polymerization. Hence the extrapolation method gives results apparently undistorted by overload.

In *Table 3* the worst agreement between the GPC and the intrinsic viscosity data occurs with the Monsanto grade. The cause of the disagreement has not been fully diagnosed. Some of it may stem from the few per cent of low molecular weight additive present in this material. As can be seen from *Figure 10* the low molecular weight end of the chromatogram has a short peak which merges into the tall polystyrene peak. In order to determine the average molecular weights of the polystyrene alone, as has been done in all the calculations, it is necessary to decide on the proportion of polystyrene in the low molecular weight tail. This decision is partly intuitive and therefore likely to be in error. Some of the disagreement for the Monsanto grade may also be due to a systematic low molecular weight calibration error because at low molecular weights no polystyrene standards were available and polypropylene gycol standards and eicosane were used. The calibration curve used is shown in *Figure 11*. There is close agreement between the original extrapolated curve and the points from *Figure 3* for the three extra polystyrene standards eluted through column set A by Tetralin at 130°C. Whenever calibration standards are physically or chemically different from the polymer under investigation the calibration has to be modified by rules that are not yet conclusively established.

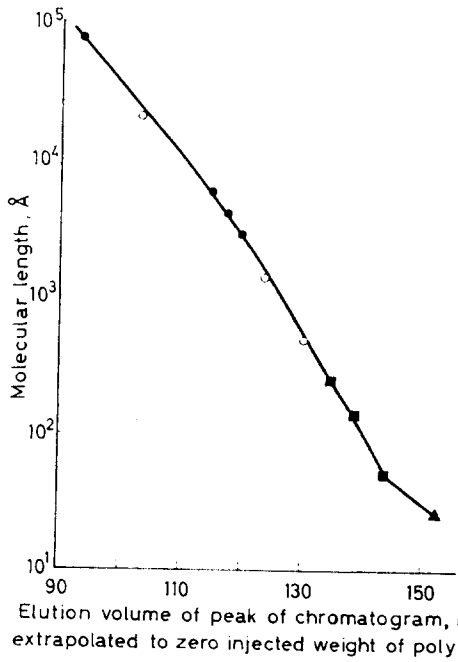


Figure 11—Calibration curve for column set A using THF at 50°C as eluent. ● polystyrene standard; ■ polypropylene glycol standard; ▲ eicosane; ○ polystyrene standard using Tetralin at 130°C

Harmon's[12] conclusion that polystyrenes and polypropylene glycols of the same molecular weight are eluted by equal volumes of THF at 50°C was based on finite weight data and may not be valid at zero injected weight. This systematic error in the low molecular weight end of the calibration curve would have greatest and most noticeable effect on the Monsanto grade because this grade has a longer low molecular weight tail than any Carinex grade. Since $\overline{M}_n$ is more sensitive than $\overline{M}_v$ to the amount and molecular weight of the polymer in the low molecular weight tail the $\overline{M}_n$ value for Monsanto Lustrex HF 55 in *Table 3* will be, on these arguments, considerably too low.

Comparative molecular weights from single chromatograms

The extrapolation procedure has the disadvantage that several GPC chromatograms for each polymer are required. If comparative distributions only are sought, it is tempting, because it is quicker, to compare single chromatograms. However, the comparison may mislead. If injected weight alone were responsible for distortion of the molecular weight distribution, then chromatograms obtained with equal injected weight would be comparable. However, this is not so because the distortion due to injected weight decreases as the molecular weight of the polymer decreases. The following example shows how equal weight GPC results can be misleading.

Table 4. Comparison of zero mg and 10 mg injected weight results from *Figure 9*

Polymer	$\overline{M}_v$ *at zero mg* $\times 10^{-3}$	$\overline{M}_v$ *by i.v.* $\times 10^{-3}$	$\overline{M}_v$ *at 10 mg.* $\times 10^{-3}$
(a) 'Carinex' HRM and MW	337	324	174
(b) 'Carinex' GP and QP	216	214	150
Ratio *a*/*b*	1·55	1·52	1·16

Single chromatogram results at 10 mg injected weight of the Carinex polystyrenes are taken from *Figure 9* and compared in *Table 4* with the zero injected weight results. The 10 mg results show that different process conditions change $\overline{M}_v$ by a factor of only 1·16 from the lowest to the highest molecular weight polymer whereas the zero injected weight results agree with intrinsic viscosity data and show the factor to be about 1·53. The same misleading effect has been found when comparing intrinsic viscosity data with gel permeation chromatography results on a series of polypropylenes when the injected weight of each polypropylene was about 19 mg.

Errors in calculation of average molecular weights from gel permeation chromatograms

The idea of the extrapolation to zero injected weight as a method of eliminating distortion due to finite weight was initially intuitive. The extrapolation gives viscosity average molecular weights which agree with those from intrinsic viscosity measurements, so it is tempting to assume that extrapolated $\overline{M}_n$ and $\overline{M}_w$ values are distortion free. However, there is no

theoretical reason why the scales on the axes in *Figure 9* need be linear. Cantow *et al.*[7] have used an extrapolation to zero injected weight plot with reciprocal molecular weight as the ordinate. Plotted this way the data in *Table 2* for Carinex HR and lower molecular weight polymers again lie on straight lines. *Figure 9*-type and Cantow-type plots give zero injected weight results for $\overline{M}_v$ and $\overline{M}_w$ which are almost identical, as shown by comparing *Tables 3* and *5*; however, for $\overline{M}_n$ a Cantow plot gives higher values than the *Figure 9*-type plot. For Carinex HRM the $\overline{M}_v$ and $\overline{M}_w$ data on Cantow

Table 5. Average molecular weights extrapolated to zero injected weight on Cantow plot

Polymer	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$
'Carinex' HRM and MW	141	—	—
'Carinex' HR	130	247	263
'Carinex' GP and QP	120	220	239
'Lustrex' HF 55	58	176	198

plots do not lie on straight lines and in order to extrapolate to an $\overline{M}_v$ comparable with the intrinsic viscosity value the data must be fitted to a strong curve as shown in *Figure 12*. Linear extrapolation on Cantow plots for $\overline{M}_v$ and $\overline{M}_w$ thus appears to be invalid at high molecular weights.

Apart from uncertainty about the scales on the axes, neither extrapolation method directly corrects for finite resolution in the gel permeation chrom-

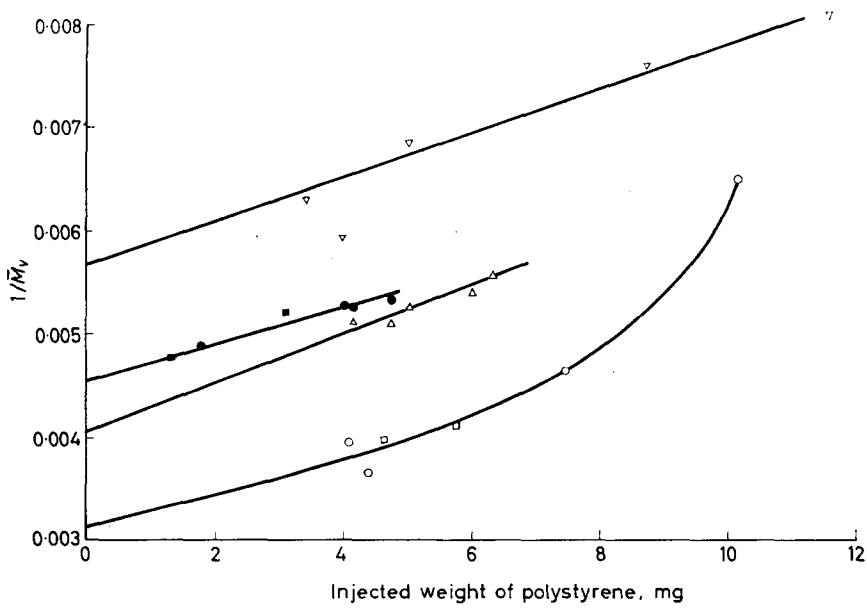


Figure 12—Extrapolation of finite weight M_v values by Cantow's method. ○ HRM nibs; □ MW nibs; △ HR nibs; ■ GP nibs; ● QP nibs; ▽ HF55 nibs

atograph and fine details of the distribution are probably blurred so that extrapolated results are probably not completely distortion free.

Whatever the credibility of the extrapolation method developed at Carrington Plastics Laboratory, systematic and random errors occur when it is applied. Systematic errors in a calibration curve derived using either different or insufficient standards have already been discussed. There are also random errors in deriving a calibration curve because neither the measurement of the peak elution volume nor the extrapolation to zero injected weight are free from random error. In the extrapolation method, once the calibration curve is derived it is applied to all chromatograms obtained on that column set so that calibration uncertainty can be regarded as a systematic error. In comparing results based on different calibration curves, however, this error must properly be included in assessing the total random error in the results.

Random errors in the strip method of calculation

The strip method of calculation illustrated in *Figure 10* is an approximation which becomes more exact as the strip width is decreased. The error introduced by the approximation has been studied by making trial calculations on practical distributions using an IBM 1401 computer. Results have been obtained for $\overline{M}_w$, $\overline{M}_n$, ΣH (the cumulative strip height) and for two other distribution parameters Q and S defined as

$$Q = \overline{M}_w / \overline{M}_n \quad \text{and} \quad S = \overline{M}_n \overline{M}_z / (\overline{M}_w)^2$$

Chiang[20] shows that $S = 1$ for a log normal distribution (log molecular weight plotted against cumulative weight fraction). *Figure 13* shows distributions with $S \gtrless 1$. The distribution with a high molecular weight tail has high $S (> 1)$, the distribution with a low molecular weight tail has low $S (< 1)$.

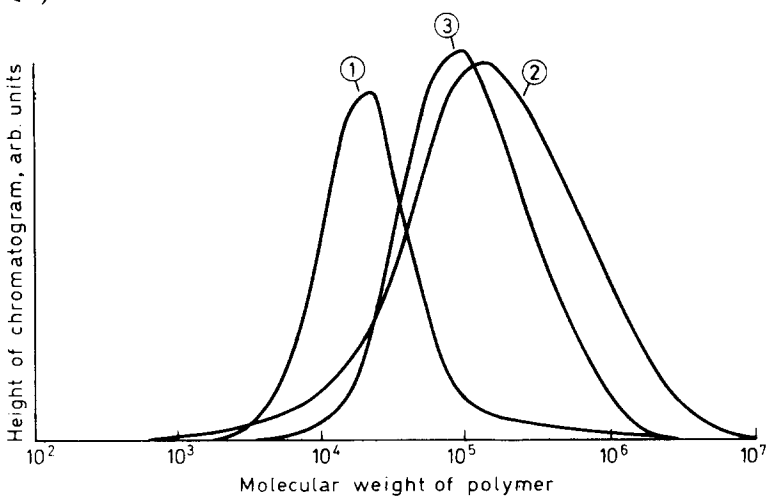


Figure 13—Molecular weight distribution with widely different S values. ① $S = 2{\cdot}27$; ② $S = 0{\cdot}490$. Distribution D in *Table 6*; ③ $S = 0{\cdot}926$. Distribution C in *Table 6*

In the strip method the chromatogram is converted into a histogram by dividing it into equal increments of elution volume and calculating $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$ and $\overline{M}_z$ by the usual expressions as shown in *Figure 10*. In practice each chromatogram is not divided into an integral number of strips but rather it is fitted on to a pre-arranged grid of strips related to calibration marks made by the GPC syphon as it empties. For example, a chromatogram exactly ten strips wide can be divided into nine whole strips plus two strips, one at each end, of width a and $(1-a)$ where $0 < a < 1$. Thus both the effect of the position of the chromatogram relative to the grid and the effect of strip width on the accuracy of the calculation must be studied. Details of four distributions upon which these effects have been studied are given in *Table 6*.

Distribution A was divided into 85 strips each 1/10 count wide, 42 or $43 \times 2/10$*, $17 \times 5/10$ and eight or nine whole counts. *Table 7* shows the effect on ΣH, $\overline{M}_n$, $\overline{M}_w$, Q and S. Distribution B was divided into $117 \times 1/10$ count strips, etc. and the effects shown in *Table 8*.

Tables 7 and *8* show that provided the strip width is less than five per cent of the total width of the distribution then the errors in the distribution parameters are less than ± 1 per cent. Strips of less than this width are used in other calculations throughout this paper.

Random errors from baseline uncertainty

Each calculation needs a chromatogram with a baseline as well as a calibration curve. The baseline is drawn in by the operator. 10 mg of one of the polystyrenes in *Figure 9* gives a maximum peak height of about 70 per cent full scale deflection with recorder sensitivity of 1×100. The combination of baseline noise and drift makes it usually difficult to judge the position of the baseline with a greater certainty than $\pm\frac{1}{2}$ per cent full scale deflection, i.e. $\pm 0{\cdot}7$ per cent peak height. For smaller injected weights the peak height is smaller and the same baseline uncertainty leads to larger proportional errors.

In Tetralin the refractive index difference between solvent and polystyrene is half that in THF and at high temperature operation (150°C) the baseline noise and drift is double that at 50°C so that, for a given injected weight, baseline uncertainty in Tetralin at 150°C is four times that in THF at 50°C.

The results of trial calculations on the effect of raising the baseline of the four distributions are shown in *Table 9*. With distributions A, B and C, which have S values close to unity, the errors due to baseline uncertainty of $\pm\frac{1}{2}$ per cent of the peak height are less than ± 3 per cent in ΣH, $\overline{M}_n$, $\overline{M}_w$ and less than ± 5 per cent in Q. The errors increase roughly in proportion with the baseline uncertainty. With distribution D, which has an S value much less than unity, the errors introduced by the same uncertainty ($\pm\frac{1}{2}$ per cent) are again less than ± 3 per cent in ΣH and $\overline{M}_w$ but have risen to up to ± 7 per cent in S and up to ± 10 per cent in Q and $\overline{M}_n$. This increased

*In 42 pairs the strips are (0 1), 2 3, 4 5, 6 7, . . ., 82 83, 84 85, where 0 1 is omitted because $H_0 = 0$. In 43 pairs the strips are 1 2, 3 4, 5 6, . . ., 83 84, 85-., where $H_{85} \neq 0$.

Table 6. Distributions used in trial calculations and summary of maximum random errors

Distribution	Q	S	Max. no. of strips	± % maximum errors due to: Strip width <5% ΣH	$\overline{M}_n$	$\overline{M}_w$	Q	S	Baseline uncertainty ±½% ΣH	$\overline{M}_n$	$\overline{M}_w$	Q	S	Baseline uncertainty ±1% ΣH	$\overline{M}_n$	$\overline{M}_w$	Q	S
A (log normal)	1·80	1·00	85	0·1	1	1	1	—	1	3	3	5	3	2	6	6	10	6
B (l.d.p.c.)	8·58	—	117															
C ('Carinex' HR)*	2·5	0·93	24						1·5	10	3	7	7	3	20	6	14	14
D (polypropylene)*	9·0	0·49	30															

*See *Figure 13.*

Table 7. Effect of strip width and position of strips relative to the chromatogram on the calculated average molecular weight—Distribution A

No. of strips	First group of strips	$\frac{\text{Strip width}}{\text{width of distribution}}$ · %	$\frac{\overline{M}_n}{\overline{M}_{n85}}$ · %	$\frac{\overline{M}_w}{\overline{M}_{w85}}$ · %	$\frac{Q}{Q_{85}}$ · %	$\frac{\Sigma H}{\Sigma H_{85}}$ · %	S
85	1	1·2	100·00	100·00	100·00	100·00	0·9978
43	1 2	2·4	99·99	100·01	100·01	100·00	0·9983
42	2 3		100·00	99·99	99·99	100·00	0·9974
17	1–5		100·03	100·05	100·01	100·00	1·0016
17	2–6		100·03	100·03	100·01	100·00	0·9993
17	3–7	5·9	100·01	99·98	99·96	100·00	0·9966
17	4–8		99·96	99·97	100·01	100·00	0·9961
17	5–9		99·96	99·98	100·01	100·00	0·9956
9	1–10		100·00	100·13	100·12	100·01	1·0058
9	2–11		100·00	100·07	100·06	100·00	1·0014
9	3–12		100·04	99·96	99·92	100·00	0·9961
9	4–13		99·92	99·98	100·06	100·00	0·9981
9	5–14	11·8	99·87	100·00	100·13	100·01	0·9981
8	6–15		100·06	99·97	99·91	99·99	0·9973
8	7–16		100·05	100·00	99·94	100·00	0·9972
8	8–17		99·99	100·00	100·01	100·01	0·9972
8	9–18		100·01	99·95	99·94	100·00	0·9941
8	10–19		100·05	99·95	99·90	—	—

Table 8. Effect of strip width and position of strips relative to the chromatogram on the calculated average molecular weight—Distribution B

No. of strips	*First group of strips*	*Strip width* / *Width of distribution*, %	$\frac{\bar{M}_n}{M_{n117}}$, %	$\frac{\bar{M}_w}{M_{w117}}$, %	$\frac{Q}{Q_{117}}$ %	$\frac{\Sigma H}{H_{117}}$, %
117	1	0·85	100·0	100·0	100·0	100·0
59	1 2	1·7	100·4	100·2	99·8	100·0
58	2 3	1·7	99·9	99·8	99·9	100·0
30	1– 4	3·4	99·4	100·0	100·7	100·0
29	3– 6	3·4	100·9	100·5	99·7	100·0
29	2– 5	3·4	99·9	99·9	100·0	100·0
29	4– 7	3·4	99·9	99·7	99·8	99·9
12	1–10	8·5	99·7	99·6	99·9	100·3
12	2–11	8·5	98·1	99·4	101·3	100·2
12	4–13	8·5	100·3	98·7	98·4	100·2
12	6–15	8·5	99·6	99·2	99·6	100·8
11	10–19	8·5	100·6	100·1	99·6	99·6
12	3–12	8·5	96·2	99·3	103·3	100·1
12	5–14	8·5	98·0	99·9	101·9	100·4
12	7–16	8·5	100·3	100·4	100·1	100·0
11	8–17	8·5	105·1	101·5	96·6	99·9
11	9–18	8·5	107·1	101·7	95·0	99·1
6	1–20	17·1	108·5	99·0	91·2	—
6	2–21	17·1	105·4	99·6	94·4	—
6	3–22	17·1	100·9	99·5	98·7	—
6	4–23	17·1	99·2	99·9	100·7	—
6	5–24	17·1	98·0	101·2	103·3	—
6	6–25	17·1	97·1	100·4	103·4	—
6	7–26	17·1	97·7	102·3	104·7	100·6
6	8–27	17·1	96·5	101·9	105·6	100·5
6	9–28	17·1	96·5	102·2	106·0	100·6
6	10–29	17·1	96·3	101·0	104·9	100·0
6	11–30	17·1	92·3	100·3	108·7	101·0
6	12–31	17·1	91·7	99·2	108·2	100·5
6	13–32	17·1	91·8	99·1	108·0	100·0
6	14–33	17·1	89·0	97·6	109·5	100·5
6	15–34	17·1	97·5	98·6	101·8	100·5
6	16–35	17·1	102·3	98·1	95·9	99·5
6	17–36	17·1	103·1	98·6	95·6	99·4
5	18–37	17·1	101·3	93·9	97·7	—
5	19–38	17·1	102·6	98·0	95·4	—
5	20–39	17·1	105·5	96·7	91·6	—

effect can be anticipated because the low S value for distribution D is due to the long low molecular weight tail shown in *Figure 13*. This tail will cause $\overline{M}_n$ to have great sensitivity to baseline uncertainty.

Since the position of the baseline may be more accurately determined at one end of the chromatogram than at the other these trial calculations on raising the baseline are idealized.

Table. 9. Effect of raising baseline upon calculated average molecular weights

Distribution as in Table 6	*% peak height that baseline is raised*	$\frac{\text{Strip width}}{\text{Width of distribution}}$, %	$\frac{\overline{M}_n}{\overline{M}_{n0}}$, %	$\frac{\overline{M}_w}{\overline{M}_{w0}}$, %	$\frac{Q}{Q_0}$, %	$\frac{S}{S_0}$, %	$\frac{\Sigma H}{(\Sigma H)_0}$, %
A	0·38	1·2	101·3	98·7	97·4	97·3	98·9
	0·75		102·0	98·0	96·1	97·8	98·0
	1·50		103·3	96·7	93·6	97·1	96·1
B	0·43	0·85	101·3	98·9	97·7	—	—
	0·87		102·6	98·0	95·5	—	—
	1·74		105·5	96·7	91·6	—	—
C	0·31	5	102·0	99·3	97·3	100·5	99·1
	0·62		104·1	98·6	94·7	100·7	98·3
D	1·0	3·3	121·6	97·7	80·3	115·1	97·1

Baseline uncertainty can be reduced by injecting greater weights and using lower instrument sensitivity. However, if there are any doubts about the validity of the linear extrapolation in *Figure 9* they will have greater justification as the injected weight increases and the range of the extrapolation becomes longer.

Random errors in injected weights

In the extrapolation method it is necessary to inject a range of weights. Only the relative weights need be known precisely. It is preferable to measure the injected weight directly, which is conveniently done because

$$\text{injected weight} = \text{constant} \times \Sigma H / (\text{refractometer sensitivity}).$$

The constant can be determined from a chromatogram obtained with an injection time long enough to be effectively infinite.

Combination of errors for the extrapolation method

Assuming the extrapolation is credible, the systematic error in the work on polystyrene eluted by THF at 50°C stems from extending the calibration curves into regions in which there are no polystyrene standards. Because the GPC extrapolated results for $\overline{M}_v$ agree with intrinsic viscosity measured $\overline{M}_v$ values the systematic error is apparently negligible except for Monsanto Lustrex HF55.

Table 6 includes a summary of the maximum random errors predicted by these studies. The Carinex polymers in *Figure 9* have distributions similar to distribution C. *Table 9* shows that as the baseline rises both $\overline{M}_v$* and ΣH (used to measure the injected weight) decrease, so the maximum error due to the experimental baseline uncertainty may be represented by the diagonal line through each point in *Figure 9*. Random error due to finite strip width is relatively unimportant and is not shown.

*Since $\overline{M}_w \doteqdot \overline{M}_v$ it is valid to apply the data for $\overline{M}_w$ to $\overline{M}_v$.

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