Quantitative Size Exclusion Chromatography of Polypropylene II: Analysis Systems

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Synopsis

Quantitative size exclusion chromatography (SEC) was considered a system with the following components: sample preparation, fractionation, detection, calibration, and resolution correction. Four systems were evaluated: I was 3 columns with "conventional single detector interpretation"; II was 4 columns with concentration correction and detector assessment; III was concentration correction applied to the data of I; IV was two development "mixed bed" columns. Analysis of polystyrene standards included calculation of their molecular weight averages and use of the Glöckner "T" measure of resolution as well as "specific resolution index." Systems I and III provided the best high molecular weight results. System IV allowed 12–20 min analysis times and provided a highly linear calibration curve with very good reproducibility; however, it showed significantly worse resolution at high molecular weights. Plots of molecular weight averages determined from SEC versus their known true values were particularly useful. Concentration correction using the Rudin model moved different concentration data toward a common universal calibration curve and generally lowered molecular weight averages. Narrow polystyrene standards required relatively high concentrations for precise molecular weight averages and therefore, their averages were not good indicators of the need for concentration correction. Analysis of polypropylene samples corroborated the lower high molecular weight resolution of System III. Concentration correction did significantly change the polypropylene molecular weight distribution but did not affect the result of the kinetic model fitting.

INTRODUCTION

The previous article in this series[1] described the development of a method of quantitatively analyzing polypropylene by size exclusion chromatography (SEC) at high temperature (145°C). A SEC with only a single detector (a differential refractometer) was used. The results of the analysis were employed in an investigation of the intentional degradation of polypropylene by reactive extrusion.[2-5]

The analysis method developed closely followed conventional practice with two exceptions: the use of very long heating times for sample preparation and the extensive use of the ordinates of the molecular weight distribution (rather than molecular weight averages) in interpretation. The former allowed dissolution of stable aggregates. The latter avoided both the need for resolution correction and inaccuracies due to column dilution effects.

The objective of this article is to show the results of selecting options other than those selected in the initial analytical development. The paper begins by introducing a "system" viewpoint of quantitative SEC. The options involved

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are contained within the components of the system. Primary options are then summarized with three new systems defined and tested.

THEORY

The SEC Quantitative Analysis System

One way of organizing the variety of options available is to consider quantitative SEC as a series of steps containing the options and coupled together to provide the needed information.[6] The steps (i.e., the "components") in this "system" are:

Fractionation. Separation by molecular size in solution.
Detection. Determination of the concentration of each molecular size.
Calibration. Determination of the molecular weight of each molecular size.
Resolution correction. Computational enhancement of experimental resolution.

Assessment of experimental resolution is a part of fractionation. Also, in the particular case of high temperature SEC, "sample preparation" is an additional step which must be separately defined and examined before any other.

Selection of options to form different systems is the subject of this paper. Reference 6 examines the topic more generally for SEC and high performance liquid chromatography (HPLC). Here, selection is based upon the idea of optimally matching the SEC analysis to the needs of the reactive extrusion investigation. The first quantitative SEC analysis system hereafter called System I, was defined in Ref. 1 so that the data could be processed rapidly and an initial, tentative solution to the reactive extrusion elucidation obtained.[2,3] Now, each step in the analysis (and simultaneously, in the engineering model) can be re-examined. If justified, new SEC systems can be defined and tried in turn. In this paper, three such systems are involved. Note that a new "system" may simply involve recalculating existing data with different interpretation options. New experimental work may or may not be involved. The remaining paragraphs in this section summarize the primary SEC options considered for the new systems. No new options were considered for sample preparation or resolution correction.

Fractionation

Adequate resolution and absence of molecular weight degradation are the main concerns. It was assumed that the degradation problems were overcome by the measures developed in Ref. 1 (notably addition of antioxidant to the sample solution). However, a recent paper by Warner et al.[7] motivated a closer investigation of resolution options. They described the performance of columns packed with a development "mixed bed" packing. These columns are intended to provide high resolution with the convenience of a linear calibration curve. More importantly, Warner and co-workers demonstrated that they avoid chromatogram distortions which can occur when conventional columns are connected together. This distortion originates from a short-range mismatch in calibration curves of individual columns and is not normally evident

in injection of narrow standards. It only becomes evident when artificial shoulders in broad chromatograms are observed. This was of particular interest here because of our emphasis on individual heights of the molecular weight distribution.

Resolution is composed of two parts: the desirable separation of molecules of different molecular weights by the calibration curve and the undesirable spreading of molecules of the same molecular weight by axial dispersion. Major complications encountered in trying to assess resolution are the polydispersity of commercially available "monodisperse" samples and the variation of resolution with molecular weight. This latter point is a complication because it means that examining axial dispersion of a small molecule (say toluene, known to be truly one molecular weight) may provide very little information applicable to polymer molecules.

There have been many attempts to circumvent these difficulties. Glöckner[8] in particular has surveyed the resolution assessment measures available and proposed one which may be satisfactory. It is represented by the letter "T" and is given by:

$$T = \left[\frac{M_1}{M_2}\right]^{1/R_{corr}} \tag{1}$$

where M_1 and M_2 are the weight-average molecular weights of the narrow standards with $M_1 > M_2$. [For narrow standards, peak molecular weights could as easily be used. Glockner states no preference but his nomenclature suggests the weight average.] R_{corr} is Bly's resolution index:[9]

$$R_{corr} = \frac{2(t_2 - t_1)}{\dfrac{W_1}{P_1(a)} + \dfrac{W_2}{P_2(a)}} \tag{2}$$

where t_1 and t_2 are the peak retention times for narrow standards 1 and 2, respectively; W_1 and W_2 are the corresponding widths at the baseline; $P_1(a)$ and $P_2(a)$ are the true polydispersity values.

As Glöckner points out, the T value has a physical meaning. It indicates the ratio of molecular weights which would be separated with 4σ resolution. For example, $T = 4$ means that two monodisperse polymers with a 1 : 4 ratio of molecular weights would be almost completely separated. Therefore, smaller values of T are more desirable than larger values. Direct application of the error propagation equation[6,10] suggests that reproducibility (2σ limits) of T will be about $\pm 18\%$ and is worse at high values of T.

In evaluation of their commercial 5 μm and 10 μm "mixed bed" columns, Warner et al.[7] used the following measure:

$$R_{sp} = \frac{0.25}{\sigma D} \tag{3}$$

where σ is the standard deviation of the peak [width at baseline = 4σ, assuming a Gaussian peak and a truly monodisperse sample (Ref. 6 provides a

discussion of this)]. D is the slope of the calibration curve (log M versus retention volume). This definition is closely related to one proposed earlier by Hamielec[11] and by Yau et al.[12] Error propagation analysis indicates that the reproducibility of R_{sp} should be much better than T (probably about the same as the estimation of peak width at baseline (about 5%)).

A more direct way of assessing resolution is to simply plot the molecular weight averages obtained from the SEC chromatogram and uncorrected for axial dispersion versus the corresponding values known for the standards. An advantage of this method is that, when done for narrow polystyrene standards, it shows the effective range of the calibration curve as well as the results of axial dispersion. When data from standards similar to the polymer of interest are used, the method provides direct information on the needed results of the analysis. A weakness of the method is that is does not show correction factors (such as σ) which can be used in resolution correction methods. [However, such measures are readily calculated from the averages.[6]]

Detection

As seen in Refs. 3 and 5, in this study the actual heights of the molecular weight distribution were used instead of molecular weight averages in development of the degradation kinetic model. Also, in the investigation of antioxidant effects, normalized chromatograms were examined. The reason for this is that although averages are the most common results requested from SEC, they are among the least accurate and least precise information available from the chromatogram.

Molecular weight averages are weighted integrals over the whole chromatogram which emphasize the curve tails and are therefore very sensitive to axial dispersion effects and calibration curve fits. This emphasis on the tails of the chromatogram means that they are also readily affected by baseline position and by noise. Moment analysis plots,[6] first proposed by Boni,[13] are a useful way of examining some of these sensitivities. These are plots of the integrand in the definition of the average versus retention time. For example, since $\overline{M}_w$ is defined by:

$$\overline{M}_w = \int_0^\infty W_N(t)M(t)\,dt \tag{4}$$

or in terms of the molecular weight distribution $W_N(\log \mathrm{M})$ versus log M:

$$\overline{M}_w = \int_0^\infty W_N(\log \mathrm{M})M d\log \mathrm{M} \tag{5}$$

The moment analysis plot would be a plot of $W_N(\log \mathrm{M})\,M$ versus log M. Similarly, the moment analysis plot for $\overline{M}_n$ would be a plot of $W_N(\log \mathrm{M})/M$ versus log M. To plot these graphs on the same page as the molecular weight distribution, all curves are normalized before plotting. That is, the ordinate plotted for the moment analysis plot of $\overline{M}_w$ (denoted $W_N(\log \mathrm{M}, \overline{M}_w)$) is:

$$W_N(\log \mathrm{M}, \overline{M}_w) = \frac{W_N(\log \mathrm{M})M}{\int_0^\infty W_N(\log \mathrm{M})M d\log \mathrm{M}} \tag{6}$$

Moment analysis plots dramatically show the effect of noise and at the same time indicate which parts of the original molecular weight distribution are being emphasized by the molecular weight average calculation.

Although computers connected to chromatographs have been commonplace for many years, with the flood of new microcomputers into the laboratory, concerns that the computer is faithfully recording what the SEC is transmitting have greatly increased. Two simple tests that the chromatographer can apply to the data are: plots of the chromatogram area versus injected concentration; plots of normalized chromatograms at different detector sensitivities and computer sampling rates. The first mentioned can check the linearity of the detector. When done with computer-stored data, it also tests the various data conversion and amplification steps in the computer. One difficulty encountered with this test is that the minimum accurate area is not sufficiently small to critically test lower detector responses. A solution to this is to plot specific area fractions of peaks of samples at different injected concentrations of the same standard versus their injected concentrations. In the second test, plotting normalized chromatograms, the chromatographer can see the distortions caused in the peak as sampling rate and sensitivity are varied. This interpretation assumes that the peak shape is unchanged by increased concentration over the range of concentrations examined.

Calibration

In Ref. 1 it was assumed that all injected samples were at infinite dilution. Although likely a good assumption for samples giving "broad" chromatograms, it is not for those with narrow chromatograms (i.e., narrow molecular weight distribution polystyrene standards). The latter have smaller hydrodynamic volumes due to "molecular crowding" because they are not significantly diluted in the columns. Among the many attempts to correct for this effect, the Rudin model[14] appears as a practical and effective one. According to this model, the true hydrodynamic volume, V_h, is given by:

$$V_h = \frac{4\pi[\eta]M}{9.3 \times 10^{24} + 4\pi N_0 c_{\text{inj}}([\eta] - [\eta]_\theta)} \tag{7}$$

where

$$[\eta]_\theta = K_\theta M^{0.5}$$

$K_\theta = 7.203 \times 10^{-2}$ cm^3/g for polystyrene

c_{inj} = concentration of polymer in the injection loop (g/cm^3)

N_0 = Avogadro's number

The true hydrodynamic volume can be plotted from the standards and the curve used assuming infinite dilution conditions for the broad molecular weight distribution unknowns.

TABLE I
Analysis Systems

System	Fractionation	Detection	Calibration	Resolution Correction
All systems	$\overline{M}_n$ vs. $\overline{M}_n(a)$ & $\overline{M}_w$ vs. $\overline{M}_w(a)$ Plots; Glöckner T calculated	Differential Refractometer; Distribution heights emphasized over averages	Universal calibration	None
I	$10^6, 10^4, 500$ Å	Moment analysis plot		
II	$10^6, 10^4, 500,$ 100 Å	Detector linearity, Sensitivity & sampling rate assessment	Rudin model concentration correction	
III	Same columns as I		Rudin model concentration correction	
IV	2 Development "mixed bed" columns; R_{sp} calculated	Moment analysis plot		

EXPERIMENTAL AND COMPUTATIONAL OPTIONS SELECTED

A Waters 150C high temperature size exclusion chromatograph with 1,2,4-trichlorobenzene (TCB) at 145°C as the mobile phase was used.[1] The flow rate was 1 mL/min. The data system and the materials analyzed were the same as previously reported.[1] Table I shows a summary of the systems examined here. System I was described previously.[1] Systems II through IV are detailed in the following paragraphs.

System II

Experimentally, this system was the same as System I except one column was added to form the new combination: PL-Gel 10 μm particle size, 1×10^6, 1×10^4, 500, 100 Å pore size. Polypropylene sample preparation was done using the results of System I and is described in Ref. 1. Computationally, the following changes were made: (a) concentration correction was carried out [Eq. (7) for narrow standards]; (b) detector sensitivity was systematically varied to see its effect on results; (c) detector linearity was examined by plotting peak area versus concentration injected and by plotting well defined area segments of curves versus their respective injected concentrations. (Apparent column degradation prematurely terminated work on this system.)

System III

This system involved revisiting data obtained from System I and applying the Rudin model concentration correction to obtain a new calibration curve,

recomputing molecular weight distributions obtained from the extrusion process and reapplying the kinetic model. Molecular weight averages of polystyrene standards were also recalculated.

System IV

Experimentally this system was similar to System II except two development "mixed bed" (PL-Gel 15 μm mixed 30 cm) columns replaced the four previous ones. Also, smaller quantities of polymer were injected. Polystyrene standards were injected at 0.10 wt% (100 μL) and 0.02 wt% (75 and 125 μL).

Polypropylene samples were all injected at 0.20 wt% (100 μL) except for one sample (an undegraded, extruded PD 888) which was later repeatedly injected at 0.10 wt% (100, 75, 50, and 25 μL) to check for concentration effects.

Computationally, the following changes were made: no concentration correction was done; both the T parameter and R_{sp} [Eqs. (1) and (3)] were calculated. The latter were compared with the values published by Warner et al.[7]

RESULTS AND DISCUSSION

Analysis of Polystyrene Standards

Figures 1 and 2 show universal calibration curves obtained in this work. Figure 3 summarizes the molecular weight calibration curves for polypropylene derived from the universal curves for Systems I through IV. (System III uses the concentration corrected System I curve.)

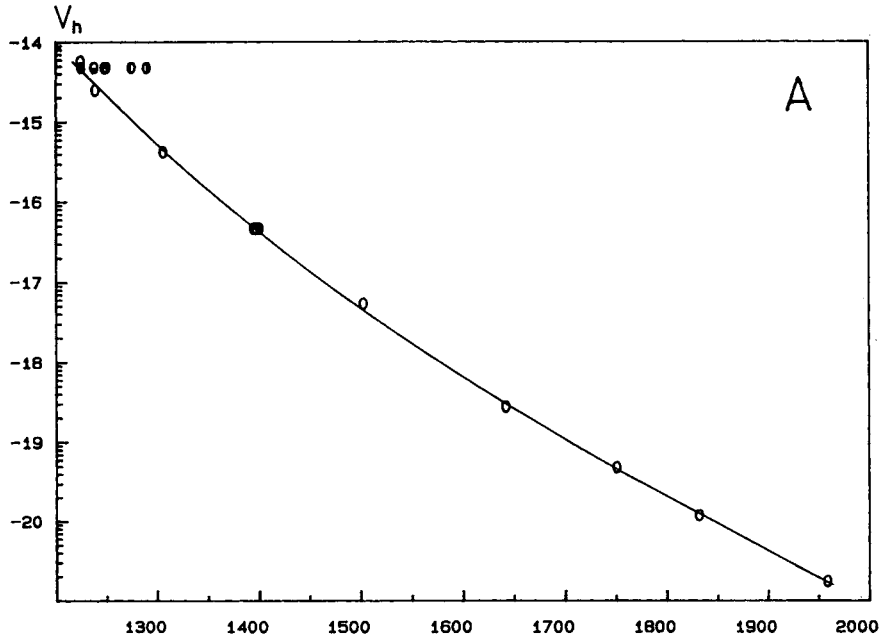

Fig. 1A. Universal calibration curve for System II. Concentration of polystyrene standards: (●) 0.03 wt%; (◒) 0.05 wt%; (◓) 0.08 wt%; (○) 0.10 wt%; (◐) 0.15 wt%; (◑) 0.20 wt%. All 200 μL injections.

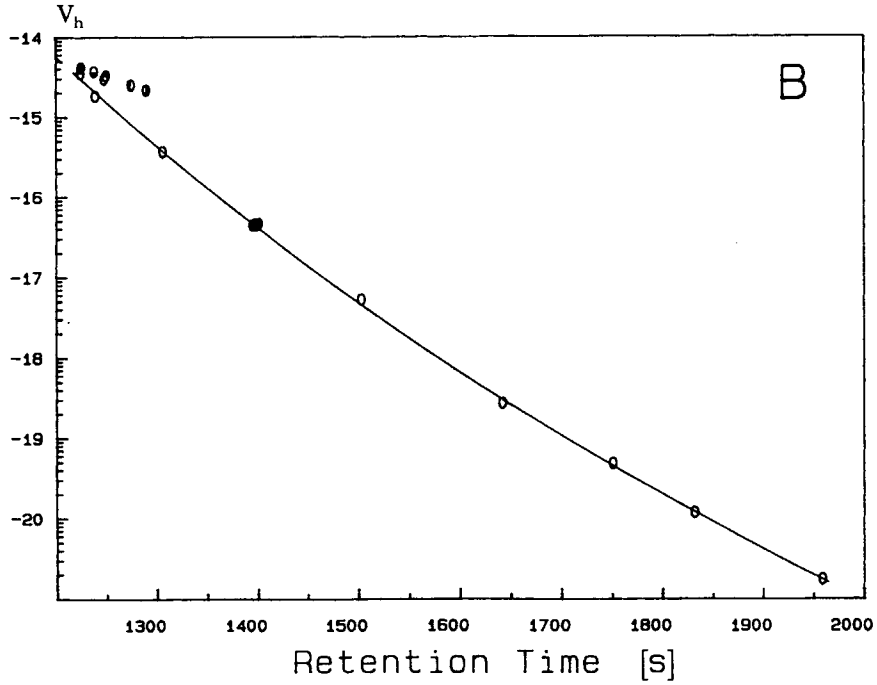

Fig. 1B. Universal calibration curve for System II: corrected for concentration using the Rudin model. Symbols for concentration of polystyrene standards: same as for Figure 1A.

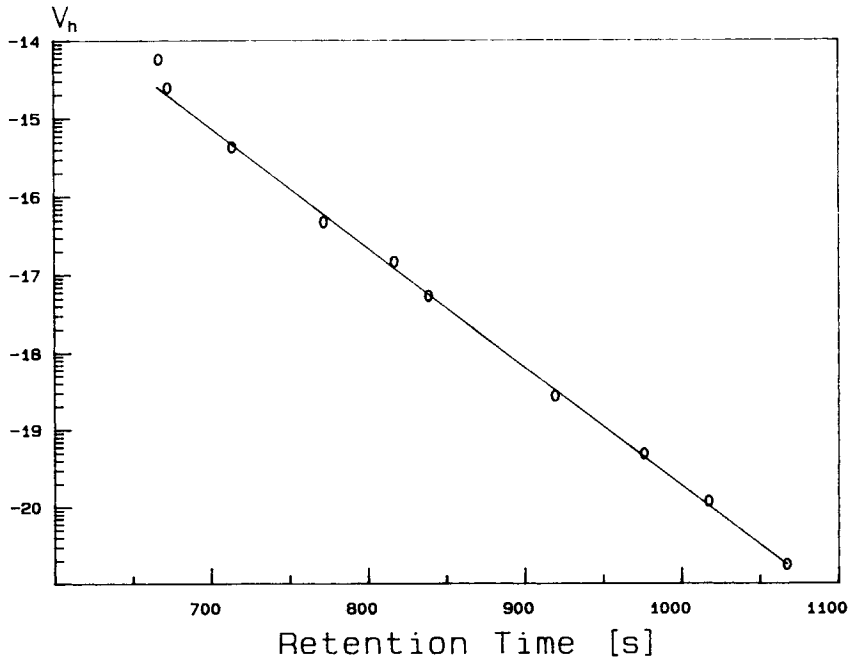

Fig. 2. Universal calibration curve for System IV.

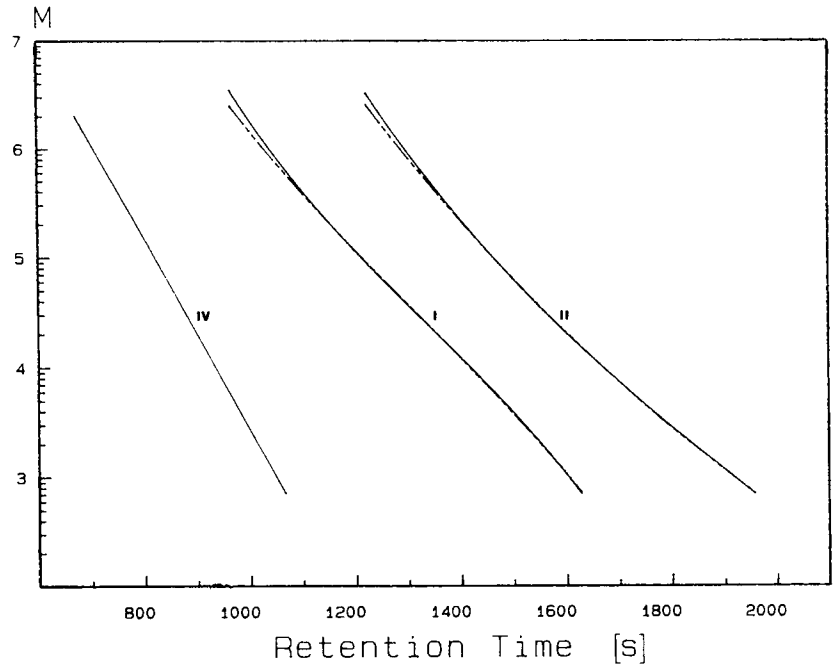

Fig. 3. Polypropylene molecular weight calibration curves for Systems I to IV. (Dashed line indicates concentration corrected curve.)

Figure 4A shows the resolution as measured by T [Eq. (1)] for all systems plotted as a function of peak molecular weight.

Resolution as measured by R_{sp} [Eq. (3)] was examined only for the two-column set (System IV). R_{sp} plotted against peak molecular weight is shown in Figure 4B. Also shown are the values obtained by Warner et al.[7]

Figures 5 and 6 show SEC molecular weight averages plotted against the values known for the standards.

These results showed that the three-column set used for the data of Systems I and III provided by far the best resolution at very high molecular weights. The calibration curves shown in Figures 1 and 3 demonstrate that this column set can separate polymer up to at least 3×10^6 in molecular weight. Figure 4 shows that both separation and axial dispersion are also likely acceptable up to about that value. T values [Fig. 4A] increase with molecular weight but are equal to or better than all of the other column sets.

The four-column set showed about the same separation as the three-column set with a slightly lower slope on the calibration curve at low molecular weights (as would be expected because of the additional 100 Å column). No significant difference from System I was evident on the molecular weight average plots (Fig. 5). T values [Fig. 4A] appeared slightly poorer than the three-column set. Concentration correction was tried on the data from this four-column set. The calibration curve was significantly changed (Figs. 1 and 3) with points of different concentration being moved toward a common curve. Mechanisms not included in the Rudin model (such as viscous fingering and shear degradation) may have affected very high concentrations and very high molecular weights.

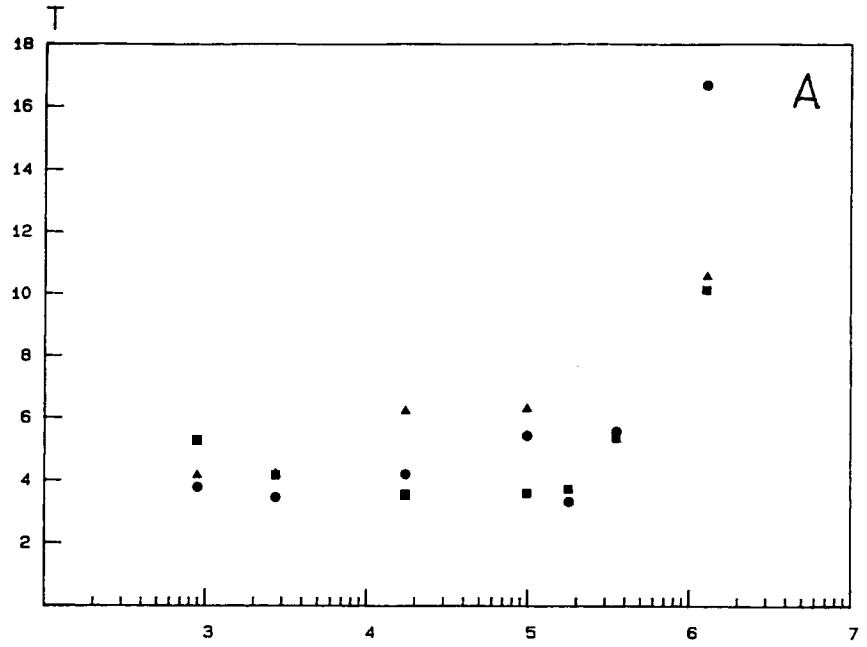

Fig. 4A. T versus peak molecular weight (M_p): (■) System I; (▲) System II; (●) System IV.

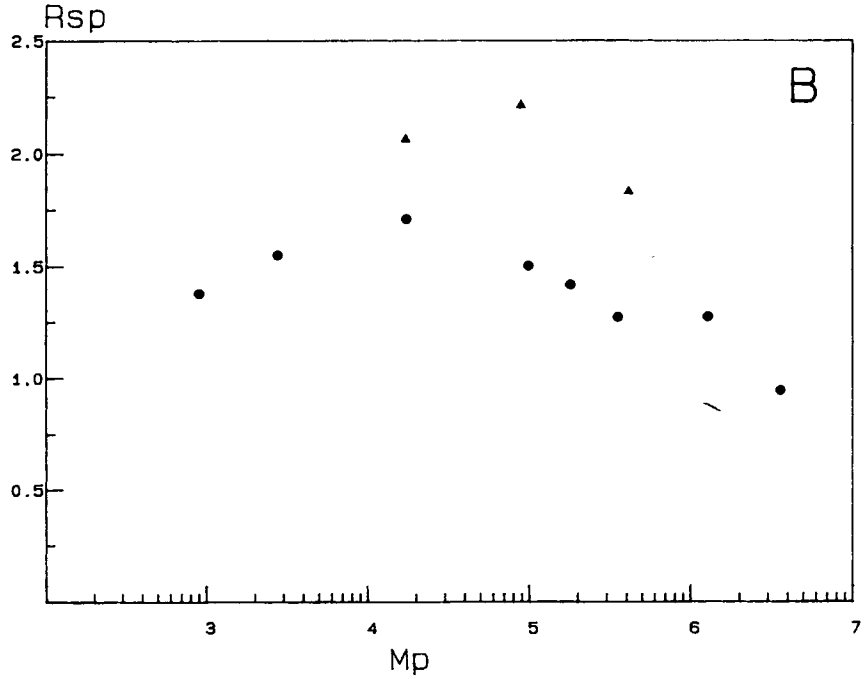

Fig. 4B. R_{sp} versus peak molecular weight (M_p): (●) System IV; (▲) Warner et al.[14]

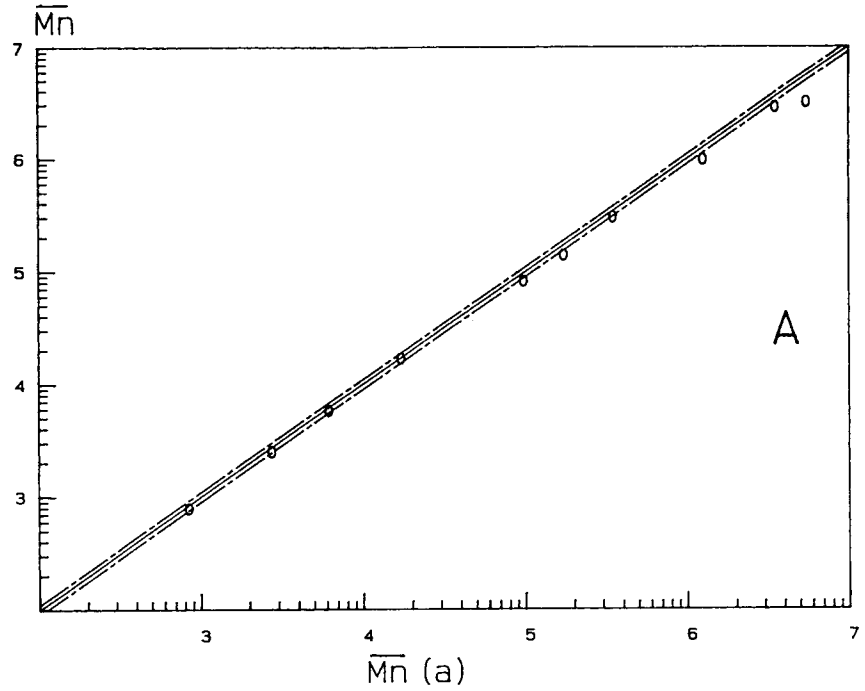

Fig. 5A. SEC Number-average molecular weight values ($\overline{M}_n$) versus corresponding absolute values for standards ($\overline{M}_n(a)$): System II. (Dashed lines bracketing diagonal indicate $\pm 10\%$ limits.)

Molecular weight averages of narrow polystyrene standards were all made worse by the correction. They were about 10% lower at the high molecular weight end than is shown in Figure 6. This actually must be expected because the narrow standards, unlike the broad polypropylene samples, cannot be correctly assumed to be at infinite dilution. That is, SEC molecular weight averages from narrow standards cannot be simply compared against true values to test the adequacy of the concentration correction.

The most correct calibration curve to use for calculating the molecular weight averages of narrow standards is the calibration determined at the same concentration as the standards. Likely the best test of the need for concentration correction is to see whether the concentration corrected calibration curve superimposes points from different injected concentrations.

Investigations carried out with System II aimed at examining the linearity of the detector all demonstrated excellent linearity.

In experimenting with different data sampling rates, too low a rate resulted in molecular weight averages which were sensitive to sampling rate and at very low rates, an obviously poor approximation to the real chromatogram. Very high sampling rates produced a higher noise level. This was because the computer software was in fact always sampling at a constant rate of 20 samples/s. The "sampling rate" which could be controlled was the number of points actually stored for the curve. These points were determined by averaging the points actually collected in order to provide the number specified. When this number approached 20 stored points/s, little or no averaging could

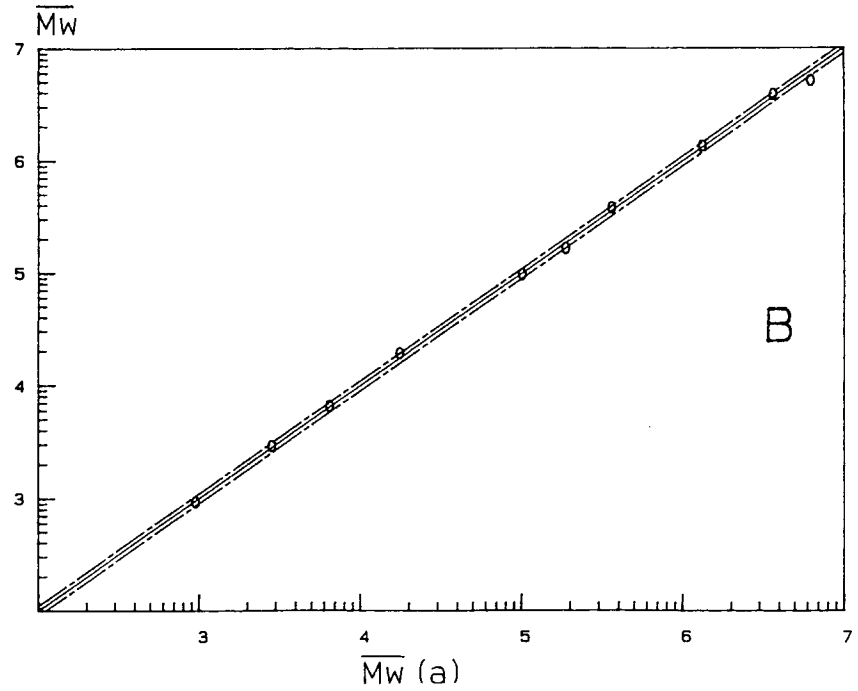

Fig. 5B. SEC weight-average molecular weight values ($\bar{M}_w$) versus corresponding absolute values for standards ($\bar{M}_w(a)$): System II. (Dashed lines bracketing diagonal indicate ±10% limits.)

be done, so "noise filtering" was decreased. In this work it was found that a specification of 0.5 stored points/s was most generally useful.

Figure 7 shows the result of changing SEC sensitivity. Too low a sensitivity caused a "stepped chromatogram." This was because voltage changes were too small for the A/D converter to distinguish. The sensitivity used for System I was quite sufficient for good accuracy and very near optimal for the system.

The two-column set of System IV allowed 12–20-min analysis times and showed a highly linear calibration curve (Figs. 2 and 3) which provided a good random scatter of data points about a plot of residuals.[6] Also, despite the steepness of the calibration curve, reproducibility was very good. Table II shows peak retention time reproducibility for these columns and, as well, shows that these peak times were only sensitive to concentration beyond 1×10^6 molecular weight. It should be noted that Warner and co-workers[7] were able to use much lower concentrations [0.02 wt% (20 μL)] with their ultraviolet (UV) detector than we were able to use with our differential refractometer. T values obtained for this column set were slightly worse than the other two-column sets [Fig. 4A]. R_{sp} values were also slightly worse than those of Warner et al.[7] [Fig. 4B]. This latter result is reasonable in light of our larger column packing (15 μm compared to the 10 μm of Warner et al.[7]) and higher injected concentrations. Despite their lower precision, T values were preferred to R_{sp} values for examining resolution. Because of the presence of the slope of the calibration curve in its definition, R_{sp} tended to provide a smoothed value of the resolution compared to the point-to-point estimates

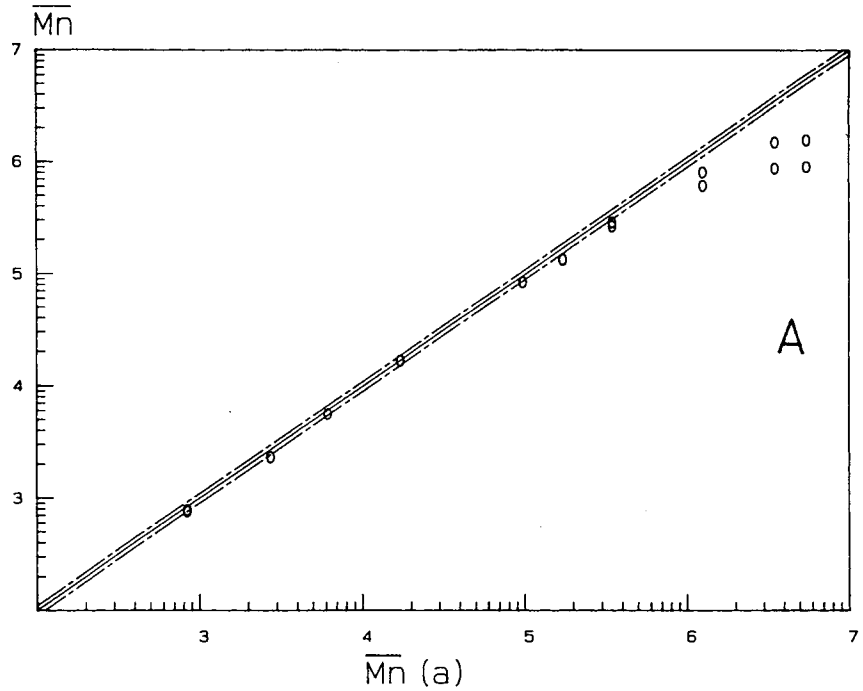

Fig. 6A. SEC number-average molecular weight values ($\overline{M}_n$) versus corresponding absolute values for standards ($\overline{M}_n(a)$): System IV. (Dashed lines bracketing diagonal indicate $\pm 10\%$ limits.)

resulting from T calculation. Also, by using σ values measured directly from the width of the normalized chromatograms, the polydispersity of the standards is ignored. This results in a dependence of the values obtained upon the actual standards employed in the study.

Figure 6, showing molecular weight averages, demonstrated that the accuracy and reproducibility were on a par with the three-column set up to a molecular weight of about 350,000. Beyond that point the SEC $\overline{M}_n$, and to a lesser extent, $\overline{M}_w$, values for the standards are lower than the known values. This could be partly due to concentration effects. At least 100 μL of 0.10 wt% polystyrene was necessary for the average molecular weights of narrow standards to be determined. Peak retention times could be accurately obtained for much more dilute samples (Table II). However, it was considered notable that the SEC $\overline{M}_n$ values were significantly lower beginning at 350,000. These values would depend mostly upon molecular weights at the peak molecular weight or lower. Concentration effects ("overcrowding effects") appear insignificant below 350,000 (Table II). The calibration curve (Figs. 2 and 3) is not as pessimistic as the molecular weight average plots. It indicates good separation at least up to 1×10^6 molecular weight. Thus, axial dispersion effects may be increasing before the calibration curve begins tailing up and they may also be caused by higher concentrations.

One complicating factor is that a straight line was used as calibration curve (in accordance with one of the expected advantages of such columns). At 0.10 wt% injected concentration, one more point slightly deviated from this line (at

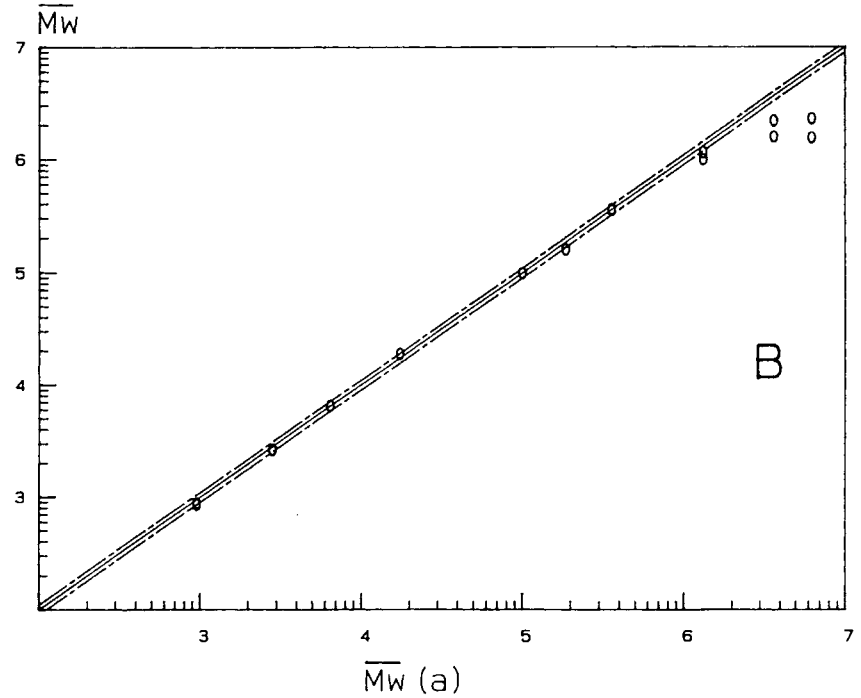

Fig. 6B. SEC weight-average molecular weight values ($\overline{M}_w$) versus corresponding absolute values for standards ($\overline{M}_w(a)$): System IV. (Dashed lines bracketing diagonal indicate $\pm 10\%$ limits.)

molecular weight 1.27×10^6) than at the lowest concentration. Only the lowest concentration points are shown in Figure 2. The others are in Table II. To determine whether or not this choice of calibration curve was causing the lower molecular weight averages the calibration points at 0.10 wt% injected concentration were fit by a curved calibration line (a cubic equation in retention time), and the molecular weight averages recalculated. The values remained significantly lower than the true values beginning at 350,000.

System III involved application of the Rudin model to the data of System I. The results obtained were very similar to those of System II with the correction placing different lower concentrations on the same calibration curve.

Analysis of Polypropylene

When attempts were made to analyze polypropylene using System II (employing the four-column set), nonreproducible results and large pressure fluctuations began to be obtained. Whether this was caused by degradation of the newly added 100 Å column or degradation of other columns or for other reasons, has not yet been determined.

When System III was used (i.e., when the Rudin model concentration correction was applied to the data of System I), significantly different molecular weight distributions resulted. However, it was found that in fitting the degradation kinetic model, no difference in the single "parameter" (the

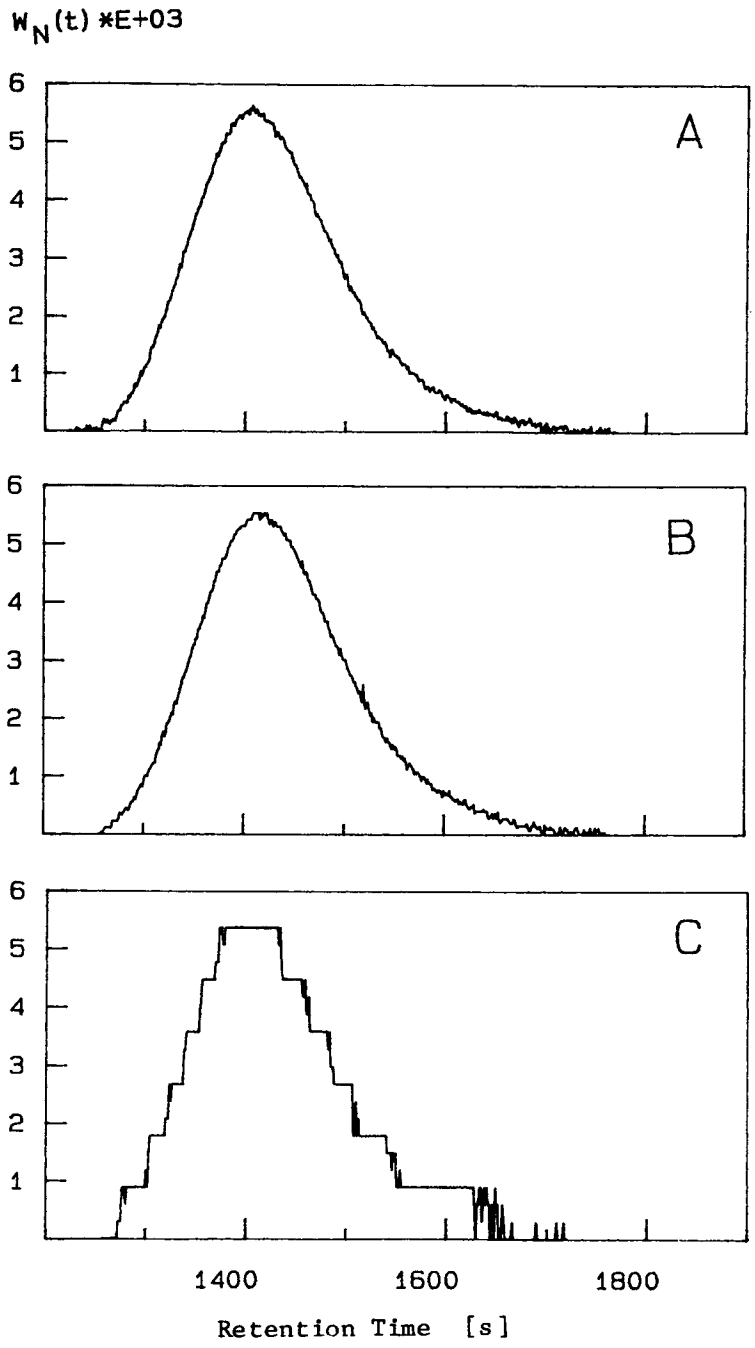

Fig. 7. Effect of sensitivity change on SEC chromatograms. Sensitivity settings: (a) 256; (b) 64; (c) 8.

TABLE II
Peak Retention Times[a] of Polystyrene Standards for Mixed Bed Columns

Std designation (TSK)	Peak molecular weight ($\times 10^{-4}$)	0.02 wt% (75 μL)	0.02 wt% (125 μL)	0.10 wt% (100 μL)	0.10 wt% (100 μL)
F-700	581.	666	—	708	686
F-380	354.	672	678	704	685
F-128	127.	713	714	719	717
F-40	34.9	772	775	775	776
F-20	17.7	816	816	818	817
F-10	9.77	838	842	841	841
F-2	1.70	919	921	920	920
A-5000	0.62	976	975	973	—
A-2500	0.27	1017	1018	1016	1018
A-1000	0.0889	1067	1073	1071	1074

[a]All peak retention times are in seconds.

"initiator efficiency") resulted. This was explained by noting that for the range of distributions obtained, the model depended not upon the absolute value of the molecular weight distributions but rather on the change of molecular weight distribution in the extruder. By subtracting the molecular weight distributions, Figure 8 shows this change for the most extreme conditions as measured with and without the Rudin model correction. The difference attributed to the concentration correction is within the experimental error shown in Ref. 1.

The above results do not eliminate the desire for absolute accuracy. The more accurate the results, the more we can be certain that the kinetic model actually describes what is occurring in the extruder. Also, results and conclusions become more universally applicable.

Figure 9 shows normalized molecular weight distributions and moment analysis plots for $\bar{M}_w$ for Systems III and IV, respectively [Eq. (6)]. As seen in Figure 9A, for the three-column set, about 15% of the normalized molecular weight distribution's area and 30% of the area under the moment analysis plot depend upon molecular weight values above one million. In contrast, Figure 9B shows that the analogous curves for System IV (the two-column set) appear narrower and of lower molecular weight. $\bar{M}_w$ decreased from 360,000 in System III to 200,000 in System IV. [Without concentration correction (i.e., for System I), the $\bar{M}_w$ was 400,000.] The lower results for System IV are attributed to the lower high molecular weight resolution of that system as discussed above.

Other explanations are less likely. For example, the presence of undissolved aggregates in the System III samples is improbable considering the exhaustive sample preparation investigation and the superposition of results for extruded undegraded and unextruded undegraded samples. The broader appearance of the System I chromatogram is unlikely to be some type of distortion caused by column mismatch since it occurs at the highest molecular weights. Concentration effects on polypropylene analysis on System IV were investigated

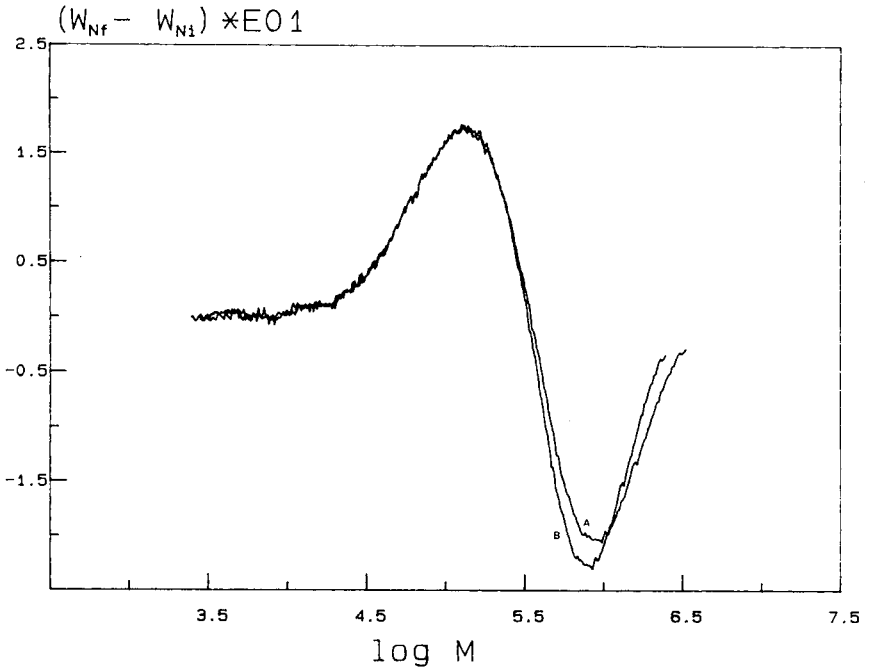

Fig. 8. The change in molecular weight distribution caused by degradation during reactive extrusion: (A) with Rudin model concentration correction applied to the SEC data; (B) no concentration correction.

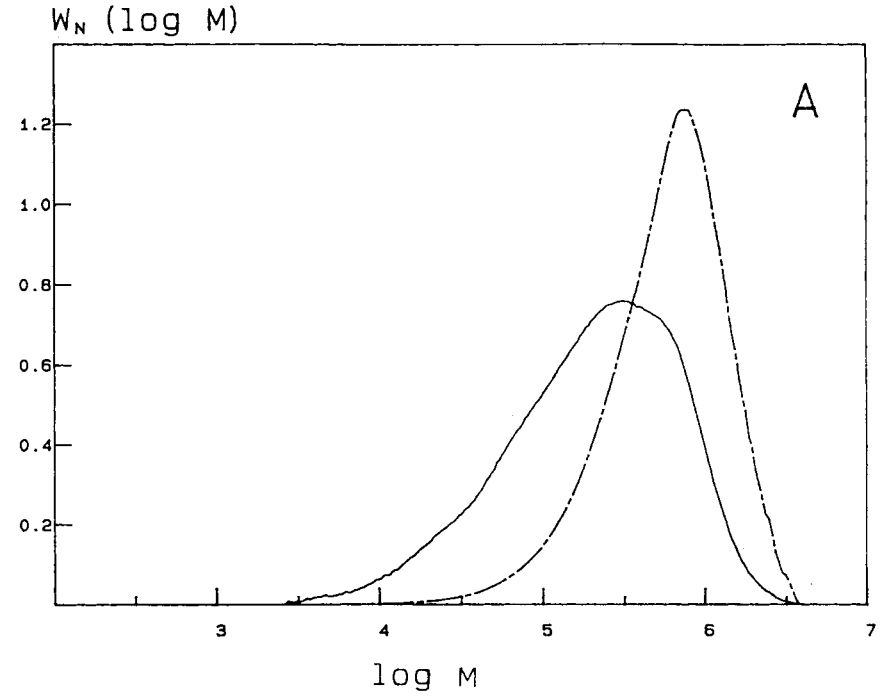

Fig. 9A. Molecular weight distribution (solid line) and moment analysis plot (dashed line) for $\overline{M}_w$: System III.

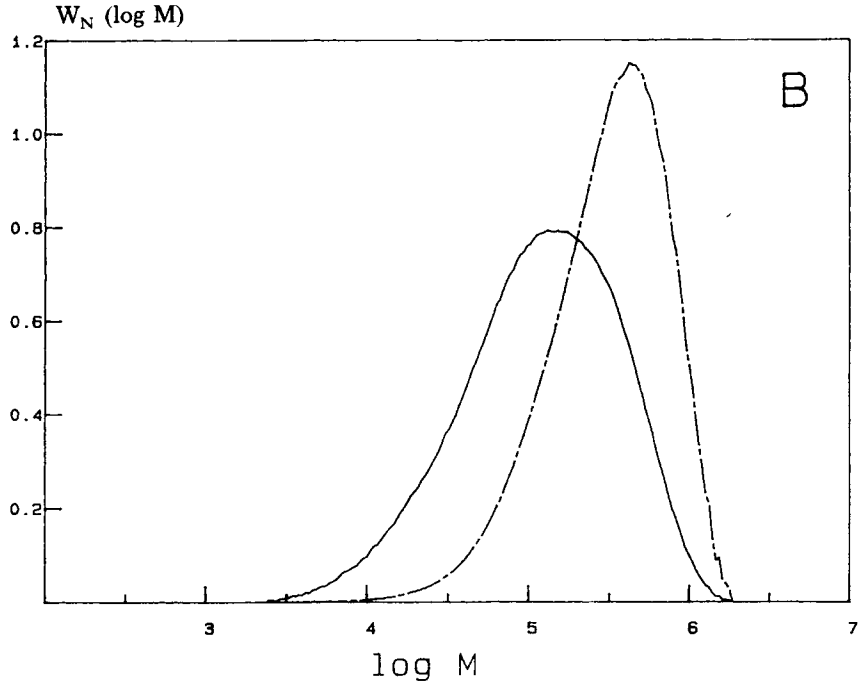

Fig. 9B. Molecular weight distribution (solid line) and moment analysis plot (dashed line) for $\overline{M}_w$: System IV.

by injection of 0.10 wt% (100, 75, 50, 25 μL) of undegraded, extruded polypropylene. This was also a check for sampling error. The only effect found was a decreased signal to noise ratio in the response caused by the lower peak height. Fitting the System IV calibration curve with a curve beyond the linear portion was examined. Results could readily be improved. However, uncertainty at the high molecular weight end was very high.

Very recently the manufacturer of this development "mixed bed" set (System IV) has confirmed that the columns contained lower pore size gel than the 10^6 Å column used in Systems I and II.[15]

At this point, the calibration procedure deserves closer attention. Alternative choices of Mark Houwink constants and other methods of calibrating (e.g., utilizing broad molecular weight distribution polypropylene standards) are being examined.

CONCLUSIONS

The study involved successively defining and trying three SEC quantitative analysis systems in addition to the previously defined System I. It was found that Systems I and III both provided results which could be used for kinetic model development. System III likely provided the most accurate results but tests of that accuracy awaits comparison with polypropylene standards.

Development "mixed bed" columns were found to provide high resolution, very rapid analysis (12–20 min), and a linear calibration curve. However, for polystyrene, resolution appeared to be significantly less above 1×10^6 molecular weight and perhaps above 350,000. Lower molecular weights measured on a

very high molecular weight polypropylene sample were attributed to this decreased resolution.

Plots of $\overline{M}_n$ and $\overline{M}_w$ determined by SEC versus the values known for the standards are sensitive indicators of resolution. A difficulty encountered in using narrow standards is the relatively high concentration needed for the refractometer to give precise chromatogram heights for molecular weight average calculation. Higher concentrations than those used to simply discern peak retention time are necessary.

The Rudin model concentration correction moved points obtained at different injection concentrations toward a common universal calibration curve. Molecular weight averages calculated from standards were not a good test of the need for concentration correction because they could be calculated only for relatively high concentrations.

Although the Rudin model concentration correction was found to significantly affect the polypropylene molecular weight distributions obtained, the kinetic model "initiator efficiency" value estimated was unaffected. This was attributed to the change in molecular weight distribution from raw polypropylene to degraded product being the same whether corrected or uncorrected SEC data were used.

The Glöckner "T" factor provided a good measure of resolution across the molecular range but precision was probably $\pm 18\%$ or worse and increased with the value of T.

The R_{sp} factor provided values in reasonable agreement with the literature. However, it tended to provide a "smoothed" estimate of resolution. Also, it included σ, a value which is difficult to obtain accurately for polymers because of the polydispersity of commercial standards. A dependence upon the actual standards used results.

NOMENCLATURE

D	Slope of straight line SEC molecular weight. Calibration curve (log M versus retention volume).
M	Molecular weight
M_P	Peak molecular weight of a narrow standard
M_1, M_2	Weight-average molecular weights of standards 1 and 2 [Eq. (1)].
$\overline{M}_n$	SEC number-average molecular weight uncorrected for axial dispersion.
$\overline{M}_n(a)$	Number-average molecular weight known for standard.
$\overline{M}_w$	SEC weight-average molecular weight from Eq. (4) uncorrected for axial dispersion.
$\overline{M}_w(a)$	Weight-average molecular weight known for standard.
N_o	Avogadro's number.
$P_1(a)$, $P_2(a)$	Polydispersities $[\overline{M}_w(a)/\overline{M}_n(a)]$ known for standards 1 and 2.
R_{corr}	Resolution index defined by Eq. (2).
R_{sp}	Resolution measure defined by Eq. (3).
T	Resolution measure defined by Eq. (1).

t	Retention time.
t_1, t_2	Peak retention times of standards 1 and 2.
V_h	Hydrodynamic volume.
$W_N(\log M)$	Ordinate of molecular weight distribution with log M abscissa.
$W_N(t)$	Normalized chromatogram height assuming perfect resolution.
W_{Nf}	$W_N(\log M)$ after reactive extrusion (at 0.04 wt% initiator).
W_{Ni}	$W_N(\log M)$ before reactive extrusion.
$W_N(\log M, \bar{M}_w)$	Ordinate of moment analysis plot for $\bar{M}_w$ and log M abscissa [Eq. (6)].
W_1, W_2	Width of normalized chromatogram at baseline for standards 1 and 2.
$[\eta]$	Intrinsic viscosity.
$[\eta]_\theta$	Intrinsic viscosity for a theta solvent.
σ	Standard deviation (0.25 $(W_1 + W_2)/2$ in Eq. (3)).

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