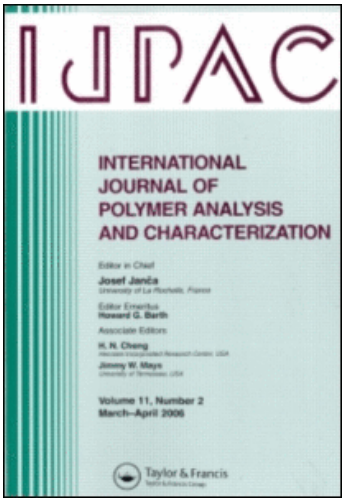

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Evaluating Size Exclusion Chromatography Fractionation*

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Traditional methods of evaluating fractionation in size exclusion chromatography (SEC) include number of theoretical plates, resolution indices and calculation of molecular weight averages. Most recently, fractionation evaluation has become evaluation of local polydispersity where "local polydispersity" is molecular variety at a particular retention volume. The three published methods for determining local polydispersity using triple-detector SEC are examined. All have two major uncertainties: the degree to which the observed local polydispersity affect the whole polymer molecular weight averages and the origin of the local polydispersity. New methods of answering these questions are examined using the SEC analysis of polymer blends. One method utilizes a plot where the area under the curve is the total number of moles of polymer. Calculation of this curve with equations containing different assumptions provides the needed significance test over the range where all three detectors have sufficient sensitivity. Determining the origin of local polydispersity utilizes the application of axial dispersion correction to experimental chromatograms to see if it can be the cause. Sensitivity of the methods is an issue for local polydispersity caused by molecules of different composition being present. Large differences in specific refractive index increment are then necessary.

Keywords: Fractionation; SEC; Local polydispersity; Triple-detector

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INTRODUCTION

Fractionation is the most fundamental aspect of any chromatographic method. For size exclusion chromatography (SEC), fractionation means separation according to size in solution. Evaluation of SEC fractionation can be an assessment of whether or not such separation is taking place. That is not the case here. This paper assumes that size separation is occurring and focuses instead upon methods of determining whether or not the separation is adequate to the need. Following a brief review of traditional methods of evaluating fractionation, we concentrate upon further developing the most recent group of methods, which seek to elucidate "local polydispersity" using triple-detector SEC.

THEORETICAL DEVELOPMENT

Traditional Methods of Evaluating SEC Fractionation

The most well known fractionation evaluation method is calculation of the number of theoretical plates N from

$$N = 16\left(\frac{t_R}{W}\right)^2 \tag{1}$$

where t_R is the peak retention time from the chromatogram of a small molecule (*e.g.*, toluene) and W is the width of the chromatogram at the base as measured by the intersection of tangents drawn through the inflection points of the peak. Plate count can be expressed on a per unit length of column basis or as a height of column equivalent to a theoretical plate.

The number of theoretical plates is often used to detect column packing degradation. However, in SEC it is really only a measure of "band spreading" by axial dispersion. It provides no guidance as to what molecular sizes can be separated. Also, the small molecule chromatogram is assumed to be a symmetrical, (Gaussian) shape: skewing can greatly influence the value of W in Eq. (1).

Resolution includes both band spreading and the amount of separation of two "truly monodisperse" (*i.e.*, single molecular size)

peaks. There have been several resolution indices proposed to provide a measure of resolution by taking both of these quantities into account. The index R_s proposed by Hamielec[1] is based upon an analytical solution of the Tung axial dispersion equation

$$R_s = \frac{2}{\sigma^2 D_2^2} \tag{2}$$

where σ is the standard deviation of the chromatogram of a "truly monodisperse" sample and D_2 is the slope of the SEC molecular weight calibration curve (plotted as $\ln M$ *versus* v). The equation assumes that the observed chromatogram (which may not be Gaussian) is the sum of such "truly monodisperse" sample chromatograms where each of these component chromatograms has a Gaussian shape with a constant value of σ. It also assumes a linear calibration curve over the range of elution of the chromatogram. For such a situation, the value of R_s can be related quantitatively to the percent error in M_n and M_w caused by axial dispersion. In theory the equation could be applied to different narrow-molecular-weight distribution samples eluting over the whole range of retention volumes of interest and plotted *versus* retention volume to show the variation of resolution. One difficulty, which this method shares with many others, is obtaining the value of σ for different polymer molecular weights: the narrow-molecular-weight distribution standards widely available for calibration are not "truly monodisperse" and methods of calculating σ from their molecular weight averages encounter significant error from uncertainties in the averages. Also, if the resolution index is found to change significantly with retention volume then it is not apparent what value to use for a broad-molecular-weight distribution sample. Often, for simple molecules (*e.g.*, homopolymers) with molecular weights less than one million, and if molecular weight sensitive detectors are not being used, the correction is negligible.

Currently the most common method of determining whether or not resolution is sufficient is to calculate M_n, M_w and possibly M_z from a broad-molecular-weight distribution standard. If the values obtained agree with previously known values for the standard then resolution is considered acceptable. The validity of this conclusion depends to a large extent on how closely the standard resembles the unknowns to be analyzed. The main advantage of this method is that much more than

resolution of the system is being tested. Furthermore, since it is generally molecular weight averages that are required from the analysis of unknowns, the method focuses upon the desired final outcome instead of some intermediate resolution index. A wide variety of problems can cause discrepancies in the molecular weight averages. In fact, a systematic approach was published, which employs an inspection of molecular weight averages in a very systematic way to ensure that multidetector systems were functioning correctly. [2] Such a method is important if molecular weight averages are used as a resolution indicator because, particularly with multidetector systems, identical significant errors can have totally different origins.

It is also possible to calculate the molecular weight averages of narrow-molecular-weight distribution standards from their respective chromatograms and to compare these with the vendor-supplied values. This can show how resolution varies with molecular weight. However, the comments above apply with respect to the many sources of error in calculated molecular weights and the difficulty in making practical use of the resolution information. Also, when narrow standards are injected, concentration effects on accuracy are of increased concern.

Local Polydispersity

Two trends are motivating more accurate evaluation of SEC fractionation: the increasing use of triple-detector SEC (*e.g.*, a chromatograph equipped with a concentration detector, such as a differential refractive index (DRI), viscometer (DV) and light scattering (LS) detector) and more interest in the quantitative analysis of complex polymers (*e.g.*, copolymers, branched polymers, stars). The result is that now SEC fractionation evaluation has become the evaluation of local polydispersity.

Local polydispersity is molecular variety at a particular retention volume v_i. Examples include variety in molecular weight, specific refractive index increment (dn/dc), branch frequency, branch length, molecular size, composition and copolymer sequence length. Axial dispersion can cause different molecular sizes to be present at a particular retention volume. This can result in local polydispersity in a variety of other molecular properties too. However, the cause of local polydispersity that is of prime concern is that which results from

molecular heterogeneity. This refers to the possibility that, for complex polymers, different combinations of composition and molecular weight, or branching and molecular weight, or branching, composition and molecular weight can result in the same molecular size in solution. Thus, local polydispersity from molecular heterogeneity can be present even when chromatographic resolution (*i.e.*, size resolution) is perfect. There are three published methods for evaluating local polydispersity using a triple-detector size exclusion chromatograph.

Methods of Determining Local PD

All three of the previous methods for evaluating local polydispersity are based upon the same three equations.

For DRI:

$$c_i = \frac{W_i}{\beta(dn/dc)_i} \tag{3}$$

where c_i is concentration at v_i, W_i is the baseline-corrected non-normalized DRI chromatogram height at v_i, β is the DRI instrument constant and $(dn/dc)_i$, is the specific refractive index at v_i. The $(dn/dc)_i$ is normally assumed constant with some average value used in the equation.

For the LS detector

$$M_{w,i} = \frac{R(\theta)_i}{\alpha P(\theta)_i (dn/dc)_i^2 c_i} \tag{4}$$

where $M_{w,i}$ is the local weight average molecular weight, $R(\theta)_i$ is the excess Rayleigh scattering (the output of the LS detector) at v_i, $P(\theta)_i$ is the particle scattering function at v_i and α is the LS detector constant. Again, normally $(dn/dc)_i$ is assumed constant and an average value is used. Also, at low angles and/or molecular sizes that are small as compared to the wavelength of the light used, $P(\theta)_i$ is unity.

For the DV detector

$$[\eta]_i = \frac{\eta_{sp,i}}{c_i} \tag{5}$$

where $[\eta]_i$ is the local value of intrinsic viscosity and $\eta_{sp,i}$ is the local value of the specific viscosity (the output of the detector). Equation (3) when combined with the generalized universal calibration curve results in an expression for $M_{n,i}$

$$M_{n,i} = \frac{J_i c_i}{\eta_{sp,i}} \tag{6}$$

where J_i is the hydrodynamic volume in solution.

In the "chromatogram comparison method" [3,4] an expression for the DRI chromatogram height is obtained by setting the local M_n value equal to the local M_w value. That is, Eq. (4) is set equal to Eq. (6). With $(dn/dc)_i$ considered constant for all the molecules at v_i (although it may be a different value at different values of v_i), an expression for W_i^*, the DRI chromatogram height assuming no local polydispersity in molecular weight, dn/dc or $P(\theta)$, is obtained

$$W_i^* = \beta\left(\frac{\eta_{sp,i}R(\theta)_i}{\alpha P(\theta)_i J_i}\right)^{1/2} \tag{7}$$

In this method W_i^* is compared to W_i. A difference between the two indicates the presence of local polydispersity.

In the "conventional calibration curve comparison method", [4] plots of $\log M_{w,i}$ *versus* v_i from Eq. (4) and $\log M_{n,i}$ *versus* v_i obtained from Eq. (6) are compared. Differences in shape and relative location indicate local polydispersity. For example, the distance between the curves is $\log M_{w,i} - \log M_{n,i}$ which is $\log(M_{w,i}/M_{n,i})$. We have recently shown how a molecular weight calibration curve corresponding to the assumption of no local polydispersity of any type can also be calculated. [5]

In the "universal calibration curve comparison method" [6,7] the same derivation as was used for Eq. (7) is used except that the universal calibration curve is considered as the unknown rather than the W_i values. Thus, an expression for J_i^*, the value of the hydrodynamic volume if no local polydispersity was present is

$$J_i^* = \beta^2\left(\frac{\eta_{sp,i}R(\theta)_i}{\alpha P(\theta)_i W_i^2}\right) \tag{8}$$

In a recent assessment using polymer blends to generate chromatograms containing known local polydispersity at each retention volume,[5] it was found that all three of these methods could detect local polydispersity in dn/dc if the difference between the dn/dc values of the polymer blend components was sufficiently large. Using plots of residuals it was possible to distinguish regions where local polydispersity was greater than signal noise. However, two questions remained: how significant was the observed local polydispersity (*i.e.*, was it worthwhile elucidating in more detail) and what was the origin of the observed local polydispersity.

Determining the Significance of Local Polydispersity

Since M_n and M_w are the most common quantities calculated from an SEC chromatogram, we would prefer to define a significant local polydispersity as that which has a significant effect on either of these two molecular weight averages. However, as will be seen below, defining the situation for M_n is much more feasible than defining the impact of local polydispersity on M_w.

There are actually four equations that are available for calculation of M_n when a triple-detector SEC system is involved. The first is the usual equation that is used when a molecular weight calibration curve is available and a concentration chromatogram has been obtained

$$M_n = \frac{m}{\sum_{i=j}^{k}(c_i/M_i)\Delta v_i} \tag{9}$$

where m is the mass injected. The summation runs from $i=j$ to $i=k$ where, for an accurate M_n of the whole polymer, j should correspond to the lowest molecular weight present in the sample and k the highest.

Goldwasser[8] showed that M_n could be calculated from the viscometer detector, the universal calibration curve and the mass injected

$$M_n = \frac{m}{\sum_{i=j}^{k}(\eta_{sp}/J_i)\Delta v_i} \tag{10}$$

This method of obtaining M_n at first appears very attractive because no assumptions regarding local polydispersity have been made and

variation in dn/dc across the chromatogram do not affect the result. However, Balke *et al.*[9] showed that inaccurate M_n values often resulted from the use of Eq. (10) for three reasons: the viscometer sometimes was insufficiently sensitive to detect the lower molecular weights in the sample; axial dispersion mixes molecules of different size at the same retention volume; and inter-detector volume still causes difficulties because the universal calibration curve is constructed from peak retention volumes selected from the output of the concentration detector and is used together with the chromatogram from the viscosity detector.

When a low-angle laser light scattering detector is used, M_n is calculated from the following equation:

$$M_n = \frac{m}{\sum_{i=j}^{k}((\alpha c_{AP,i}^2 P(\theta)_i (dn/dc)_i^2)/(R(\theta)_i))} \tag{11}$$

where

$$c_{AP,i} = m\frac{W_i}{\sum_{i=j}^{k} W_i \Delta v_i} \tag{12}$$

Equation (11) is conventionally used with $P(\theta)$ and dn/dc considered as constant with retention volume. Then the equation assumes no local polydispersity in any molecular property (molecules are identical at a particular retention volume) and no variation in $P(\theta)$ or dn/dc across the chromatogram either. If dn/dc varies across the chromatogram than the value obtained for $c_{AP,i}$ from Eq. (12) will be incorrect.

Radke *et al.*[10] pointed out that if the definition of the true local concentration c_i, from Eq. (3) is substituted into Eq. (11) for $c_{AP,i}$, then the equation which results allows an accurate calculation of M_n using the light scattering detector assuming no local polydispersity. Variation in dn/dc across the chromatogram would not influence the result. The equation obtained was

$$M_n = \frac{m}{\sum_{i=j}^{k}((\alpha W_i^2 P(\theta)_i)/(\beta^2 R(\theta)_i))\Delta v_i} \tag{13}$$

where W_i is the height of the DRI chromatogram at retention volume v_i. α and β are instrument constants for the light scattering and concentration detectors, respectively.

Thus, considering the above equations and ignoring concerns about sufficient detector sensitivity, axial dispersion and interdetector volume, Eq. (10) should provide the most accurate values of M_n since its result is unaffected by either local polydispersity in dn/dc or variation in dn/dc across the chromatogram. Equation (13) should provide the second most accurate values assuming $P(\theta)$ is constant everywhere (it is unity for low angles) since it is unaffected by variation in dn/dc across the chromatogram but is affected by local polydispersity in dn/dc. Finally Eq. (11) will provide the least accurate values because its result is affected by both local polydispersity in dn/dc and variation in dn/dc across the chromatogram.

The lack of sensitivity for the viscometer detector is a serious obstacle to obtain accurate M_n values from Eq. (10). It would be expected to be an even worse problem for Eqs. (11) and (13) since the light scattering detector is generally even less sensitive than is the viscosity detector to the presence of low molecular weights. This problem was circumvented by applying these equations only over a range where the detectors are sensitive.

For any retention volume range, the value of M_n for the molecules in that range is the ratio of the mass of polymer eluting over that range to the total number of moles of polymer eluting over the range. Eqs. (10), (11) and (13) do not attempt to calculate total mass eluted. Instead, the numerator, m, common to all three, is the known total sample mass injected. The mass, m_v over a limited range of retention volumes would be the same for all equations but it is unknown since it depends upon the shape of the molecular weight distribution. Thus, it is not possible to calculate the actual value of M_n over this limited range since, in general, we do not know the mass of the polymer eluting over that range. However, we can determine the ratio of M_n over that limited range using Eq. (11) or (13), to the value of M_n obtained over that range using the most accurate equation, Eq. (10).

For example, considering the two most accurate equations, Eqs. (10) and (13)

$$\frac{M_{n,\text{Eq. (13)}}}{M_{n,\text{Eq. (10)}}} = \frac{m_v}{(\text{Mol})_{\text{Eq. (13)}}} \frac{(\text{Mol})_{\text{Eq. (10)}}}{m_v} = \frac{(\text{Mol})_{\text{Eq. (10)}}}{(\text{Mol})_{\text{Eq. (13)}}} \tag{14}$$

In Eq. (10), the denominator is the total number of moles over the range v_j to v_k retention volumes. It can be considered as the area under

a plot of η_{sp}/J *versus* v over that range of retention volumes. Similarly, the number of moles over the range of interest for Eq. (13) is the area under a plot of $\alpha W^2 P(\theta)/(\beta^2 R(\theta))$ *versus* v. Thus, ratioing the M_n values obtained from Eq. (13) to those obtained from Eq. (10) yields:

$$\frac{M_{n,\text{Eq. (13)}}}{M_{n,\text{Eq. (10)}}} = \frac{(\text{area under}(\eta_{sp}/J) \textit{ versus } v)}{(\text{area under}(\alpha W^2 P(\theta)/\beta^2 R(\theta)) \textit{ versus } v)} \tag{15}$$

$$\frac{M_{n,\text{Eq. (13)}}}{M_{n,\text{Eq. (10)}}} = \frac{\sum_{i=j}^{k}(\eta_{sp,i}/J_i)\Delta v_i}{\sum_{i=j}^{k}(\alpha W^2 P(\theta)/\beta^2 R(\theta))\Delta v_i} \tag{16}$$

Similarly, the values of M_n obtained from Eq. (11) to those obtained from Eq. (10) yields

$$\frac{M_{n,\text{Eq. (13)}}}{M_{n,\text{Eq. (10)}}} = \frac{(\text{area under}(\eta_{sp}/J) \textit{ versus } v)}{(\text{area under}(\alpha c_{AP,i}^2 P(\theta)(dn/dc)^2/R(\theta)) \textit{ versus } v)} \tag{17}$$

$$\frac{M_{n,\text{Eq. (13)}}}{M_{n,\text{Eq. (10)}}} = \frac{\sum_{i=j}^{k}(\eta_{sp,i}/J_i)\Delta v_i}{\sum_{i=j}^{k}(\alpha c_{AP,i}^2 P(\theta)(dn/dc)^2/R(\theta))\Delta v_i} \tag{18}$$

If Eq. (10) provides the "true" value, the percent error when either Eq. (11) or (13) are used is calculated from

$$\text{Percent Error Over Range} = 100\left(\frac{M_{n,\text{Eq. (10)}} - M_{n,\text{Eq. (11) or (13)}}}{M_{n,\text{Eq. (10)}}}\right) \tag{19}$$

It is possible to attempt the same type of analysis for M_w. However, the value of dn/dc always intrudes into the equations.[10] We have no equations for M_w which are not dependent upon both local polydispersity in dn/dc and variation of dn/dc across the chromatogram.

Origin of the Observed Local Polydispersity

When local polydispersity is detected by any of the above methods it can be due to many factors, such as molecular heterogeneity and axial dispersion. Other possibilities are errors in the use of multidetector SEC, and range from incorrect interdetector volume, injection concentrations, detector response constants through the value of dn/dc.

The previously published method systematic approach is directed at setting up multidetector systems so as to prevent such errors.[2] The method also provides an effective interdetector volume that effects some degree of axial dispersion correction, as well as accounting for the volume between detectors. The method was shown to work well for broad-molecular-weight distribution polymers but was not suitable for polymers with a narrow-molecular-weight distribution. More recent publications have confirmed this conclusion.[11]

Once the systematic approach has been used, finding the origins of local polydispersity consists of analysis of linear homopolymers individually to eliminate any possibility of local polydispersity due to molecular heterogeneity and the use of mathematical simulation to see the effect of axial dispersion. In the present work, the method described in the previous section then is used to see whether or not significant local polydispersity is observed for these linear homopolymers. The conventional comparison method then is used to see the effect of axial dispersion. This particular method is useful because there have been many simulations of the effect of axial dispersion on the molecular weight calibration curve determined from different detectors.[12, 13] Also, correction equations are available readily so that they can be applied to the actual data obtained to discover the effect of different degrees of axial dispersion on the actual values obtained. For example, Hamielec's solution of the Tung axial dispersion equation has provided equations for local weight average molecular weight, local number average molecular weight and local intrinsic viscosity[14]

$$\frac{M_K(v, uc)}{M(v)} = \frac{F[v-(k-1)D_2(v)\sigma(v)^2]}{F[v-(k-2)D_2(v)\sigma(v)^2]} \exp\left\{\frac{(2K-3)}{2}(D_2(v)\sigma(v))^2\right\} \tag{20}$$

$$\frac{[\eta](v, uc)}{[\eta](v)} = \frac{F[v-aD_2(v)\sigma(v)^2]}{F[v]} \exp\{(aD_2(v)\sigma(v))^2/2\} \tag{21}$$

where $M_K(v, uc)$ is the Kth local molecular weight average uncorrected for axial dispersion, $M(v)$ is the local molecular weight average corrected for axial dispersion, $K=1, 2$ corresponds to number and weight average molecular weight, respectively. F is the chromatogram height, $[\eta](v, uc)$ is the uncorrected local intrinsic viscosity, $[\eta](v)$ is the

corrected local intrinsic viscosity, and a is the Mark–Houwink exponent. D_2 and σ were defined earlier.

Given the calibration curve obtained from the injection of narrow-molecular-weight distribution standards and, if necessary, universal calibration, the only unknown in these equations is the standard deviation σ of a truly monodisperse standard. By trying different values of this standard deviation value and generating the corrected calibration curve, we can decide whether or not it is likely that axial dispersion is causing the observed local polydispersity.

EXPERIMENTAL

SEC experimental conditions used are the same as in previous publications.[2] The LS detector was a Precision Detectors PD2000 operating at 670 nm and at 15° and 90° (Only the 15° data were used here with $P(\theta)$ equal to unity. Although not considered necessary in this work, for very high molecular weights, the actual value of $P(15)$ can be obtained by using both the 15° and 90° data.[15,16]). A Viscotek (Houston, TX) H502A DV and a Waters Corporation (Milford, MA) 411 DRI detector were also employed in the SEC system.

Eluent was uninhibited tetrahydrofuran at a nominal flow rate of 1 mL/min with acetone as an internal flow marker. Three Polymer

TABLE I Polymers analyzed

Code	*Polymer*	*dn/dc* [*ml/g*]	M_n	M_w
PDMS800K	poly(dimethyl siloxane)	0.003	508,000	813,000
PMMA80K	poly(methyl methacrylate)	0.087	43,100	80,500
LPE	linear polyester	0.123	27,800	51,700
BPE	branched polyester	0.123	5,660	191,000
PVA	poly(vinyl acetate)	0.055	79,200	220,000
PS	polystyrene	0.180	125,800	292,000
PTBS	poly(2,4,6-tribromostyrene)	0.124	241,000	634,000
PVC	poly(vinyl chloride)	0.109	57,200	122,000

TABLE II Percent effect of using Eqs. (13) and (11) instead of Eq. (10)

Maximum retention volume [*mL*]	*Component* 1	*Equation* (13)	*Equation* (11)	*Component* 2	*Equation* (13)	*Equation* (11)	*Blend* (*Eq.* (13))	*Blend* (*Eq.* (11))
18.5	PMMA 80 K	−7.33	−7.33	PDMS	–	–	−31.8	−34.1
19.5	LINEAR POLYESTER	4.03	4.04	BRANCHED POLYESTER	−7.07	−7.07	−2.11	−7.13
18.5	PMMA 400 K	−5.28	−5.29	PVC	10.24	10.24	−17.2	−20.17
18.5	PMMA 400 K	−5.28	−5.29	PVA	6.89	6.88	−8.97	−7.69
18.5	PMMA 80 K	−7.33	−7.33	PVC	10.24	10.24	−13.9	−10.06
18.5	PVA	6.89	6.88	PVC	10.24	10.24	9.31	12.76
18.5	PMMA 80 K	−7.33	−7.33	PVA	6.89	6.88	−8.31	−1.26
17.5	PS	1.86	1.86	PTBS	1.89	1.88	−9.43	−13.2

Laboratories (Amherst, MA) Plgel mixed-C columns, 7.5 × 250 mm, were used and sample concentrations were typically ~ 1.5 mg/mL of total polymer, injected as a volume of 100 μL. Details of the polymers analyzed for this study are shown in Table I. Polystyrene was obtained from Aldrich Chemical Company (Milwaukee, WI) and the remaining polymers, except linear and branched polyesters, were obtained from American Polymer Standards (Mentor, OH). Molecular weight and *dn/dc* values in Table I were measured in these laboratories by SEC.

The linear polyester was prepared from dimethyl terephthalate (0.95 mol), dimethyl glutarate (0.05 mol) and neopentyl glycol (1 mol) and the procedure has been described previously.[17] The branched polyester contained 0.05 mol pentaerythritol branch agent and 0.95 mol neopentyl glycol, combined with the above molar concentrations of di-acids. Table II shows the 50 : 50 by weight polymer blends analyzed. As before, polymer blends are used in this study because the region of local polydispersity originating from molecular heterogeneity can be defined exactly as the overlap region between the two component chromatograms.

RESULTS AND DISCUSSION

Analysis of Polymer Blends Using the Chromatogram Comparison Method

It was previously shown that the large *dn/dc* differences between PMMA80 K and PDMS800 K resulted in this blend being the most easily analyzed by all three of the local polydispersity detection methods. Figure 1 shows five different DRI chromatograms for this polymer blend. Curves A and B are the chromatograms of the individual polymer components injected separately. Curve C is the experimental DRI chromatogram of the blend of the two while curve D (indistinguishable from curve C in this case) was obtained by adding the component chromatograms together in a 50 : 50 ratio. Curve E is the DRI chromatogram obtained from Eq. (7). It is the chromatogram that would be obtained if there were no local polydispersity in this blend. The region of local polydispersity in this case is the range of retention volumes where the component chromatograms overlap. It is

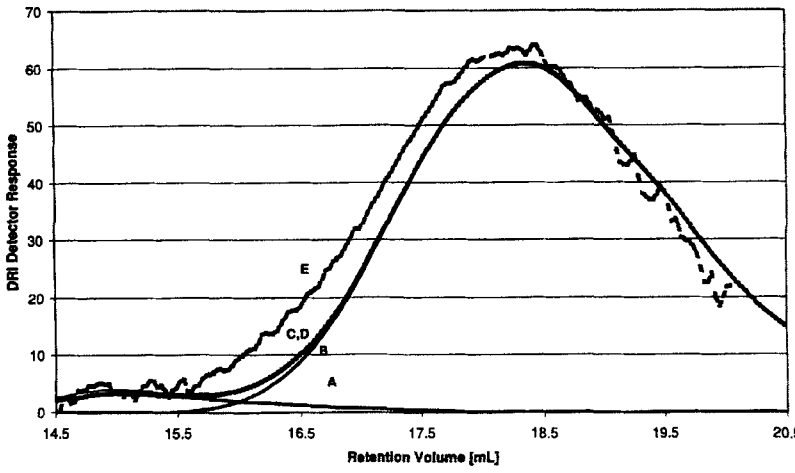

FIGURE 1 DRI chromatograms for the PMMA80 K/PDMS800 K blend. A: PDMS; B: PMMA80 K; C: PDMS + PMMA80 K experimental; D: PDMS + PMMA80 K calculated by summing components; E: PDMS + PMMA80 K from Eq. (7).

in this region that two different molecular components are present at each retention volume. On the scale of the plot it appears to be from about 15.5 to 17.5 mL. A comparison of curves C and E suggests that the range actually extends to 18.5. The superposition of curves C and D suggests that the SEC system itself appears to be functioning quite well.

A second example of the application of the chromatogram comparison method is shown in Figure 2. There we see the PMMA400 K/PVC blend exhibiting local polydispersity from about 16 to 18 mL. Observed local polydispersity evident from the differences between curves E and C beyond this range of retention volumes is uncertain because curves C and D do not superimpose sufficiently well.

Analysis of Changes in M_n Over the Sensitive Elution Range

From Table II and Figure 3 it can be seen that, not unexpectedly, it is the PMMA80 K/PDMS800 K that gave the greatest error in M_n over the elution volume range where the detectors are most sensitive. A -31.8% difference was found in the difference between the M_n of

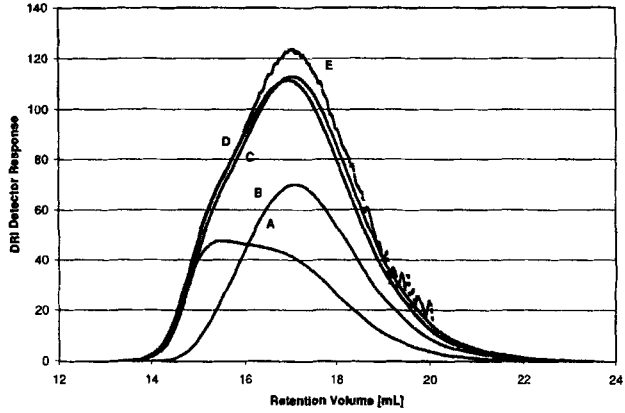

FIGURE 2 DRI chromatograms for the PMMA400 K/PVC blend. A: PMMA400 K; B: PVC; C: PMMA400 K + PVC experimental; D: PMMA400 K + PVC calculated by summing components; E: PMMA400 K + PVC from Eq. (7).

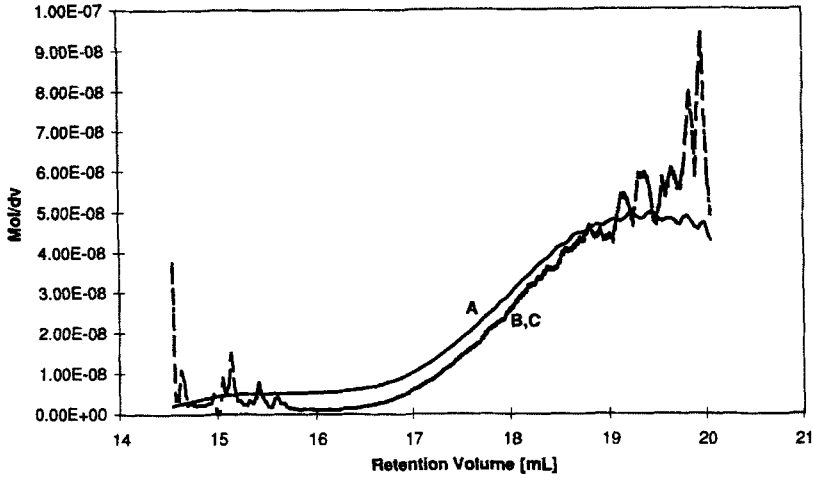

FIGURE 3 Moles per retention volume increment for the PMMA 80 K/PDMS 800 K blend plotted using the denominator of A: Equation (10); B: Equation (13); C: Equation (11).

polymer eluting from the lowest retention volume to 18.5 mL obtained from Eq. (10) as compared to the value obtained from Eq. (13) Judging from the complete lack of local polydispersity effects on the PMMA 80 K homopolymer component shown in Figure 4 (there was

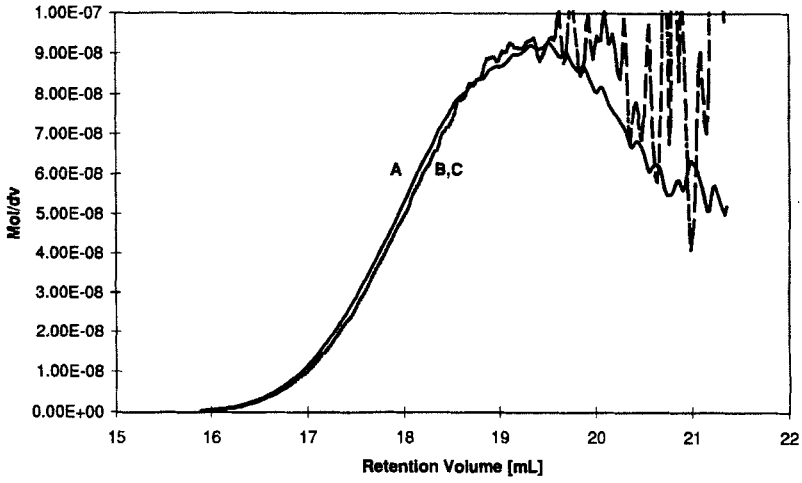

FIGURE 4 Moles per retention volume increment for PMMA 80 K plotted using the denominator of A: Equation (10); B: Equation (13); C: Equation (11).

no LS chromatogram for the low *dn/dc* PDMS component), this difference is probably due to the very high local polydispersity. When Eq. (10) was used instead of Eq. (11), a value of −34.1% was obtained. This value is apparently due to the effects of both local polydispersity in *dn/dc* and variation in *dn/dc* across the chromatogram, but the small difference from that obtained using Eq. (13) indicates that the effect of variation in *dn/dc* across the chromatogram was not significant.

As is evident from Table II, practically all of the other blends showed no significant difference between the blend results and the results of analyzing the linear homopolymer components individually. The primary exception is the PMMA400 K/PVC blend (Fig. 5). In that case use of Eq. (13) caused a −17.2% change and Eq. (11) resulted in a −20.2% change. Analysis of the PMMA 400 K homopolymer revealed no significant effect of equation selection (Fig. 6). However, analysis of the PVC homopolymer showed a significant 10.2% difference (Fig. 7). Since there cannot be any local polydispersity caused by variation in *dn/dc*, Eqs. (11) and (13) result in exactly the same values. Of all the cases examined, this one has the most uncertain origin and is discussed below.

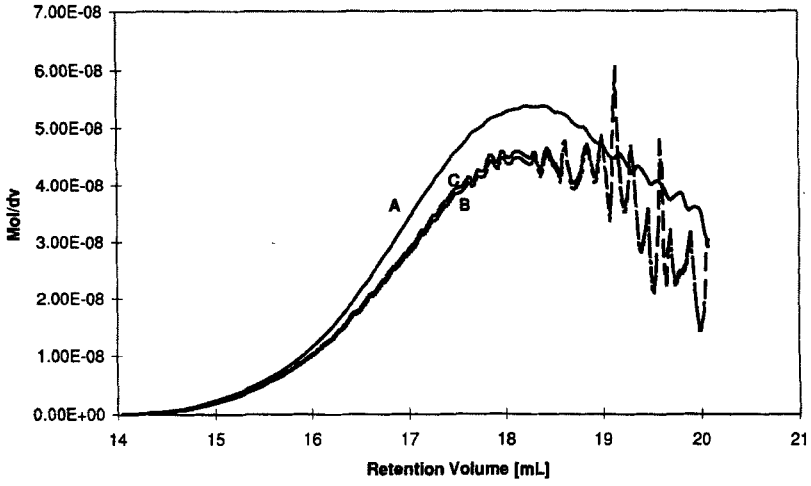

FIGURE 5 Moles per retention volume increment for the PMMA 400 K/PVC blend plotted using the denominator of A: Equation (10); B: Equation (13); C: Equation (11).

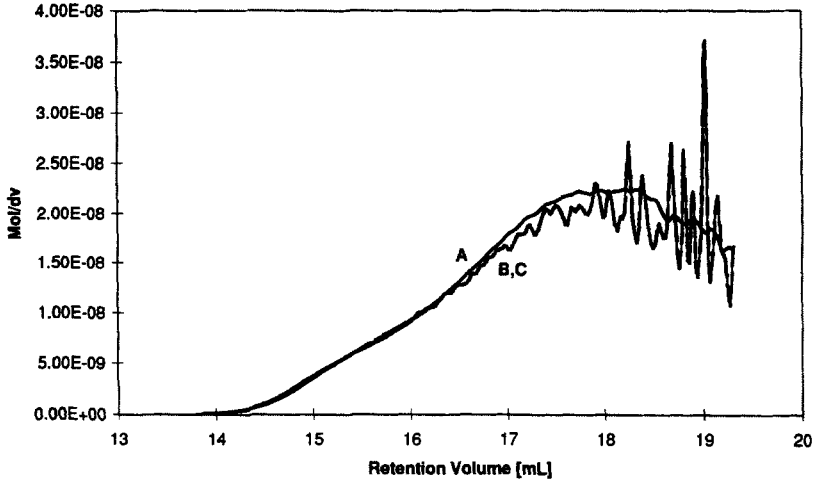

FIGURE 6 Moles per retention volume increment for PMMA 400 K plotted using the denominator of A: Equation (10); B: Equation (13); C: Equation (11).

Origin of the Observed Local Polydispersity in PVC Homopolymer

The large differences in results for the PVC homopolymer obtained from Eqs. (10) and (13) led to the hypothesis that axial dispersion

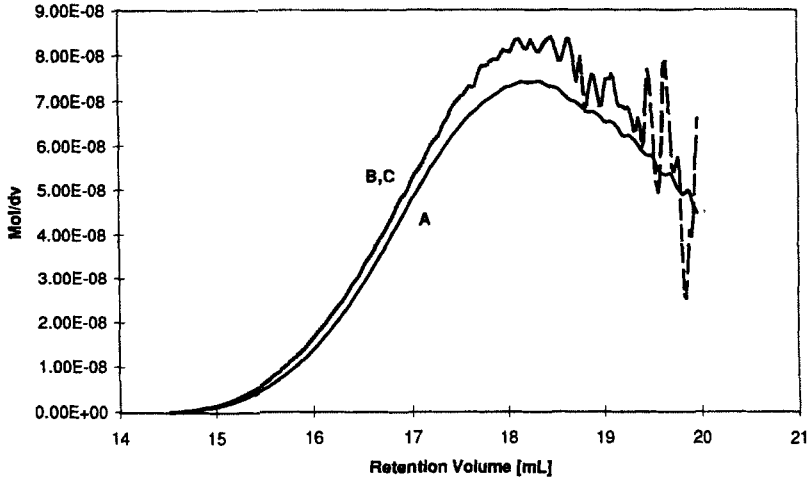

FIGURE 7 Moles per retention volume increment for PVC plotted using the denominator of A: Equation (10); B: Equation (13); C: Equation (11).

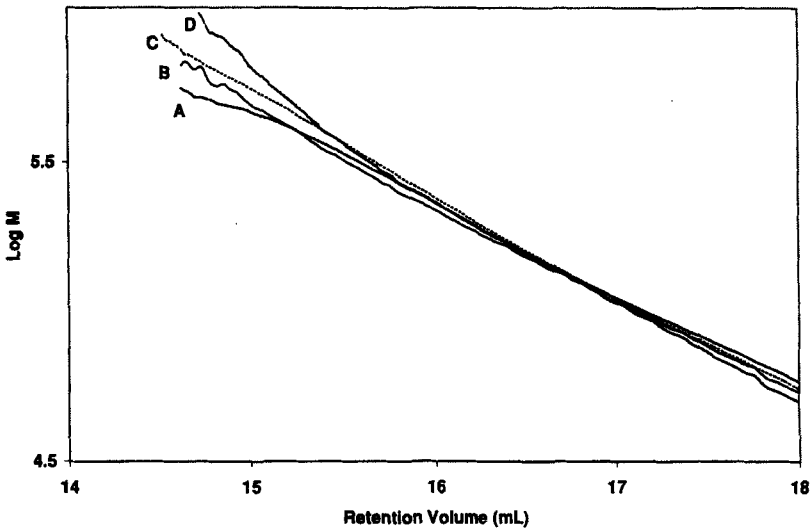

FIGURE 8 Rotation of local average molecular weights as a function of the standard deviation (σ) of the chromatogram of a monodisperse sample for PVC data. A: M_n ($\sigma = 0.359$); B: M_w ($\sigma = 0$); C: M_n ($\sigma = 0$); D: M_w ($\sigma = 0.359$).

acting on the pure PVC homopolymer was an important source of the local polydispersity observed for the PVC blend. To examine this possibility, Eqs. (20) and (21) were applied with different assumed

values of the standard deviation (σ) of the Gaussian spreading function (*i.e.*, the chromatogram of a monodisperse sample). The universal calibration curve was used with the corrected local [η] values to obtain corrected local M_n values. The logarithm of these corrected M_w and M_n values were plotted as corrected calibration curves shown in Figure 8. The original curves for M_w and M_n actually showed M_n exceeding M_w at low retention volumes! The corrected curves for one specific value of σ are shown to illustrate that indeed the corrections do allow the local M_w curve to rotate clockwise and the M_n curve to rotate counterclockwise: Both curves overlap at approximately a value of $\sigma = 0.23$. Similar results have been demonstrated by Gillespie *et al.*[18] It was interesting to note that the correction equation previously published for local M_n was not applicable here because the value of local M_n was determined by using local [η] with the universal calibration curve, rather than by using a detector that could determine M_n directly.

CONCLUSIONS

Evaluation of the local polydispersity is an increasingly important part of evaluating SEC fractionation. It is possible to detect the presence of local polydispersity by employing triple-detector SEC; however, sensitivity can be an issue. Large differences in *dn/dc* amongst molecules present at a given retention volume are desirable for high sensitivity. Determining the significance of observed local polydispersity was examined by computing the effect of different equations on the change in the estimated value of the whole polymer M_n evaluated over the range of elution where significant detector sensitivity was evident. Two polymer blends of the eight examined displayed significant local polydispersity: a poly(methyl methacrylate) (PMMA80 K)–poly(dimethyl siloxane) (PDMS800 K) blend and a poly(methyl methacrylate) (PMMA400 K)–poly(vinyl chloride) (PVC) blend. The result for the first blend was attributed to the large *dn/dc* difference between the blend components: the PMMA80 K sample had a *dn/dc* of 0.087 while the PDMS had a *dn/dc* of 0.003. Separate SEC analysis of the components of the second blend showed that the PVC component was contributing very significantly to the

observed local polydispersity. A simulation study using different assumed degrees of axial dispersion revealed that axial dispersion could be the cause.

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