Local Polydispersity Detection in Size Exclusion Chromatography: Method Assessment

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ABSTRACT: Local polydispersity is the term describing the variety of molecules present at the same retention volume in size exclusion chromatography (SEC) analysis. In the analysis of a linear homopolymer, local polydispersity is generally attributed to the effect of axial dispersion: it can cause molecular size variety (i.e., imperfect resolution) at each retention volume and thus local polydispersity in the molecular weight. In the analysis of polymer blends (copolymers and branched polymers), it is possible to have local polydispersity, even when the resolution is perfect, because molecules of different compositions (or degrees of branching) can have the same molecular size in solution. Conventional SEC interpretation assumes no local polydispersity if the axial dispersion effects are negligible. Three methods are currently available for detecting local polydispersity by using a combination of differential refractive index, light scattering, and viscometer detectors: the chromatogram comparison method, the conventional calibration curve comparison method, and the universal calibration comparison method. Here we experimentally assess these three methods using polymer blends and emphasize the chromatogram comparison method. All three are shown to be useful for assessing triple detector systems, but they are capable of detecting local polydispersity due to molecular heterogeneity only for very large differences in specific refractive index increments in the blend components. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 370–383, 2001

Key words: polydispersity; size exclusion chromatography; molecules; retention volume

INTRODUCTION

The term local polydispersity describes a variety of types of molecules present at the same retention volume in an analysis by size exclusion chromatography (SEC). Because conventional interpretation of SEC chromatograms assumes that no variety is present, if there is significant local polydispersity it can be a serious source of error. The most well-known type of local polydispersity is in molecular weight. One definition of this type of local polydispersity is the ratio of the local weight-average molecular weight ($M_{w,i}$, the value at a particular retention volume, v_i) to the local number-average molecular weight ($M_{n,i}$). This is exactly analogous to the well-known definition of polydispersity for the whole polymer, M_w/M_n, where M_w and M_n are the usual values obtained by averaging over the entire chromatogram. However, as seen in this article, there are other measures of local molecular weight polydispersity in addition to the ratio of the two local averages $M_{w,i}/M_{n,i}$. Also, there are many other possible sources of local variety in molecules in addition to

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the molecular weight. For example, there may be local polydispersity in specific refractive index increments (dn/dc, usually an indicator of composition local polydispersity), molecular size, branch frequency, branch length, and even copolymer sequence length.

The types of local polydispersity obtained reflect the two primary causes: axial dispersion and molecular heterogeneity. Axial dispersion refers to axial mixing of molecules in the SEC instrument, especially in the columns. Mixing of different molecular sizes means that more than one size elutes at the same retention volume. This local polydispersity in size is always accompanied by local polydispersity in the molecular weight (because size depends on the molecular weight) and possibly in other molecular properties as well. Axial dispersion is a very well known phenomenon in SEC. With modern high resolution columns axial dispersion may often be negligible. However, particularly at higher molecular weights or when larger diameter particles are used as column packing to minimize polymer shear degradation, the likelihood of it becoming a significant source of local polydispersity is increased. The second major cause of local polydispersity is molecular heterogeneity. This refers to the fact that for more complex molecules, copolymers and branched polymers or even blends of linear homopolymers, the diversity of molecules present in the sample can mean that the same molecular size can result from different combinations of molecular weight, composition, branching, and so forth. Therefore, at a particular retention volume, because the SEC separates by size in solution, local polydispersity can result, even under perfect resolution conditions. In a bicomponent polymer blend, for example, in the region of overlap of the chromatograms of the two components in the blend, two types of molecules are present (the molecules from both components) and therefore local polydispersity is present in that region.

The traditional method of examining local polydispersity is crossfractionation using two different types of liquid chromatographs. Polymer blends and copolymers were successfully crossfractionated to show the variety of molecules present at each retention volume.[1,2] Theoretical studies concluded that the local molecular weight polydispersity is expected to often be below the detection limits of molecular weight sensitive detectors.[3,4] Local polydispersity continues to be a general concern when complex molecules are analyzed, and there were recent efforts to somehow utilize triple detector SEC to determine if local polydispersity is present. The results from such a method could then be used to conclude whether or not more labor intensive cross-fractionation approaches would be worthwhile. The three detectors used were a differential refractometer (DRI), a differential viscometer (DV), and a light scattering photometer (LS). In this article we briefly summarize and compare the three main triple detector methods for determining local polydispersity published thus far. We then focus on further development and assessment of these methods with emphasis on one in particular, the chromatogram comparison method.

THEORETICAL DEVELOPMENT

Methods of Determining Local Polydispersity

The three methods currently proposed to reveal the presence of local polydispersity by interpreting the results of triple detector SEC analysis are the chromatogram comparison method,[5,6] the conventional calibration curve comparison method,[6] and the universal calibration comparison method.[7,8] All three of these methods are based on manipulations of the basic detector equations. The equation for the DRI is the following:

$$c_i = \frac{W_i}{\beta\left(\frac{dn}{dc}\right)_i} \tag{1}$$

where c_i is concentration at v_i, W_i is the baseline corrected unnormalized DRI chromatogram height at v_i, β is the DRI instrument constant, and $(dn/dc)_i$ is the specific refractive index at v_i. In conventional use of this equation, $(dn/dc)_i$ is assumed constant everywhere and some average value is used in the equation.

The equation for the LS detector (assuming the second virial coefficient term negligible) is the following:

$$M_{w_i} = \frac{R(\theta)_i}{\alpha P(\theta)_i \left(\frac{dn}{dc}\right)_i^2 c_i} \tag{2}$$

where $R(\theta)_i$ 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 de-

tector constant. In the conventional use of this equation $(dn/dc)_i$ is assumed constant everywhere and an average value is used. Also, at low angles and/or molecular sizes that are small compared to the wavelength of the light used, $P(\theta)_i$ is unity.

The equation for the DV detector is the following:

$$[\eta]_i = \frac{\eta_{sp_i}}{c_i} \tag{3}$$

where $[\eta]_i$ is the local value of the intrinsic viscosity and $\eta_{sp,i}$ is the local value of the specific viscosity (the output of the detector). Combining eq. (3) with the generalized universal calibration curve[9] we obtain an expression for $M_{n,i}$:

$$M_{n_i} = \frac{J_i c_i}{\eta_{sp_i}} \tag{4}$$

where J_i is the hydrodynamic volume in solution.

In the chromatogram comparison method eq. (2) is set equal to eq. (4). 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^*, which is the DRI chromatogram height assuming no local polydispersity in the molecular weight, dn/dc, or $P(\theta)$, is obtained:

$$W_i^* = \beta\left(\frac{\eta_{sp_i} R(\theta)_i}{\alpha P(\theta)_i J_i}\right)^{1/2} \tag{5}$$

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, plots of $\log M_{w,i}$ versus v_i from eq. (2) and $\log M_{n,i}$ versus v_i obtained from eq. (4) 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 $\log(M_{w,i}/M_{n,i})$.

In the universal calibration curve comparison method the same derivation is used as for eq. (5), 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 obtained if no local polydispersity is present, is obtained:

$$J_i^* = \beta^2\left(\frac{\eta_{sp_i} R(\theta)_i}{\alpha P(\theta)_i W_i^2}\right) \tag{6}$$

The universal calibration curve comparison method was the first published attempt to use triple detector SEC to determine local polydispersity.[7,8] It was presented as a general equation for diagnosing the adequacy of SEC fractionation.

In examining the above methods, it is immediately evident that the conventional calibration curve comparison method is less developed than the other two because no expression for a "no local polydispersity reference" curve was derived. The next section presents such a derivation.

No Local Polydispersity Molecular Weight and Intrinsic Viscosity Calibration Curves

This derivation depends upon the idea that all three of the detectors must be viewing the same local concentration values if the interdetector volume has been correctly determined. Thus, if eqs. (2) and (3) are each rearranged to be explicit in local concentration and these two expressions are set equal to each other [assuming no local polydispersity in $P(\theta)$ and dn/dc], then

$$\frac{[\eta]_i}{M_{w_i}} = \frac{\alpha \eta_{sp_i} P(\theta)_i \left(\frac{dn}{dc}\right)_i^2}{R(\theta)_i} \tag{7}$$

Now, we can represent the group of quantities on the right-hand side of eq. (7) by defining E_i.

$$E_i \equiv \frac{\alpha \eta_{sp_i} P(\theta)_i \left(\frac{dn}{dc}\right)_i^2}{R(\theta)_i} \tag{8}$$

Then

$$\log[\eta]_i = \log E_i + \log M_{w_i} \tag{9}$$

A separate equation can be obtained for $[\eta]_i$ from the definition of the generalized universal calibration curve:

$$\log[\eta]_i = \log J_i - \log M_{n_i} \tag{10}$$

Now, for no local polydispersity in the molecular weight,

$$M_{w_i} = M_{n_i} = M_i^* \tag{11}$$

Therefore, solving eqs. (9) and (10),

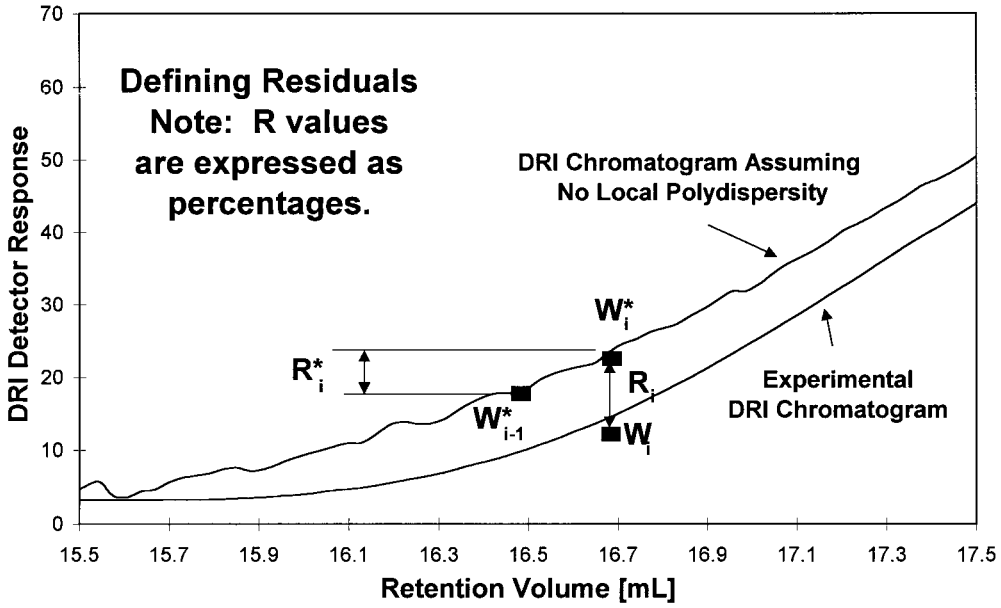

Figure 1 A definition of the residuals for the chromatogram comparison method.

$$\log M_i^* = 0.5(\log J_i - \log E_i) \tag{12}$$

$$\log[\eta]_i^* = 0.5(\log J_i + \log E_i) \tag{13}$$

Equations (12) and (13) respectively describe the local molecular weight and local intrinsic viscosity values that, when plotted versus v_i, provide calibration curves that assume no local polydispersity in the molecular weight, *dn/dc* or $P(\theta)$.

It can be seen from the above that discerning the differences between curves is a fundamental aspect of all three methods for determining local polydispersity using triple detector SEC. The presence of random error in these curves, particularly in those calculated from two or three detector responses, needs to be distinguished from the systematic error caused by the presence of local polydispersity. This topic is examined in the next section.

Distinguishing Significant Signal from Random Noise

Residuals can be used to quantify the difference between one curve and another, and they can also be used to define random noise. Figure 1 shows two residuals defined with respect to the two chromatograms involved in the chromatogram comparison method. These residuals are the distance between the two chromatograms (R_i) and the distance between consecutive data points on one curve (R_i*), which is the no local polydispersity curve. The R_i* is affected by two properties of this curve: the "high frequency" noise that we wish to quantify and the longer term trend of the curve, a property that is not of interest.

In use, the R_i and R_i* are both expressed as percentages by the following equations:

$$R_i = 100\,\frac{W_i - W_i^*}{W_i} \tag{14}$$

$$R_i^* = 100\,\frac{W_{i-1}^* - W_i^*}{W_{i-1}^*} \tag{15}$$

Each type of residual is then plotted versus v_i so that the systematic error and random error can be compared at each retention volume. Note that because the R_i* are affected by the longer term trend of the curve, in interpreting these residuals we ignore the average R_i* value and the slope of R_i* versus v and rather focus on the magnitude of the random scatter of these values.

The differences in the sensitivities of the three detectors relative to each other is a primary source of random noise in the calculated no local polydispersity curves. This is the subject of the next section.

Different Detector Sensitivities

Figure 2 shows the normalized chromatograms of the blend of linear and branched polyesters (LPE,

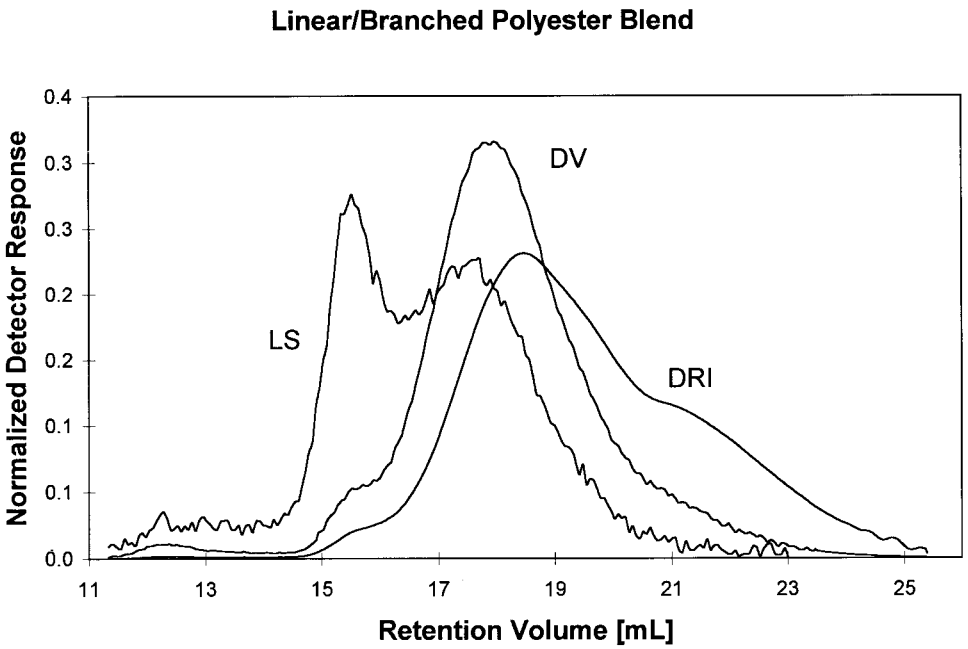

Figure 2 Normalized chromatograms of a blend of linear and branched polyesters: LS, light scattering; DV, viscometer; DRI, differential refractive index.

BPE) for the LS, DV, and DRI detectors. The DRI detector response extends much further into the high retention volume region than either of the other two detectors, while the LS detector shows unmatched low retention volume sensitivity. This situation is well recognized in the published literature. It can easily be seen that when all three detectors must be used together there is only a narrow range of retention volumes where all three have a reasonable level of signal to noise (approximately 15.5–21 mL in Fig. 2). This is reflected in strong noise at each end of the calibration curves obtained from the DV and LS detectors (plots of $\log [\eta]_i$ and $\log M_{w,i}$ vs. v_i, respectively). Another way of viewing this problem is to consider it as the problem of extrapolating such calibration curves to include a wider range of retention volumes. If that could be done successfully, then the DV, LS, and DRI chromatograms could actually be generated in the low signal regions from the calibration curve extrapolations. Furthermore, eqs. (12) and (13) actually show us that extrapolations of these two types of calibration curves are not independent. The extrapolated values, $\log [\eta]_i^{\text{extrap}}$ and $\log M_{w,i}^{\text{extrap}}$, must obey the following equation:

$$\log[\eta]_i^{\text{extrap}} = \log E_i + \log M_{w_i}^{\text{extrap}} \qquad (16)$$

Polymer blends were used in this work. As a result, the calibration curves obtained assuming no local polydispersity often appeared more distorted than did "normal" calibration curves. Finding the best equation combined with the need for finding the correct weighting factors in the fitting was a problem reserved for later study. Here the limited range of retention volumes available with the three detectors was accepted (no extrapolation was done) and the chromatograms were all truncated when the signal reached 1% of the peak value.

A final problem that was examined here was distinguishing local polydispersity originating from a molecularly heterogeneous sample from the local polydispersity originating from other causes. This is discussed in the next section.

Distinguishing Polydispersity Originating from Causes Other Than Molecular Heterogeneity

As mentioned above, in addition to the molecular heterogeneity of the sample, local polydispersity can also be caused by axial dispersion. Also, incorrect specification of the interdetector volume, injection concentration error, incorrect detector constants, incorrect *dn/dc* values, and violations of universal calibration can all result in apparent local polydispersity. To distinguish local polydispersity originating from the sample heterogeneity from local polydispersity originating from other causes the strategy to be examined here was to analyze "simple" polymers (such as linear ho-

Table I Polymers Analyzed

Designation	Polymer	dn/dc	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

mopolymers) that were unlikely to have local polydispersity due their molecular heterogeneity. If the presence of local polydispersity was then indicated then it was due to one or more of the other causes mentioned above.

EXPERIMENTAL

The SEC experimental conditions used here were the same as in previous publications.[5,6] A 757 Spectroflow spectrophotometric UV detector (data not used here) and a Precision Detectors PD2000 LS detector operating at 15 and 90° were used. [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.[10,11]] A Viscotek H502A DV and a Waters 410 DRI detector were employed in the SEC system. The eluent was uninhibited tetrahydrofuran at a nominal flow rate of 1 mL/min. Acetone was used as an internal flow marker. Three Polymer Laboratories PLgel mixed-C columns (7.5 × 250 mm) were used. Sample concentrations were typically ~1.5 mg/mL of total polymer, which was injected as a volume of 100 μL. The details of the polymers analyzed for this study are shown in Table I. The pure components and the following 50:50 weight blends were analyzed: poly(methyl methacrylate) (M_w = 80,500, PMMA80K)/poly(dimethyl siloxane) (M_w = 813,000, PDMS800K), LPE/BPE (described previously),[12] and PMMA80K/poly(vinyl acetate) (PVA). Polymer blends were used in this study because the region of local polydispersity originating from molecular heterogeneity could be exactly defined as the overlap region between the two component chromatograms.

RESULTS AND DISCUSSION

Analysis of PMMA80K/PDMS800K and Its Components

The large dn/dc differences between PMMA80K and PDMS800K caused this blend to be the most easily analyzed by all three of the local polydispersity detection methods. Figure 3 shows the DRI chromatograms of the 50:50 weight blend and the individual components. The much smaller PDMS peak reflects its much smaller dn/dc value. The region of overlap between the two peaks shown in the figure is the region of local polydispersity to be determined by the methods (local polydispersity is present from about 15.5 to 17.9 mL).

Figure 4 shows the result of applying the chromatogram comparison method to this blend. From this figure, the region where the two chromatograms differed corresponds to this retention volume region. Figure 5 shows the two residuals (R_i and R_i*) for this analysis plotted versus the retention volume as a continuous line and as individual data points, respectively. The R_i line departs strongly from zero in the expected range of retention volumes with large noise excursions between 14.5 and 15.5 mL. The random high frequency of the individual point values of R_i* confirm that those excursions may be attributed to random error in the W_i*.

Figure 6 shows the application of the conventional calibration curve comparison method to the PMMA80K/PDMS800K analysis. The no polydispersity calibration curve is located about midway between two calculated calibration curves, assuming $P(\theta)$ was unity and dn/dc constant. The distance between these latter two curves is the logarithm of the local polydispersity in molecular weight ($M_{w,i}/M_{n,i}$). Again, the retention volume range from 15.5 to 17.9 mL corresponded to the region where all of these calibration curves were separate. At lower retention volume values, random noise accounted for the difference. At higher retention volumes the curves were superimposed.

Figure 7 shows the application of the universal calibration curve comparison method. A significant difference between the no local polydispersity curve and the curve obtained in the usual way from the injection of narrow molecular weight distribution standards is readily evident in the range of 15.5–17.9 mL. Figure 8 shows the

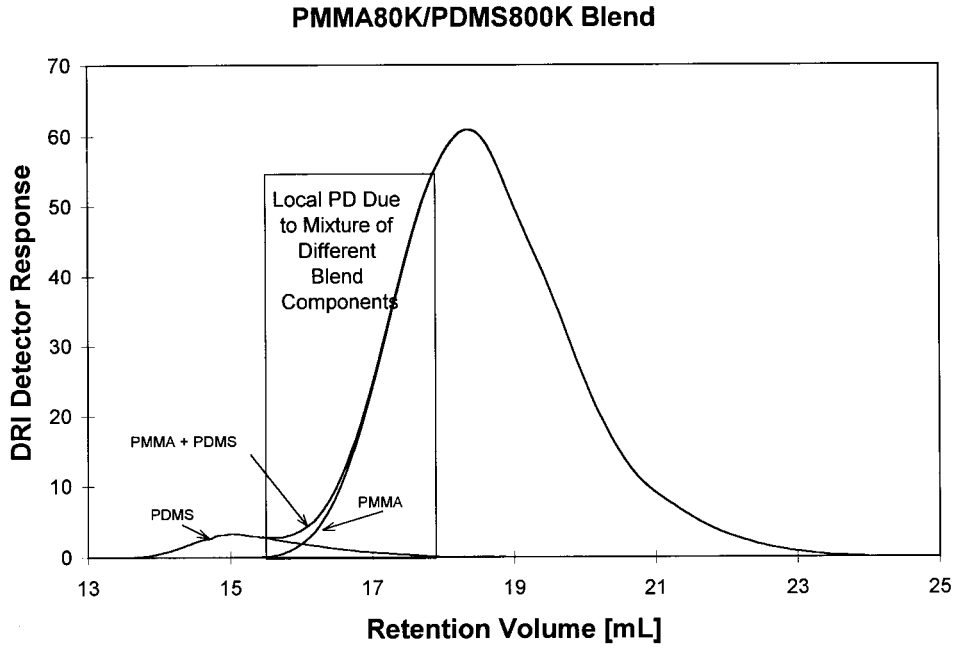

Figure 3 DRI chromatograms of a 50 : 50 weight PMMA80K/PDMS800K blend and each component.

plots of residuals that demonstrated that this deviation exceeded the random error. These residuals were defined analogously to those for the chromatogram comparison method [eqs. (14) and (15)], except that the universal calibration curves (J_i, J_i*) were used instead of the DRI chromatograms (W_i, W_i*). A comparison of Figure 5 and Figure 8 indicates that the chromatogram com-

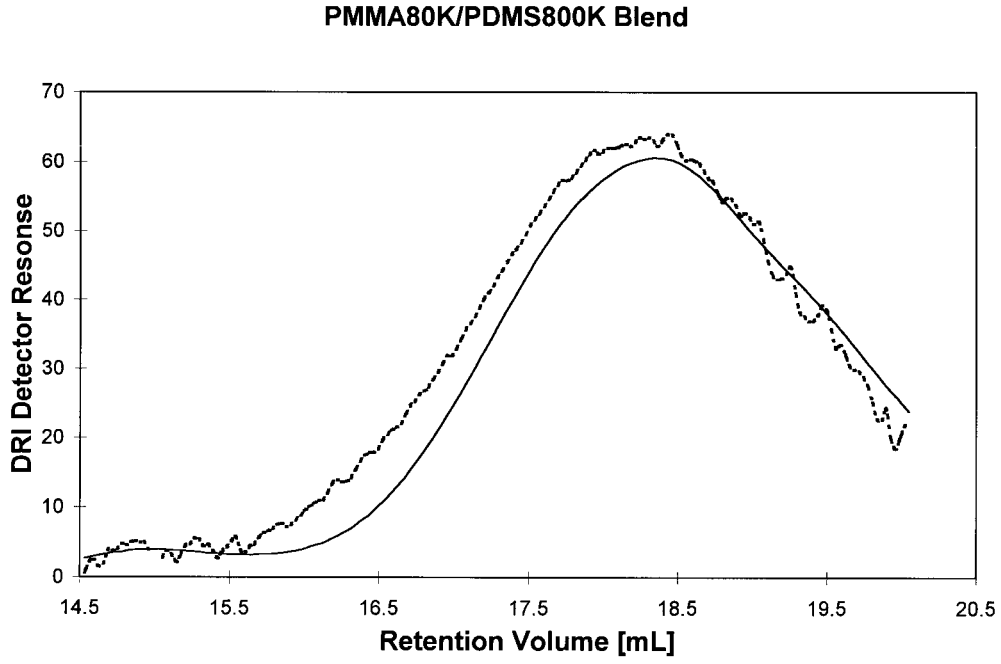

Figure 4 The application of the chromatogram comparison method to the PMMA80K/PDMS800K blend: (- - -) W_i^*; (—) W_i.

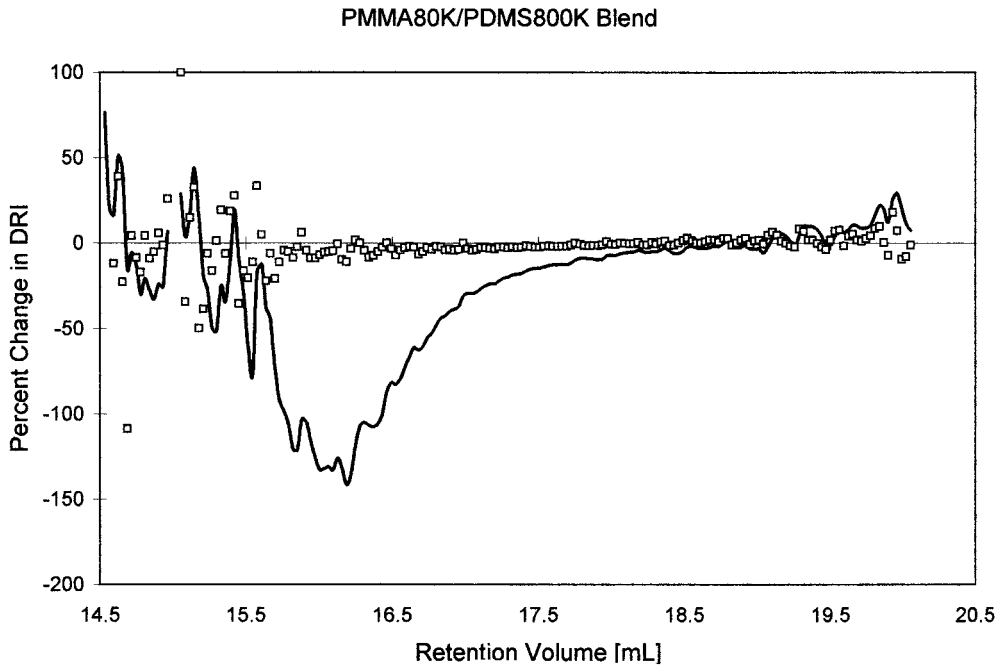

Figure 5 The residuals for the application of the chromatogram comparison method to the PMMA80K/PDMS800K blend: (□) R_i^*; (—) R_i.

parison method resulted in a maximum of 140% distance between the two curves while the universal calibration curve comparison method resulted in a maximum of 500% distance. However, the maximum random noise also increased from 75 to 210%. The topic of the relative sensitivity of these three methods is thus not clear at this time and will be the subject of a future publication.

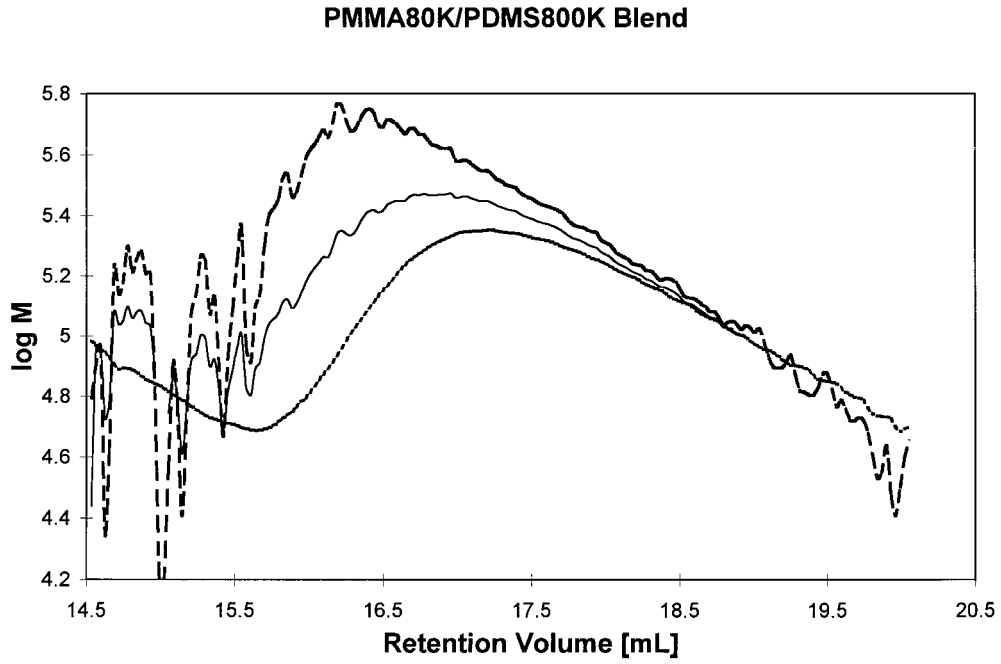

Figure 6 The application of the conventional calibration curve comparison method to the PMMA80K/PDMS800K blend: (– – –) $M_{w,i}$; (—) M_i^*; (- - -) $M_{n,i}$.

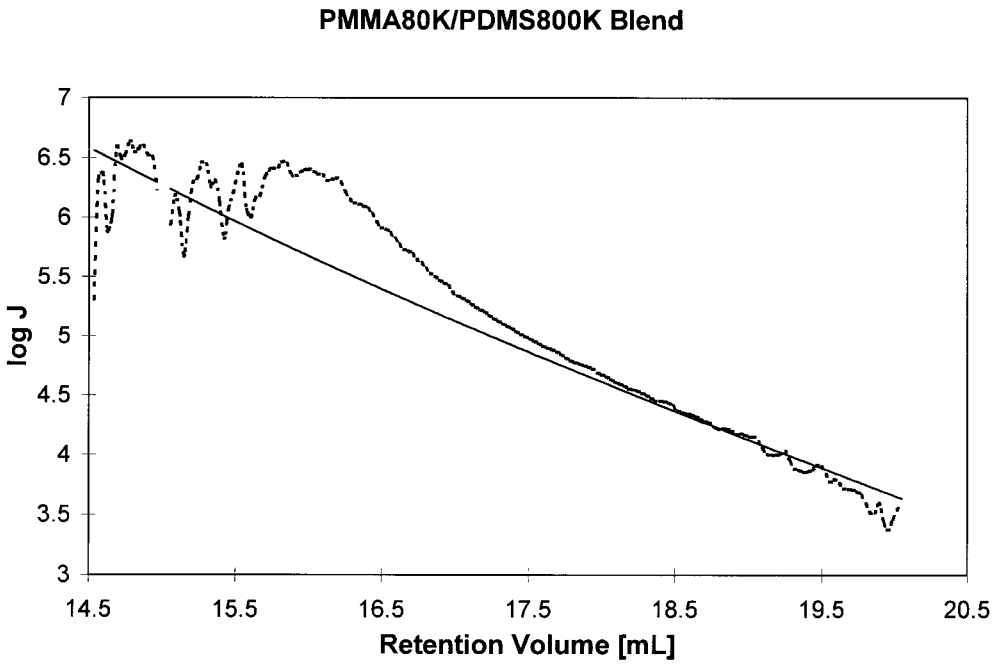

Figure 7 The application of the universal calibration curve comparison method to the PMMA80K/PDMS800K blend: (- - -) J_i^*; (—) J_i.

To further investigate the possible causes of local polydispersity other than sample molecular heterogeneity, pure PMMA homopolymer (PMMA80K) was examined. [Pure PDMS800K could not be examined in this way because essentially a zero light scattering signal was obtained.] Figure 9 shows the plots of residuals for PMMA80K analyzed using the chromatogram comparison method. The R_i values

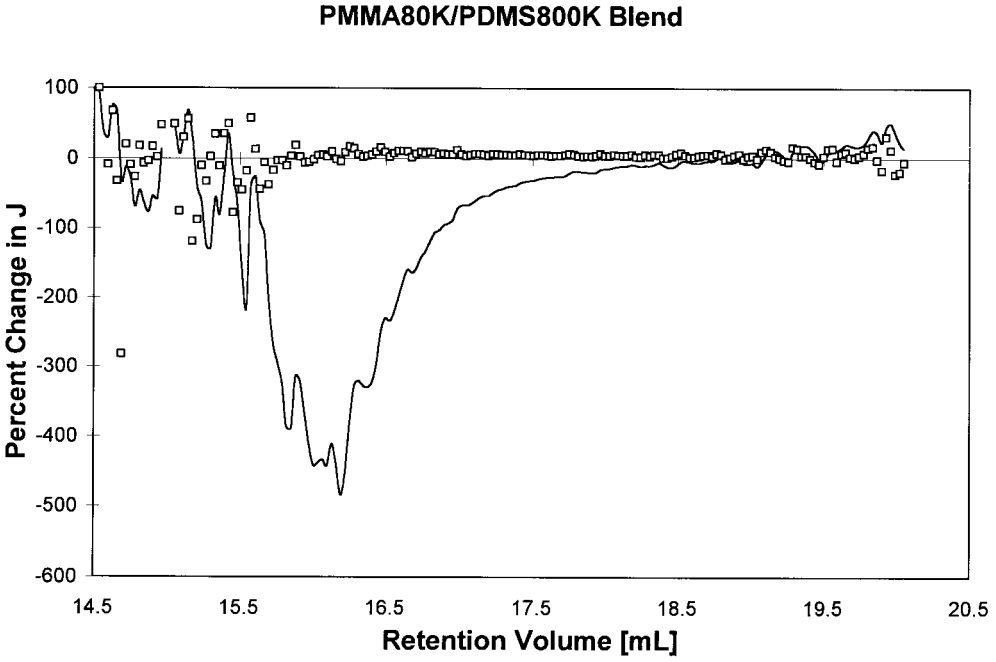

Figure 8 The residuals for the application of the universal calibration curve comparison method to the PMMA80K/PDMS800K blend: (□) R_i^*; (—) R_i.

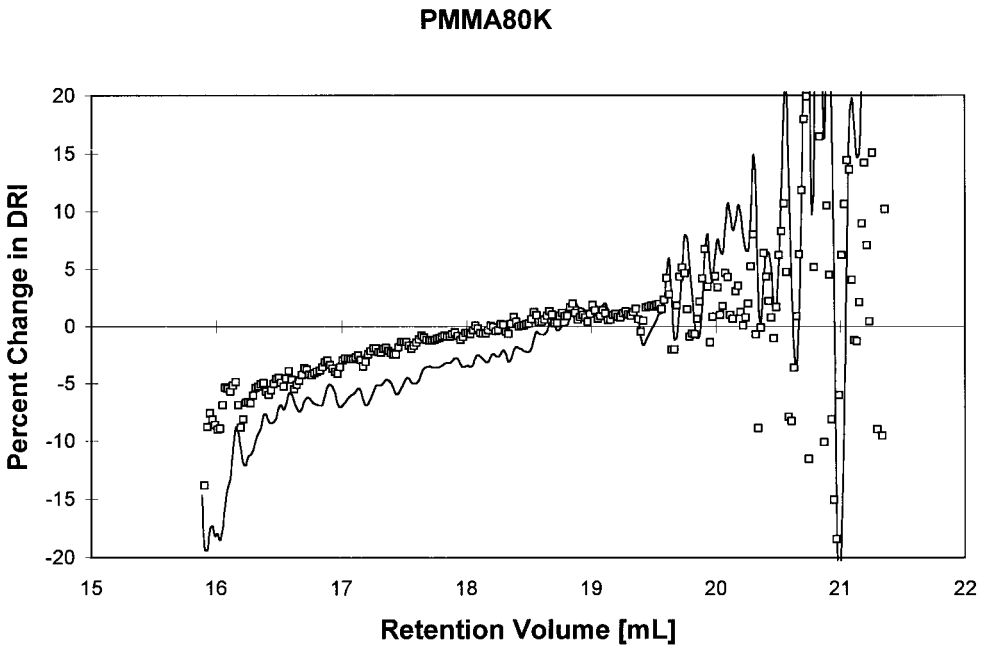

Figure 9 The residuals for the application of the chromatogram comparison method to the PMMA80K homopolymer: (□) R_i^*; (—) R_i.

showed that such undesired sources of local polydispersity could generate approximately a 20% difference between the no local polydispersity and experimental DRI chromatograms. However, the R_i^* values (ignoring the slope of the data because it was due to the shape of the no polydispersity chromatogram) showed that at about 16 mL the random scatter was approximately 10%. Thus, the actual discernible difference between the curves was approximately 10% (i.e., 20 − 10% noise). This was much less than the 140% maximum difference observed when the chromatogram comparison method was applied to the polymer blend data.

Analysis of LPE/BPE and Its Components

Figure 10 shows the DRI chromatograms of a 50:50 blend of LPE and BPE, as well as the chromatograms of the components. Both components had the same *dn/dc* value, and $P(\theta)$ (15°) was considered as unity for both. Thus, the local polydispersity in the molecular weight was the only molecular heterogeneity present. Figures 11–13 show the application of the chromatogram comparison method with plots of residuals for the blend and the blend components. It is evident that the difference between the chromatograms may exceed random error (compare the residuals in Fig. 11) but does not exceed the difference between the curves ascribable to causes other than molecular heterogeneity (evident from the residuals of the blend components). That is, in this case the molecular weight heterogeneity was not sufficient to be detectable.

Analysis of PMMA80K/PVA and Its Components

Figure 14 shows the DRI chromatograms of the PMMA80K/PVA and its components. The region of overlap (i.e., the range of retention volumes containing significant local polydispersity) is from approximately 15.6 to 22 mL. Figure 15 shows the plot of residuals for this blend after application of the chromatogram comparison method and Figure 16 shows the same plot for PVA. The plot of residuals for PMMA80K was previously shown as Figure 9. Again it is evident that, as for the LPE/BPE blend, although the difference between the chromatograms is above the random noise level (at least in the 17–18 mL region, Fig. 15), it did not exceed deviation from causes other than molecular heterogeneity (Figs. 9, 16). Although these two polymers are drastically different chemically, their *dn/dc* values and molecular weight variety did not differ sufficiently to allow local polydispersity due to molecular heterogeneity to be detected at any retention volume.

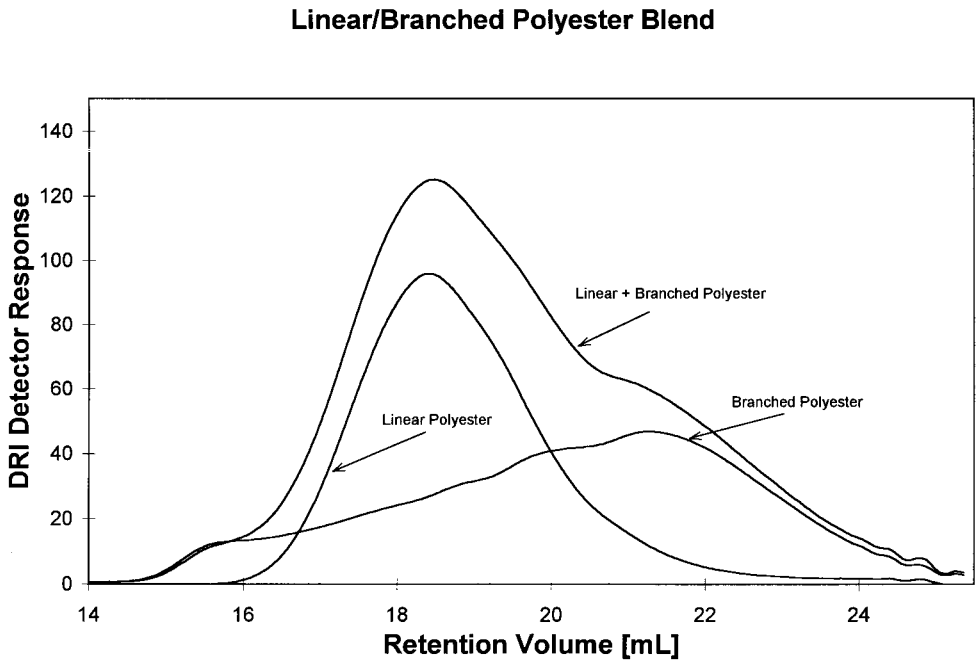

Figure 10 A DRI chromatogram of the blend of a linear polyester and a branched polyester and DRI chromatograms of the individual components.

CONCLUSIONS

Three methods for assessing local polydispersity using triple detector SEC are available. These are the chromatogram comparison method, the conventional calibration curve comparison method, and the universal calibration curve comparison method. All three meth-

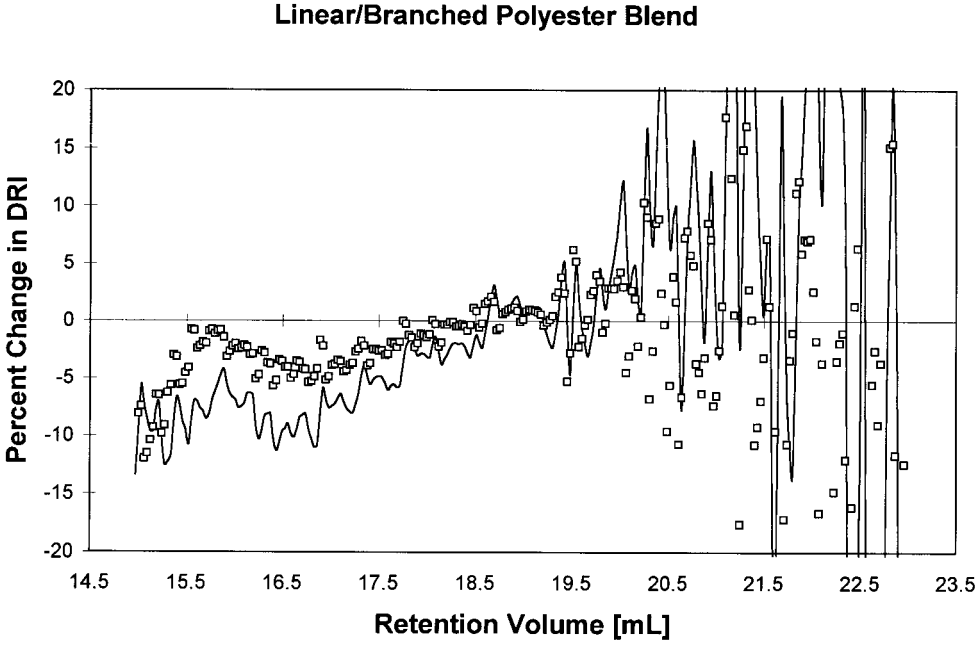

Figure 11 The residuals for the application of the chromatogram comparison method to the blend of a linear and branched polyester: (□) R_i^*; (—) R_i.

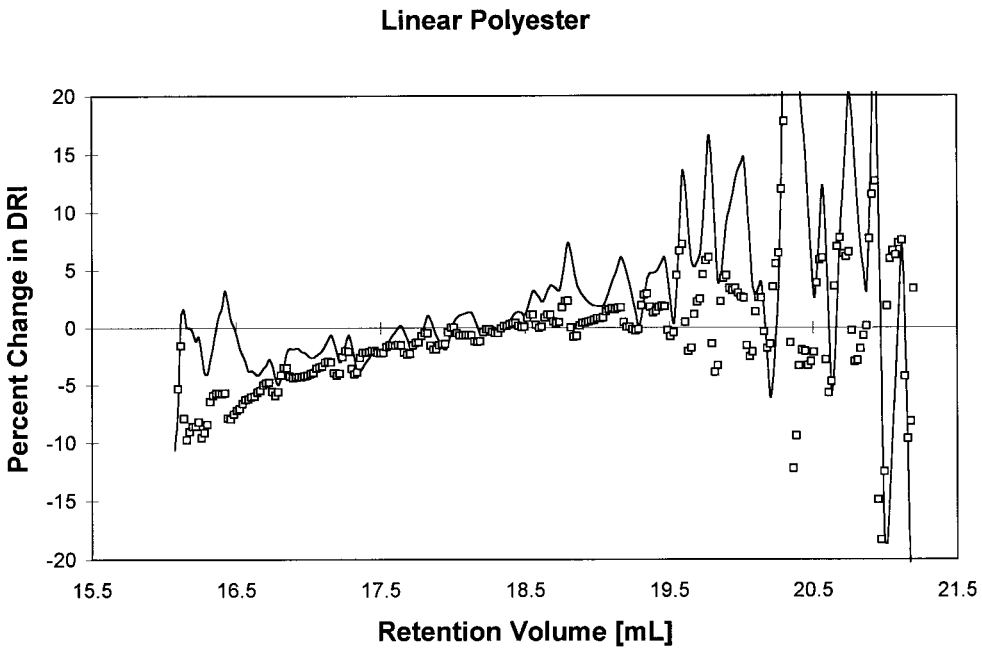

Figure 12 The residuals for the application of the chromatogram comparison method to the linear polyester homopolymer: (□) R_i^*; (—) R_i.

ods now provide a valuable system assessment with the potential for elucidating local polydispersity. One of the methods, the universal calibration comparison method, may be more sensitive than the chromatogram comparison method. However, it apparently also has more significant noise.

Two types of calculated residuals were shown to be useful for defining signal and for distinguishing signal from noise.

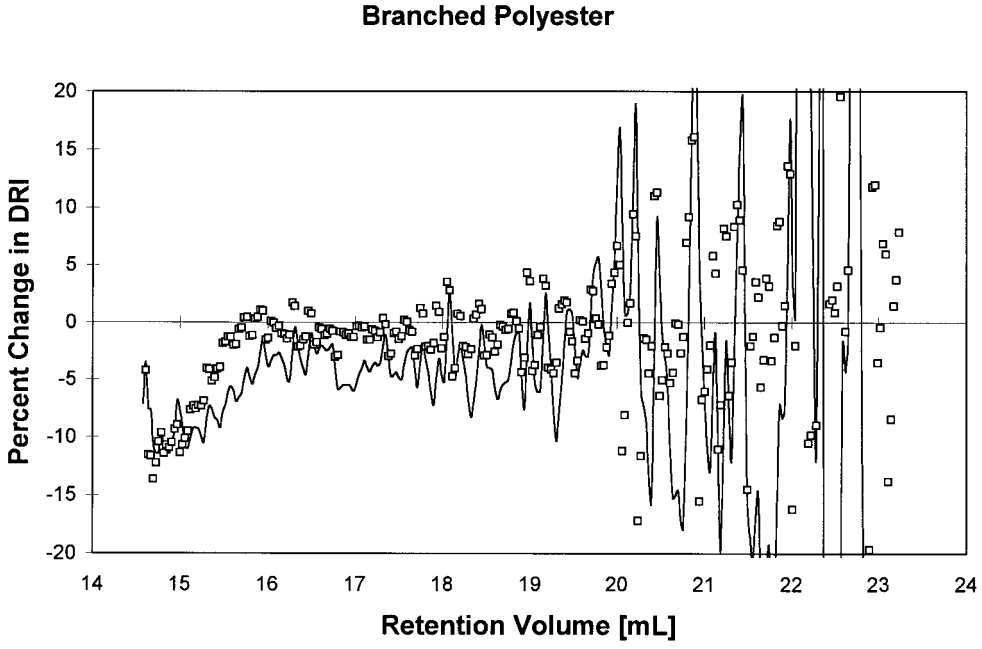

Figure 13 The residuals for the application of the chromatogram comparison method to the branched polyester homopolymer: (□) R_i^*; (—) R_i.

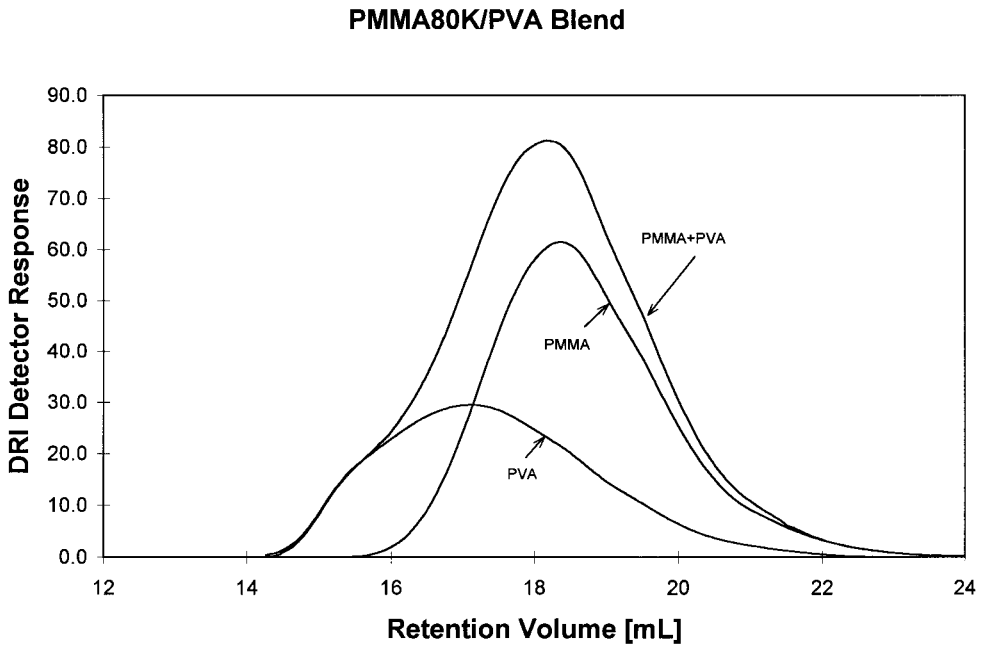

Figure 14 A DRI chromatogram of a blend of PMMA80K and PVA and DRI chromatograms of the individual components.

The different relative sensitivities of the three detectors resulted in a seriously limited range of useful retention volumes when all three detectors were used together because they were in these local polydispersity detection methods.

Application of the methods to determine local polydispersity in polymers without molecular het-

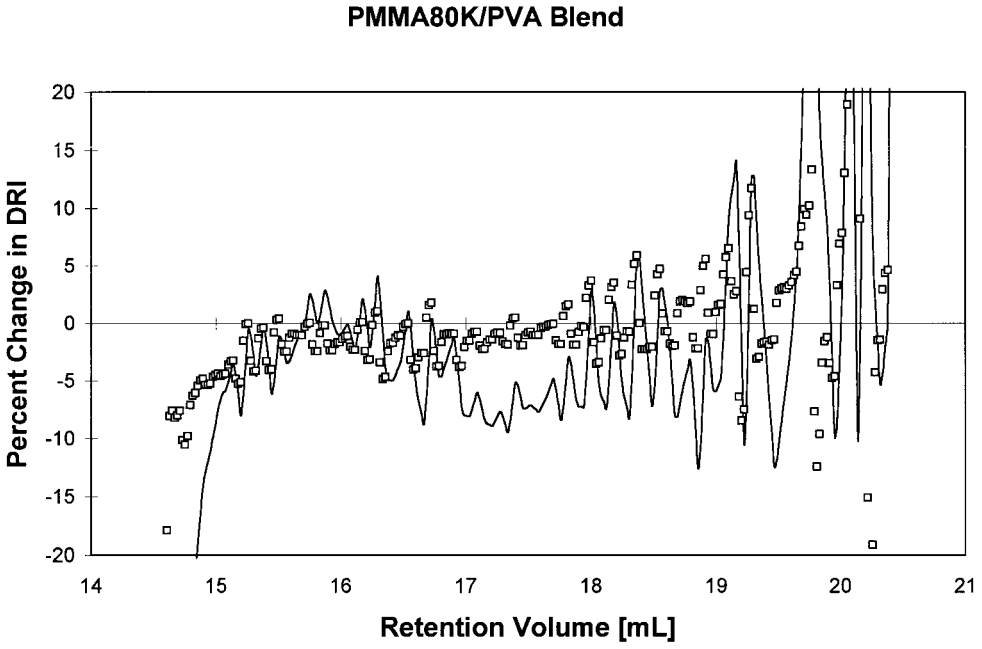

Figure 15 The residuals for the application of the chromatogram comparison method to the PMMA80K/PVA blend: (□) R_i^*; (—) R_i.

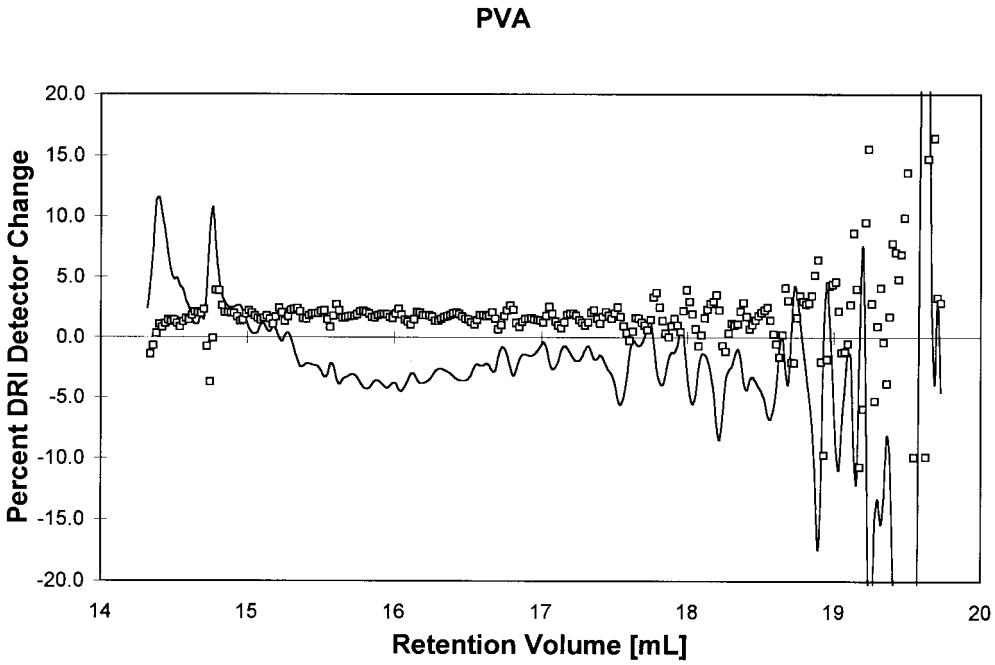

Figure 16 The residuals for the application of the chromatogram comparison method to the PVA homopolymer: (□) R_i^*; (—) R_i.

erogeneity (e.g., linear homopolymers) served to show the magnitude of local polydispersity due to effects such as axial dispersion, interdetector volume, and so forth.

Of the three polymer blends examined, only the one with a very large difference in *dn/dc* (PMMA/PDMS blend) showed local polydispersity that could definitely be attributed to molecular heterogeneity. A blend of branched and linear polyesters with identical *dn/dc* values and a blend of PMMA and PVA showed local polydispersity, but factors other than molecular heterogeneity appeared to be the cause. This result was in agreement with theoretical predictions that in copolymers extremely large differences in *dn/dc* would be necessary for experimental detection of local polydispersity by SEC.[3]

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