

Detecting Local Polydispersity with Multidetector SEC from Reconstructed DRI Chromatograms

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ABSTRACT: Local polydispersity refers to variety in the types of molecules present at the same retention volume in an analysis by size exclusion chromatography (SEC). Such variety is undesired because it can be a major source of inaccuracy in SEC interpretation. A rapid, practical, method for detecting the presence of local polydispersity is presented. In this method, data from a differential viscometer (DV) and light scattering (LS) detector are used together with a universal calibration curve to generate a differential refractive index (DRI) chromatogram for the sample, while assuming that it does not exhibit local polydispersity. This "reconstructed" DRI chromatogram is compared to the actual DRI chromatogram. It is shown that any significant difference between the two indicates the presence of local polydispersity. Plots of residuals (the difference between the heights of the two DRI chromatograms vs. retention volume) allow the significance of the local polydispersity to be assessed and the retention volume range encompassing the local polydispersity to be defined. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 831-835, 1998

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INTRODUCTION

Local polydispersity in size-exclusion chromatography (SEC) refers to variety in the types of molecules present at the same retention volume. Equations commonly used to determine molecular weight averages and molecular weight distribution assume no local polydispersity (i.e., they assume that all molecules are identical at each retention volume). This assumption can lead to considerable inaccuracy in the presence of local polydispersity.

Axial dispersion as a source of local polydispersity in SEC has been recognized for many years, and a wide diversity of methods have been developed to correct for its effect.¹⁻³ With high-resolu-

tion columns this source of error is generally considered less serious: whole polymer molecular weight averages (i.e., averages including all the molecules present) of polydisperse linear homopolymers calculated from DRI chromatograms are often within 5% of values determined using other methods. However, there remain some areas of concern: SEC of very high molecular weight polymers, for example. Also, it is possible that local molecular weight averages and local intrinsic viscosity values (those values determined for the molecules present at each retention volume) may be inaccurate, and this inaccuracy does not reflect in the whole polymer values determined from the DRI detector.

A second source of local polydispersity arises from the chemical structure of the sample, even with perfect resolution. For example, polymer molecules with different amounts of branching can have the same SEC retention volume but

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different molar masses. Also, polymer molecules with different chemical composition, such as in polymer blends and in compositionally heterogeneous copolymers, may coelute. Such compositional local polydispersity can be very troublesome. Depending on the variation in the specific refractive index increments (dn/dc values) across the chromatogram and within a chromatogram retention volume "slice," widely different and inaccurate results can be obtained from DV, LS, and DRI detectors. In some instances, each type of molecule present may be detected separately from all others (by selecting a particular wavelength for a UV detector, for example). Alternatively, compositional local polydispersity may be elucidated by fractionating according to chemical composition either prior to or after the SEC separation.⁴ The necessary first step in either approach is recognition of the presence of local polydispersity.

We earlier developed a method for detecting local polydispersity based upon special sample preparation techniques.⁵ That method is useful if only one molecular weight-sensitive detector is present. However, the need for special sample preparation is a disadvantage and often limits the polymers that can be so analyzed. This article presents a simple method for detecting local polydispersity of any kind by using a multidetector SEC consisting of DRI, DV, and LS detectors. The method has recently been used in combination with the shape of molecular weight calibration curves to develop a systematic approach for assessing local polydispersity.⁶

The method generates a DRI chromatogram from the viscometry and light-scattering signals, combined with a universal calibration curve. Any differences between this generated DRI chromatogram and the experimental DRI chromatogram indicates the presence of local polydispersity. It may be used to validate SEC molar mass measurements and to identify samples that require further fractionation. Here, we show the basis for this method and two examples of its use.

THEORY

Local Concentration from the DRI Chromatogram

For any variety of molecules at a particular retention volume, the local concentration c_i (the total concentration of polymer molecules at that retention volume) is obtained from the sum of the DRI chromatogram heights of j different polymer

molecules at retention volume i , (v_i), W_{ij} , and the specific refractive index increment of the different molecules j at v_i , $(dn/dc)_{ij}$.

$$c_i = \frac{1}{\beta} \sum_{j=1}^k \frac{W_{ij}}{\left(\frac{dn}{dc}\right)_{ij}} \quad (1)$$

The DRI detector response constant β is in units of refractive index units per mV. If no local polydispersity is present that affects dn/dc (i.e., all of the molecules have identical dn/dc values), then the local concentration is given by:

$$c = \frac{W_i}{\beta \left(\frac{dn}{dc}\right)_i} \quad (2)$$

Local Number-Average Molecular Weight from the DV Detector

From Hamielec and Ouano,⁷ we know, in the presence of local polydispersity, that the DV detector provides the local number-average molecular weight,

$$M_{ni} = \frac{J_i c_i}{\eta_{sp,i}} \quad (3)$$

where J_i is hydrodynamic volume obtained from a universal calibration curve and $\eta_{sp,i}$ is specific viscosity. If local polydispersity does not affect dn/dc , then we may combine eqs. (2) and (3) so that an accurate local M_n can be calculated:

$$M_{ni} = \frac{J_i W_i}{\eta_{sp,i} \beta \left(\frac{dn}{dc}\right)_i} \quad (4)$$

Local Weight-Average Molecular Weight from the LS Detector

The local weight-average molecular weight is strongly affected by the variety of dn/dc values at a particular retention volume and is given by:

$$M_{wi} = \frac{1}{\alpha c_i} \sum_{j=1}^k \frac{R_{\theta_{ij}}}{P(\Theta)_{ij} \left(\frac{dn}{dc}\right)_{ij}^2} \quad (5)$$

where α is the light-scattering optical constant, not containing $(dn/dc)_{ij}^2$. If molecules at v_i do not vary in dn/dc and $P(\theta)$ values, then:

$$M_{w_i} = \frac{R_{\theta_i} \beta \left(\frac{dn}{dc} \right)_i}{\alpha P(\theta)_i \left(\frac{dn}{dc} \right)_i^2 W_i} \quad (6)$$

Reconstructing the DRI Chromatogram for No Local Polydispersity

If no local polydispersity is present, then the data from the DV and LS detectors can be used to obtain an estimate of the DRI chromatogram.

For the case of no local polydispersity in molecular weight, $M_{n_i} = M_{w_i}$. Equating (4) and (6) and rearranging provides an expression for the DRI chromatogram height at v_i that does not contain the specific refractive index increment, dn/dc :

$$W_{i,\text{reconstructed}} = \beta \left(\frac{\eta_{sp_i} R_{\theta_i}}{\alpha P(\theta)_i J_i} \right)^{1/2} \quad (7)$$

Equation (7) can be expected to regenerate the DRI chromatogram only if: (a) there is no local molecular weight polydispersity, (b) there is no local polydispersity of any type that causes a variety of dn/dc values or $P(\theta)$ values to be present at v_i , and (c) universal calibration applies. That is, if there is local molecular weight polydispersity, it can be detected (if it is above the random noise level) even if it does not affect dn/dc variety at v_i . Likewise, local compositional polydispersity can be detected (if there is variety in dn/dc at v_i) even if there is no local molecular weight polydispersity.

Effect of dn/dc Varying across the DRI Chromatogram

Because eq. (7) was derived for a particular retention volume, v_i , without reference to molecules at neighboring retention volumes, it follows that variation of dn/dc across the chromatogram will not affect the value of the reconstructed chromatogram height at v_i . This is demonstrated mathematically in the following paragraphs.

If there is no local polydispersity at v_i , then all molecules there are identical. They then have a single value of dn/dc , $(dn/dc)_i$ and a single value of $P(\theta)$, $P(\theta)_i$ (although both these quantities may be different at different v_i). Then from combining eqs. (7), (6), and (2) we obtain:

$$W_{i,\text{reconstructed}} = \beta \left[\frac{\eta_{sp_i} \alpha P(\theta)_i \left(\frac{dn}{dc} \right)_i^2 c_i M_{w_i}}{\alpha P(\theta)_i J_i} \right]^{1/2} \quad (8)$$

which simplifies to:

$$W_{i,\text{reconstructed}} = \beta \left(\frac{dn}{dc} \right)_i \left(\frac{M_{w_i} \eta_{sp_i} c_i}{J_i} \right)^{1/2} \quad (9)$$

Provided that there is no local molecular weight polydispersity, $M_{w_i} = M_{n_i}$, $M_{w_i}/J_i = 1/[\eta]_i$, where $[\eta]_i$ is intrinsic viscosity, and

$$W_{i,\text{reconstructed}} = \beta \left(\frac{dn}{dc} \right)_i \left(\frac{1}{[\eta]_i} [\eta]_i c_i^2 \right)^{1/2} \quad (10)$$

which immediately reduces to eq. 2 for the true DRI chromatogram. Because dn/dc is permitted to vary with i , this means that a variation of dn/dc across the chromatogram will not adversely affect the accuracy of the reconstructed DRI chromatogram. Thus, any significant residual, R_i , calculated from:

$$R_i = W_i - W_{i,\text{reconstructed}} \quad (11)$$

indicates that the assumptions that all molecules at point i have the same (dn/dc) , and that $M_{w_i} = M_{n_i}$ are incorrect. Thus, such samples contain local polydispersity over the range of retention volumes for which there is a significant value of R_i .

EXPERIMENTAL

The SEC detectors, arranged in series, are a 757 Spectroflow spectrophotometric detector (UV), a Precision Detectors PD2000 light-scattering (LS) detector operating at 15 and 90 degrees, a Viscotek H502A differential viscometer (DV), and a Waters 411 differential refractive index (DRI) detector. The columns, LS, DV, and DRI detector temperatures were maintained at 35.0°C. The eluent was uninhibited tetrahydrofuran, nominally delivered at a flow rate of 1.0 mL/min. Flow rate corrections were made using 0.2% acetone added to the sample solvent as a flow marker. Columns were three Polymer Laboratories Pgel mixed-C, 7.5 × 300 mm. A universal calibration curve was constructed using 15 narrow molecular weight distribution polystyrene standards (Polymer Laboratories) ranging from MW 580 to 2,300,000. Polymer blends at a concentration of

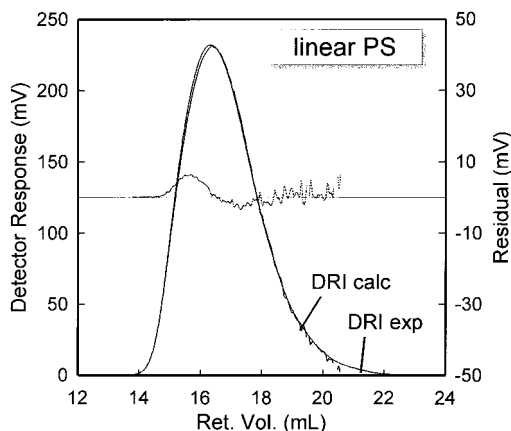


Figure 1 Reconstructed (DRI calc) and experimental (DRI exp) chromatograms for linear polystyrene. Residuals (dotted) are plotted on a second y-axis.

0.75 mg/mL of each component were injected in an injection volume of 100 μ L.

RESULTS AND DISCUSSION

Polystyrene: No Significant Local Polydispersity

Analysis of a broad molecular weight distribution linear polystyrene provides a first test of eq. (7). This material is known to not contain molecular weight or compositional local polydispersity, except for that created by axial dispersion. Axial dispersion effects are small in the SEC system employed, and the use of an effective interdetector volume^{1,2} provides some correction for imperfect resolution. In this case, the reconstructed chromatogram nearly superimposes on the experimental DRI chromatogram (Fig. 1). The plot of residuals shows that the difference to be expected between experimental and reconstructed DRI chromatograms for a sample that exhibits insignificant local polydispersity is a maximum of approximately 2.5% of the experimental DRI signal. The differences may be attributed to minor axial dispersion and the effects of detector signal noise.

Blend of Poly(2,4,6-tribromostyrene) and Polystyrene: Slight Difference in dn/dc within a Retention Volume "Slice"

A 1:1 blend of poly(2,4,6-tribromostyrene) ($dn/dc = 0.124$ at 680 nm) and polystyrene ($dn/dc = 0.180$ at 680 nm) mixes molecules at the same retention volumes (Fig. 2) with slightly different specific refractive index increments. The reconstructed DRI chromatogram (Fig. 3) does not su-

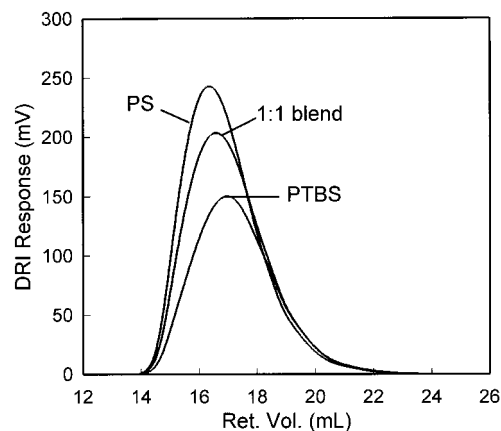


Figure 2 Experimental DRI chromatograms of polystyrene (PS), poly(2,4,6-tribromostyrene) (PTBS), and a 1:1 blend (by weight) of PS and PTBS.

perimpose on the experimental DRI chromatogram, and the plot of residuals indicates differences between 0 and 8% of the experimental DRI signal.

Blend of Poly(dimethylsiloxane) and Polystyrene: Large Difference in dn/dc within a Retention Volume "Slice"

Experimental DRI chromatograms of polystyrene, poly(dimethylsiloxane) and a 1:1 blend are shown in Figure 4. Figure 5 shows the reconstructed chromatograms for a 1:1 blend of polystyrene ($dn/dc = 0.180$ at 680 nm) with poly(dimethylsiloxane) ($dn/dc = 0.003$ at 680 nm). These polymers have nearly identical molecular size distributions. However, molecules exist at each re-

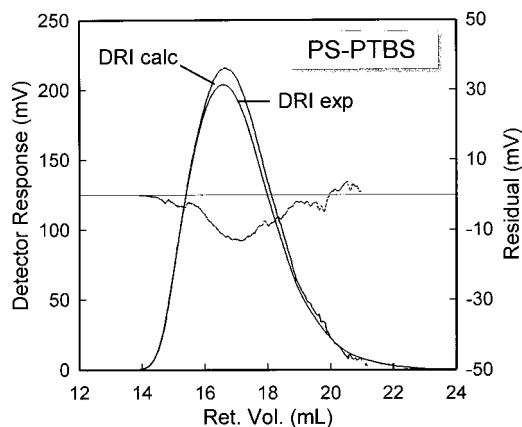


Figure 3 Reconstructed (DRI calc) and experimental (DRI exp) chromatograms for 1:1 blend of polystyrene (PS) and poly(2,4,6-tribromostyrene) (PTBS). Residuals (dotted) are plotted on a second y-axis.

tention volume with greatly different specific refractive index increments. The difference is readily seen between the reconstructed and experimental DRI chromatograms and the plot of residuals in Figure 5.

Computer Simulations

Various computer simulations were done by adding together component chromatograms to obtain the chromatogram of binary blends. Reconstructed chromatograms were calculated using eq. (7) for comparison. The "true" properties of the component chromatograms could be arbitrarily specified to test the effect on eq. (7) of having dn/dc values different within the slice and constant across the chromatogram, or constant within the slice and varying across the chromatogram while maintaining molecular weight polydispersity negligible. The results conclusively showed that the DRI chromatogram reconstructed using eq. (7) is sensitive only to dn/dc variations within the slice under these conditions. A variation in dn/dc across the chromatogram had no effect. In fact, it was the surprising result of such simulations that led to the theoretical explanation presented above.

CONCLUSIONS

Local polydispersity in molecular weight or local polydispersity that is reflected in a difference in

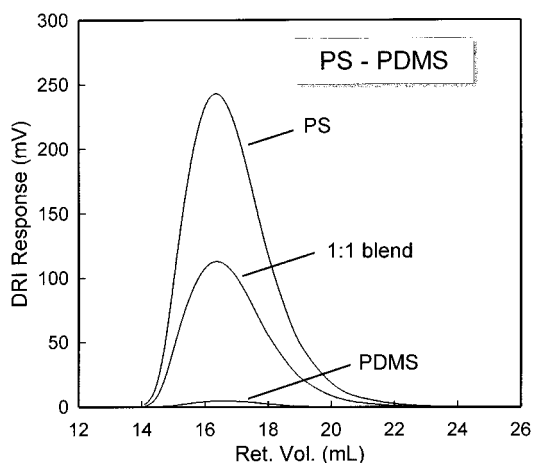


Figure 4 Experimental DRI chromatograms of polystyrene (PS), poly(dimethylsiloxane) (PDMS), and a 1:1 blend (by weight) of PS and PDMS.

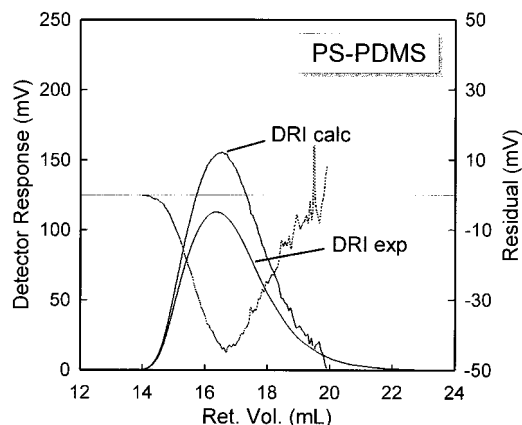


Figure 5 Reconstructed (DRI calc) and experimental (DRI exp) chromatograms for 1:1 blend of polystyrene (PS) and poly(dimethylsiloxane) (PDMS). Residuals (dotted) are plotted on a second y-axis.

refractive index among the molecules at a particular retention volume can be detected by comparing a reconstructed DRI chromatogram to the experimentally measured one. Data from a LS detector and from a DV detector in combination with a universal calibration curve are used to obtain the reconstructed DRI chromatogram. This local polydispersity detection method is both practical and rapidly accomplished. A particularly notable part of the method is that the reconstructed chromatogram is unaffected by variation in dn/dc across the chromatogram. It is affected only by molecular weight and/or dn/dc diversity within a chromatogram retention volume "slice."

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