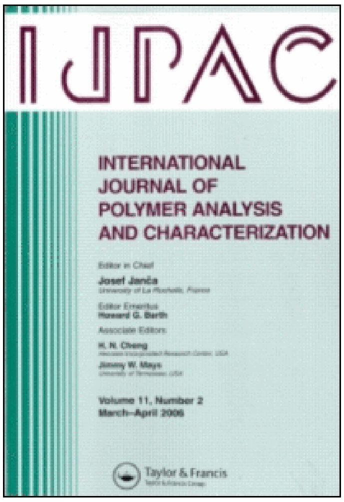

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Detecting "Perfect Resolution" Local Polydispersity in Size Exclusion Chromatography

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The objective of this work is to obtain a simple method for detecting local polydispersity. Local polydispersity is the presence of a variety of different types of molecules at the same retention volume in SEC. One source of local polydispersity is axial dispersion. However, the topic of this paper is the detection of local polydispersity which is independent of axial dispersion effects. This "perfect resolution" local polydispersity can occur because SEC separates on the basis of molecular size in solution and thus, for complex polymer molecules, such as copolymers or branched polymers, a variety of combinations of molecular weight and composition can produce the same molecular size. In conventional SEC interpretation, it is assumed that, with high resolution columns, local polydispersity is absent. Highly misleading analyses can result if this assumption is invalid. Two very simple methods were developed in this work. The first method enabled polystyrene-poly(dimethyl siloxane) blends to be examined for local polydispersity by regenerating the chromatogram after sample preparation using an adsorption cartridge and comparing it to the original concentration chromatogram. The second method involves the use of a dual detector SEC to examine the change in apparent local intrinsic viscosity caused by sample preparation utilizing precipitation. Two-dimensional solubility parameters were used for solvent/nonsolvent selection. The method was demonstrated on a polystyrene-poly(dimethyl siloxane) blend.

Keywords: Size exclusion chromatography, local polydispersity, viscometer, poly(dimethyl siloxane)

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INTRODUCTION

In size exclusion chromatography (SEC), separation is on the basis of molecular size in solution. For a linear homopolymer, such as polystyrene or polypropylene, there is a unique one-to-one relationship between each molecular size and its corresponding molecular weight. Thus, separation by molecular size is synonymous with separation by molecular weight. However, for complex polymers, copolymers and branched polymers for example, different combinations of composition (and/or branching) and molecular weight can result in the same molecular size. Thus, the one-to-one relationship between molecular size and molecular weight is then absent. This means that there then can be more than one molecular weight at the same retention volume even for high resolution separations where axial dispersion effects are negligible. The resulting variety in molecular weight at each retention volume is then a local polydispersity in molecular weight. Local polydispersity in composition and/or branching accompanies the local polydispersity in molecular weight. Since local polydispersity is normally assumed negligible in SEC interpretation, if it is present it can be a serious source of error.

The objective of this research is to devise simple, readily applied methods for determining this "perfect resolution" local polydispersity and for assessing whether or not it is sufficient to be worth pursuing with chromatographic cross-fractionation. In this paper we present two such methods and in the remainder of the paper, reference to local polydispersity is always referring to "perfect resolution" local polydispersity. The basis for both methods is sample preparation which selectively removes molecules so that local polydispersity becomes evident. Blends of polystyrene (PS) and poly(dimethyl siloxane) (PDMS) were the subjects of the study. Method I utilizes only a single concentration detector but requires detailed sample preparation knowledge to be useful. Method II requires a concentration detector and a molecular weight sensitive detector but is much more general and readily applicable as compared to Method I.

THEORY

Local Polydispersity

As mentioned above, local polydispersity in molecular weight is of major concern because conventional SEC interpretation assumes only one molecular weight is present at each retention volume once axial dispersion effects are insignificant. If local polydispersity is present, both the abscissa and the ordinate of the molecular weight distribution can be significantly affected. The abscissa, normally log (molecular weight) becomes the log (local number-average molecular weight), when universal calibration is used with a differential viscometer (DV) detector. It becomes log (local weight-average molecular weight) when a light scattering (LS) detector is used. The ordinate, normally a measure of concentration, becomes distorted if the different molecules present at a particular retention volume have different detector response factors. Therefore, even in a qualitative sense, if local polydispersity is assumed negligible when it is not, the SEC analysis readily provides a misleading, over-simplified picture of the polymer.

There are three interacting factors which are responsible for local polydispersity: more than one property distribution can be present in copolymers and in branched polymers; the SEC separates molecules according to their size in solution; and different combinations of molecular properties (*e.g.*, molecular weight and composition) can result in the same molecular size in solution. The simplest case is when two linear homopolymers are blended: if their chromatograms overlap then, by definition, there is local polydispersity in the region of overlap because in that region there are two different types of molecules at each retention volume. In practice, unlike the case of more complex polymer mixtures and copolymers, for such a simple two component blend, such local polydispersity is not a problem if two detectors can be found that respond differently to each type of polymer. The responses of the two detectors give two equations in two unknowns (the concentration of each type of polymer at each retention volume). Alternatively, if the chromatograms of the pure components are known in advance, together with the concentration of each pure component present in the blend, then the local polydispersity can be exactly defined at each retention volume. Thus, such polymer blends will be used here to develop methods of detecting local polydispersity.

Previous Attempts to Experimentally Account for Local Polydispersity

There has been a considerable amount of work directed at chromatographic cross-fractionation of copolymers.[1–8] In such cross-fractionation experiments, the objective is often to elucidate the individual molecular weight and copolymer composition distributions (as plots of concentration versus molecular weight and concentration versus composition, respectively) or the whole joint distribution (as a contour plot of molecular weight versus composition with each contour representing a different polymer concentration). With branched polymers containing short-chain branching, combinations of temperature-rising elution fractionation (TREF) and SEC have been used,[9–13] where branch frequency and molecular weight are the emphasis.

None of the above chromatographic cross-fractionation approaches is easily accomplished, they all tend to be very expensive and time-consuming. Furthermore, it is often not even known with certainty that the polymer to be analyzed deserves such special attention: it may have no significant local polydispersity. That is, for a copolymer, the whole polymer may have a very narrow copolymer composition distribution and a broad molecular weight distribution (and thus negligible local polydispersity).

Development of New Methods to Detect Local Polydispersity

The fundamental idea to be investigated here is that by comparing the chromatograms of a sample analyzed by SEC before and after a special sample preparation method has been applied, the presence of local polydispersity can be revealed. Two sample preparation methods are examined: adsorption (Method I) and solvent/nonsolvent precipitation (Method II). Also, two chromatographic systems are involved: a system with a single differential refractive index (DRI) detector (used for Method I development) and a system with a DRI detector and a DV detector (used for Method II development). The following two sections summarize each of the two methods in turn assuming that a linear copolymer and (mainly to develop the technique for more complex polymers) a blend of two linear homopolymers are to be analyzed. Then the relevant literature on polymer adsorption and precipitation, the sample preparation techniques to be used, is reviewed.

Method I: Local Polydispersity Detection Using Single Detector SEC

When a single DRI detector is used, the fundamental problem is that the detector must be assumed to respond differently to each type of polymer. Thus, if the chromatogram appears different before and after special sample preparation it may be because total concentration at a particular retention volume has been reduced and no local polydispersity is present or because composition at that particular retention volume changes (which will indicate local polydispersity) along with total concentration. Thus, Method I assumes that we know the identity of molecules that are being removed by the sample preparation method. For example, in the analysis of PS-PDMS blends, if it is known that the sample preparation method removes only polystyrene (*i.e.*, the "after chromatogram" represents only the PDMS molecules originally present possibly mixed with some polystyrene molecules), then subtraction of the "after" chromatogram from the "before" chromatogram could immediately reveal the presence of polystyrene and the extent of overlap of the two component chromatograms (the local polydispersity). The most ideal situation would be if the method removes all of the polystyrene and does not remove any of the PDMS. The more deviation there is from this ideal, the less effective the method.

If some polystyrene molecules remain after sample preparation then the sensitivity of the test is reduced. However, if any PDMS is removed then invalid results can be obtained. It is expected that the molecular weight of the PDMS will affect its removal. Removal of low molecular weight PDMS is quite likely. Thus, for this method to work, the relationship between the amount of PDMS removed as a function of molecular weight will need to be quantitatively defined. Only then can the "after" chromatogram be "reshaped" to allow for the undesired loss of PDMS.

Even if this "reshaping" can be accomplished, Method I is expected to be a very limited technique, applicable only to a specific polymer blend and not to copolymers. The use of dual detectors (*i.e.*, Method II) does not require such an exact knowledge of the sample preparation effect.

Method II: Local Polydispersity Detection Using a Dual Detector SEC

When dual detectors are used, "before" and "after" local property values at each retention volume can be obtained. For example, if two UV wavelengths are used and each polymer type absorbs UV differently, then the composition at each retention volume (local composition values) before and after sample preparation can be readily calculated. Similarly, if a DRI detector and a DV detector are used, then local intrinsic viscosity can be obtained at each retention volume. If there is no change in the local property value, then the molecules removed by the sample preparation method are identical to those remaining in the analyzed sample. Either there is no local polydispersity or the sample preparation method fails to preferentially remove one polymer type. However, if a change is observed, then those molecules removed are different than those remaining and local polydispersity is indicated.

In actual application of a DRI and a DV detector, a practical problem is encountered: the local concentration value cannot be calculated from the DRI response because the DRI is assumed to respond differently to each type of molecule. This problem is circumvented by defining an apparent intrinsic viscosity.

In a SEC separation using DRI and DV detectors, the local intrinsic viscosity can be defined as follows:

$$[\eta]_i(v) = \frac{\eta_{sp,i}(v)}{c_i(v)} \tag{1}$$

where $[\eta]_i(v)$ is the local total intrinsic viscosity of the sample, $\eta_{sp,i}(v)$ is the specific viscosity obtained from the DV detector, and $c_i(v)$ is the concentration provided by the DRI detector at each retention volume.

The output from a differential refractometer measured at each retention volume, $W_i(v)$, is proportional to the concentration at the corresponding slice, $c_i(v)$:

$$W_i(v) = K c_i(v) \tag{2}$$

where K is the proportionality constant.

If $w_{i,A}(v)$ and $w_{i,B}(v)$ are the weight fractions of A units and B units of polymer blends (A + B) or copolymer (A + B) at retention volume v_i, then:

$$W_i(v) = (K_A w_{i,A}(v) + K_B w_{i,B}(v))c_i(v) \tag{3}$$

Therefore the calculated intrinsic viscosity or "apparent intrinsic viscosity" can be written as:

$$[\eta]_{i,AP}(v) = \frac{[\eta]_i(v)}{K_A w_{i,A}(v) + K_B w_{i,B}(v)} = \frac{\eta_{sp_i}(v)}{W_i(v)} \tag{4}$$

If the precipitate contains identical molecules to those left in the solution at a particular retention volume, then $[\eta]_i(v)$, $w_{i,A}(v)$, and $w_{i,B}(v)$ (and hence $[\eta]_{i,AP}(v)$) will be unchanged at that retention volume.

Equation (4) assumes that interdetector volume has been taken into account so that the detector responses used in the equation are for the same molecules. Currently there is no widely accepted method for obtaining interdetector volume and different methods yield different results. If we assume that the effect of interdetector volume on the detector responses before and after special sample preparation is unchanged and do not attempt to account for interdetector volume, then the effect of local polydispersity should still be detectable. Similarly, if a constant "incorrect" interdetector volume is used, the method remains valid. However, in these cases, while the change in apparent intrinsic viscosity is expected to remain useful for detecting local polydispersity, the absolute values of apparent intrinsic viscosity will then reflect the effect of interdetector volume. This may be an important aspect as the method is further developed with the objective of quantitatively defining the value of the local polydispersity at each retention volume.

Sample Preparation Techniques

Adsorption and solvent-nonsolvent precipitation are the two sample preparation techniques considered for Methods I and II.

Adsorption is the most frequent mechanism used in chromatographic attempts to separate copolymer molecules by composition.[6] In adsorption of a polymer molecule, only one unit amongst thousands needs to adsorb in order that the whole molecule be retained. This causes chromatographers to utilize gradient operation in adsorption separations. There have been many reports in the literature of successful separations of copolymers according to composition with only a very small dependence of the separation on molecular weight. This suggests that adsorption on commercially available silica packed cartridges can serve as an effective sample preparation method. These cartridges are widely used for removing undesired contaminants from samples analyzed by high performance liquid chromatography (HPLC).[14–16]

Solvent selection for adsorption separations, however, is very specific to the polymer type and adsorption is very sensitive to operating conditions. One-step isocratic adsorption separation of polymers (the procedure involved here) is particularly sensitive. Thus, solvent selection can be a very empirical, trial-and-error procedure. Despite this disadvantage, it was decided to attempt to utilize adsorption as a sample preparation method because, if local polydispersity were detected, the solvent selected would assist in establishing a chromatographic cross-fractionation method.

Solvent/nonsolvent precipitation was the second sample preparation method used. This type of precipitation has been used alone and as a basis for a chromatographic separation mechanism in many studies.[6] Selection of the solvent and nonsolvent, as well as the ratio of each required for precipitation, has been greatly assisted very recently with the publication of a method proposing new two-dimensional solubility parameters.[17] These solubility parameters were used here for both of these purposes.[18]

EXPERIMENTAL

Materials

Narrow molecular weight distribution PS standards (Polymer Laboratories, Amherst, Mass.) were used for calibration of the SEC single and dual detector systems. Each sample injection volume was 100 μL. The concentrations of narrow molecular weight distribution PS standards between 3.2 × 10^6 and 3.3 × 10^3 g/mol ranged from 0.5 to 2.0 mg/mL, for high-to-low molecular weights, respectively. SRM 706 broad molecular weight distribution polystyrene standard (National Institute of Standards and Technology, Gaithersburg, Maryland) was dissolved at a concentration of 1.0 mg/mL.

As for the PDMS standards, the concentrations of narrow molecular weight distribution standards (American Polymer Standards Corporation, Mentor, Ohio) between 1.4 × 10^6 and 3.0 × 10^3 g/mol (M_w) ranged from 0.5 to 2.0 mg/mL, for high-to-low molecular weights, respectively, and the concentrations of the broad molecular weight distribution PDMS standards 6.3 × 10^5, 9.4 × 10^4 and 3.9 × 10^4 g/mol (M_w) (Aldrich Chemical Co., Milwaukee, Wisconsin), were maintained at 1.0 mg/mL.

The silica adsorption SepPak cartridges were purchased from Waters Corp. (Waters Corp., Milford, Mass.).

The syringe pump used for the adsorption experiment was a Harvard programmable model 44 (Harvard Apparatus, Inc., South Natick, Mass.).

The solvents used in this work were: toluene, tetrahydrofuran, and cyclohexane from BDH Inc. and methanol from Aldrich Chemical Co.

Size Exclusion Chromatographic Systems

Single Detector System

A single detector SEC system consisted of a model 510 pump (Waters Corp.), a 1050 series autosampler (Hewlett Packard Company, Ontario, Canada), and a model 410 differential refractometer (Waters Corp.). The column set consisted of three PLgel 10-μm mixed-bed, 300 × 7.5-mm columns (Polymer Laboratories). The mobile phase was toluene at 30 °C. Flow rate was maintained at 1 mL/min.

Dual Detector System

In this dual detector system, the SEC in the single system was equipped with a Viscotek differential viscometer Model 110 (Viscotek Corp., Houston, Texas) as a second detector in a series configuration with the DRI placed last. All other conditions were the same as for the single detector system.

Sample Preparation Methods

Adsorption

The adsorption sample preparation procedure developed was as follows:

(i) A polymer blend of PS-PDMS was dissolved in a solvent mixture of cyclohexane (CYH)—tetrahydrofuran (THF).
(ii) The silica cartridge was filled with 1 mL of polymer blend solution. (The cartridge was dry before being filled with solution. No attempt to precondition the adsorbent was made.)
(iii) The solvent mixture of CYH-THF was passed through the cartridge to elute the PDMS from the polymer blend.
(iv) Four mL of eluting solution was collected as a first fraction. PDMS was separated from the blend into this fraction. PS was retained in the cartridge at this step.
(v) THF was used to flush PS from the treated cartridge. PS is then eluted as the second fraction.
(vi) Four mL of eluting sample was collected as a second fraction.
(vii) Each fraction was then analyzed by SEC.

Solvent/Nonsolvent Precipitation

The solvent/nonsolvent combination of toluene-methanol and estimates of the ratio of each required was selected using a two-dimensional solubility parameter diagram constructed using literature solubility data.[17,19] The following sample preparation procedure was carried out:

(i) A polymer sample (blend of PS-PDMS) was dissolved in toluene and placed on a slowly rotating sample shaker overnight. The concentration was between 5–10 mg/mL.
(ii) The sample solution was removed from the shaker and the nonsolvent methanol was added to precipitate the sample (at a toluene:methanol ratio of 70:30 (v/v) for blend of PS-PDMS). The sample was allowed to precipitate overnight.
(iii) One mL of the top clear portion of sample was drawn off and dried in a vacuum oven.
(iv) The dried sample was redissolved with 1 mL of toluene and analyzed by SEC.

RESULTS AND DISCUSSIONS

Method I: Local Polydispersity Detection Using a Single Detector SEC

Because only one detector is present, this method requires extensive knowledge of what the sample preparation accomplishes. Adsorption was the sample preparation technique used in this case. The separation of PS-PDMS blends was accomplished using CYH-THF at a ratio of 90:10 (v/v) for the silica cartridge experiment.

Figure 1 shows the results: curve A is the chromatogram of the blend without sample treatment; curve B is the chromatogram after passing the sample through the silica filled cartridge (PS has been removed); and curve C is the chromatogram obtained of the material washed off the silica (PS).

Blends of PS (SRM 706) and PDMS (631K) standards (each with polydispersities of approximately two) were fractionated using the silica cartridge. The fractions were then collected and subsequently injected into an SEC. For this polymer blend, the SEC peak due to PS was completely separated from PDMS. Thus, the correction equation necessary to allow for removal of some PDMS in the sample preparation step, and therefore to "reshape" the PDMS chromatogram, could be obtained from these data.

The correction equation was obtained by fitting the value of the PDMS chromatogram heights after adsorption versus the corresponding height before adsorption at each retention volume using multiple linear regression:

$$W(v)_{\text{no adsorption}} = \beta_0 + \beta_1 W(v)_{\text{after adsorption}} + \beta_2 v + \beta_3 v W(v)_{\text{after adsorption}} \quad (5)$$

where the β_i are constant coefficients.

Figure 2 shows a comparison of three chromatograms: the original chromatogram representing pure PDMS (the upper curve); the chromatogram of the pure PDMS peak after the sample was run through an adsorption cartridge (the lower curve) and the data points resulting when the heights from the lower curve are substituted into Equation (5). Figure 2 shows the result using the PDMS standard of M_w 39,000, and similar results were obtained when either of the other PDMS standards were used. The fact that Equation (5) provides an excellent regeneration of the original PDMS chromatogram demonstrated that the use of this equation provides a method of reshaping

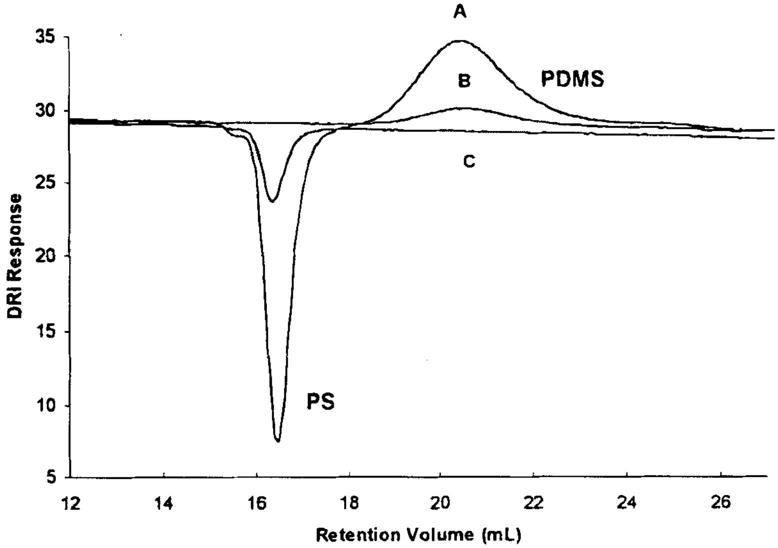

FIGURE 1 DRI chromatograms (reversed polarity) of PS-PDMS blend obtained using a silica-filled cartridge for adsorption sample preparation. A: chromatogram of the sample not subjected to adsorption; B: chromatogram of the sample after adsorption; C: chromatogram of the adsorbed polymer removed from the cartridge.

the PDMS peak from the chromatogram obtained after sample adsorption to provide a chromatogram representing all the PDMS in the original sample. Since Equation (5) was developed by fitting heights of pure PDMS chromatograms, when applied to future samples, differences between data points and the upper curve in a plot such as Figure 2 would indicate the presence of non-PDMS polymer at particular values of retention volumes.

Method II: Local Polydispersity Detection Using Dual Detector SEC

Sample Preparation by Adsorption

A local polydispersity detection method based upon dual detector SEC, Method II, was developed since it became increasingly evident that Method I was of limited applicability. By adding a DV as a second detector in the SEC system, an apparent local intrinsic viscosity can be calculated. If the value of this local property changes as a result of sample preparation, then local polydispersity is significant at the retention volume examined. That is, the molecules removed at a specific retention volume by the sample preparation step are different than those remaining. If it does not vary, then local polydispersity may or may not be significant at that point (*i.e.*, different molecules may be present but the sample preparation step did not preferentially remove one over the other).

A PS-PDMS blend was formulated to test this method. Figure 3 shows the normalized DRI chromatograms for the blend components. Since these chromatograms overlap almost completely and because each component is present in the same amount, two types of molecules are present at each retention volume over almost the whole range of retention volume (18 to 24.5 mL). That is, the blend has significant local polydispersity over this range. The exception is towards the low retention volume tail of the PS or the high retention volume tail of the PDMS where overlap is not present. However, in these areas, it can be expected that low chromatogram heights will cause considerable imprecision in the value of apparent intrinsic viscosity.

Figure 4 shows three plots for the PS-PDMS blend with no special sample preparation: a. the DRI chromatogram; b. the DV chromatogram; and c. a plot of the apparent intrinsic viscosity versus retention volume. Figure 5 shows the same set of plots for the sample after adsorption. Figure 6 shows

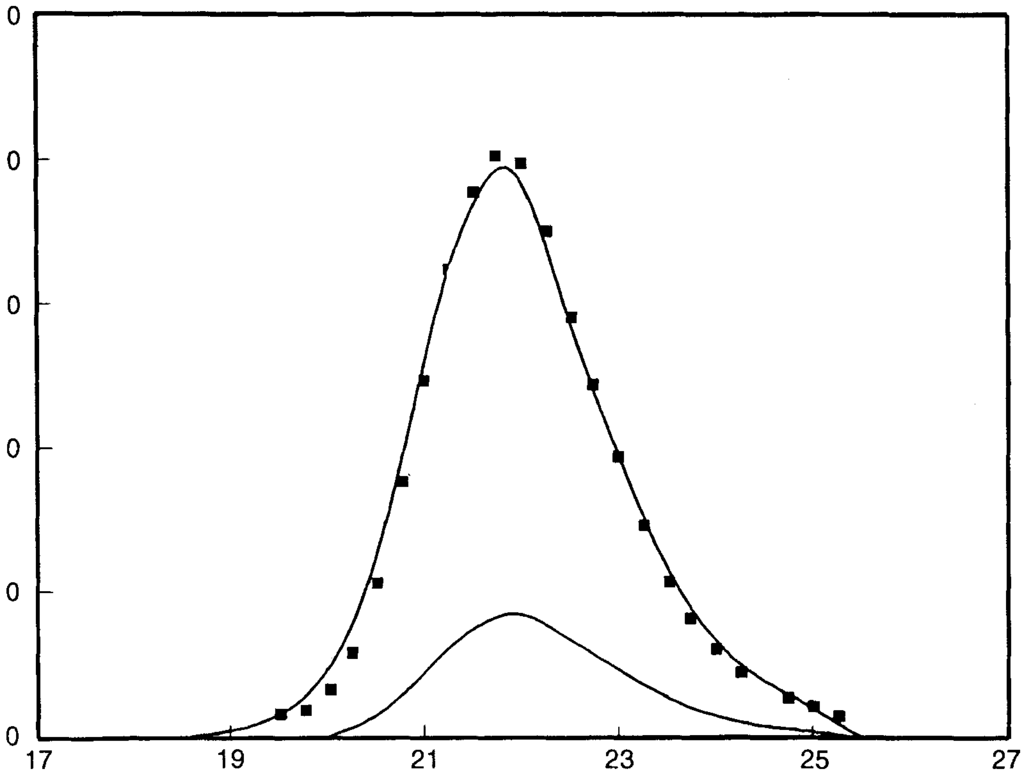

FIGURE 2 Application of Method I: regenerated chromatogram (data points) using Equation (5) is shown superimposed on the original PDMS chromatogram (Mw = 39,000) (upper curve) and the PDMS chromatogram after sample preparation (lower curve).

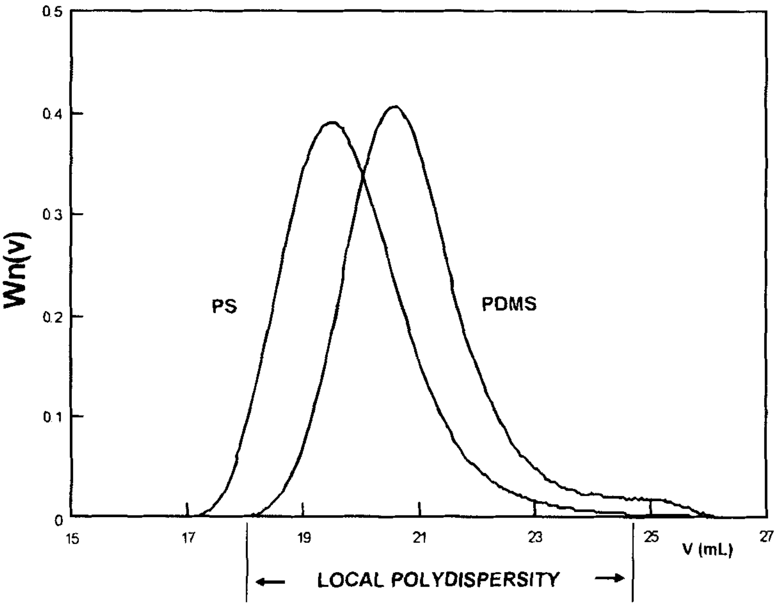

FIGURE 3 Normalized chromatograms obtained for the PS and PDMS in the blends before sample preparation: retention volume range of significant local polydispersity shown.

a superposition of the apparent intrinsic viscosity plots before and after adsorption sample treatment. The apparent viscosity results are different at practically all retention volumes, in agreement with the wide local polydispersity present.

Sample Preparation by Precipitation

Method II was also accomplished using solvent/nonsolvent precipitation as the sample preparation method. Results are shown in Figure 7: a. Figure 7a is the DRI; b. Figure 7b is the DV; and c. Figure 7c is the apparent intrinsic viscosity. The apparent intrinsic viscosity values are different from those obtained when adsorption was the sample preparation step but, most importantly, they also differ from the untreated sample over the whole retention volume range (Fig. 8). That is, they also show that the local polydispersity is significant across the range, as expected.

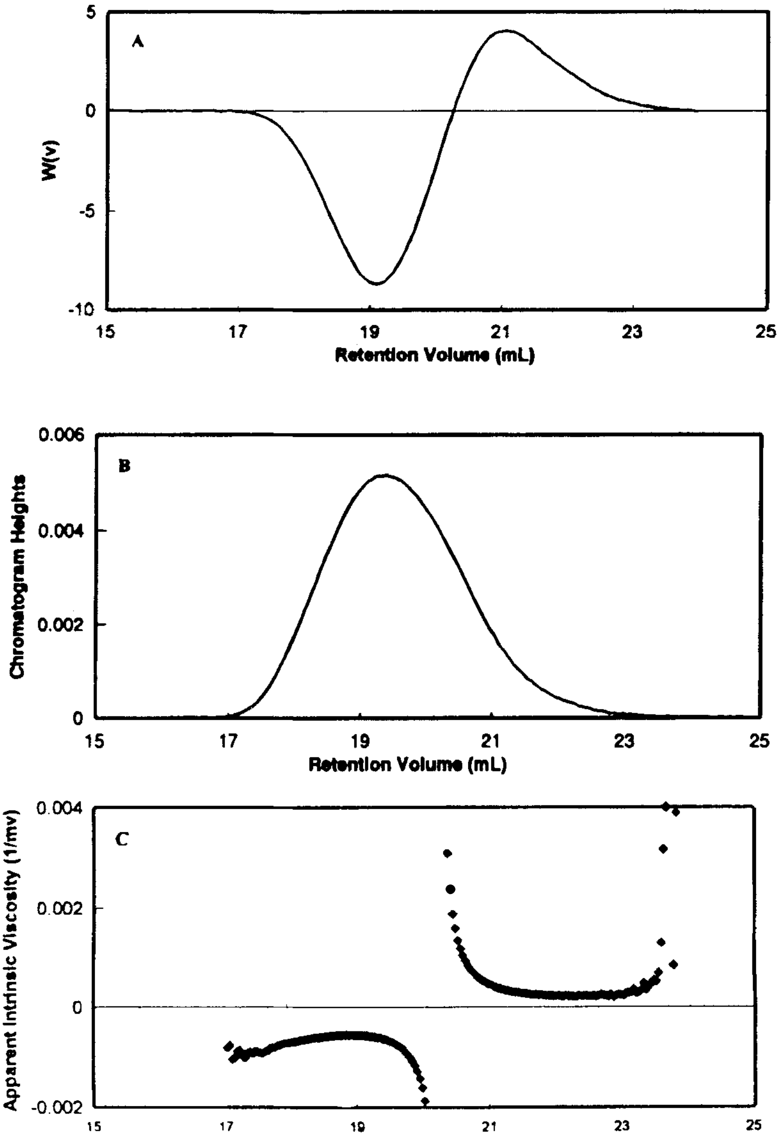

FIGURE 4 Chromatograms and apparent intrinsic viscosity obtained from DRI and DV detectors for the PS-PDMS blend before applying the adsorption-cartridge treatment. a: DRI; b: DV; c: apparent intrinsic viscosity versus retention volume.

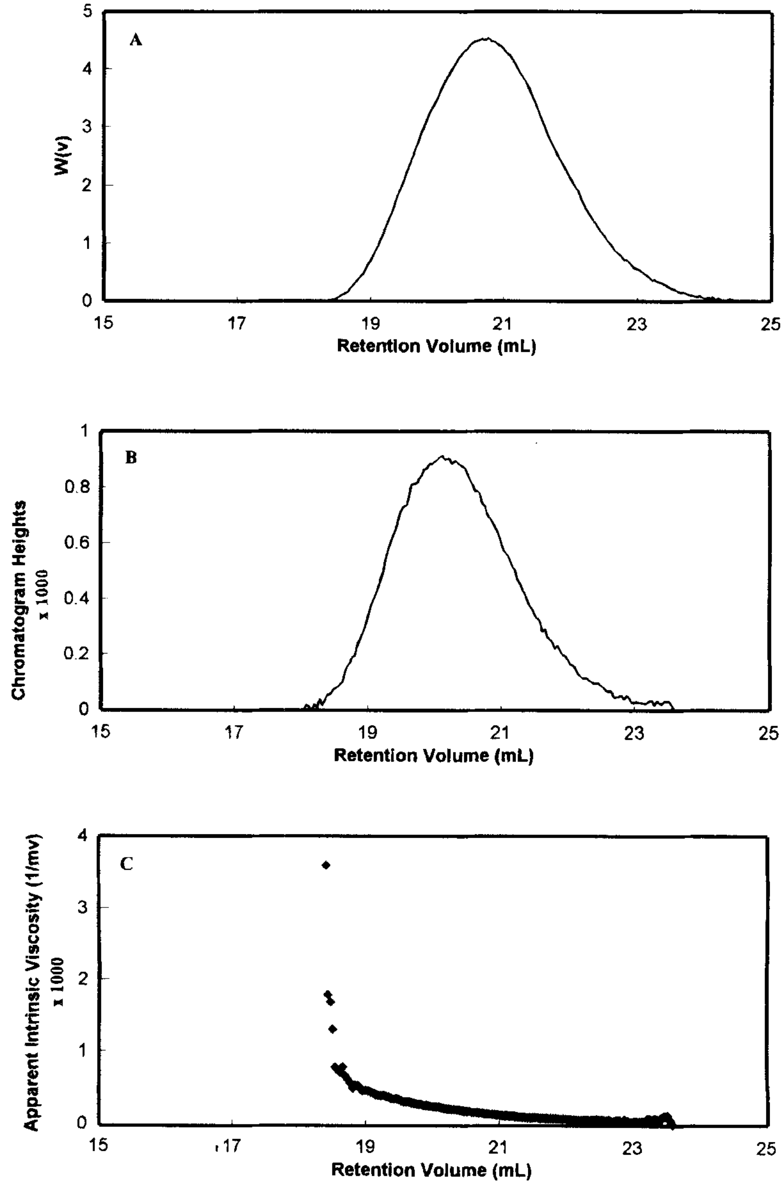

FIGURE 5 Chromatograms and apparent intrinsic viscosity obtained from DRI and DV detectors for the PS-PDMS blend after applying the adsorption-cartridge treatment. a: DRI; b: DV; c: apparent intrinsic viscosity versus retention volume.

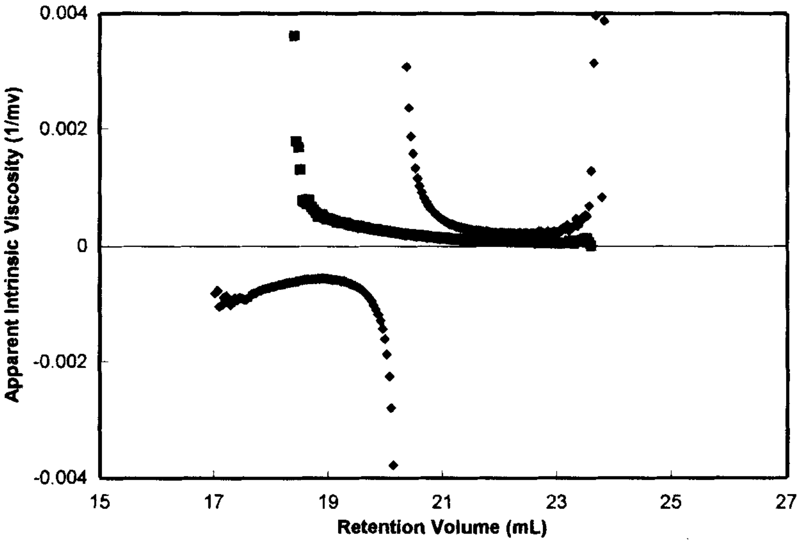

FIGURE 6 Method II: comparison of apparent intrinsic viscosities obtained for the PS-PDMS blend before and after applying the adsorption sample preparation method. ◆ before adsorption; ■ after adsorption.

CONCLUSIONS

Method I: Local Polydispersity Detection Using a Single Detector SEC

For the adsorption sample preparation method for PS-PDMS blends, an empirical equation relating the DRI chromatogram height without sample preparation to the chromatogram height after sample preparation was developed. This equation was based upon samples of PDMS of different molecular weight distributions and permitted the chromatogram after adsorption sample preparation to be regenerated. The degree to which this chromatogram superimposed on the chromatogram of the same sample without adsorption sample preparation was the degree to which local polydispersity is absent in the fractionated sample. The two difficulties with this method were that it was limited to PDMS blends and solvent selection for adsorption was difficult to accomplish.

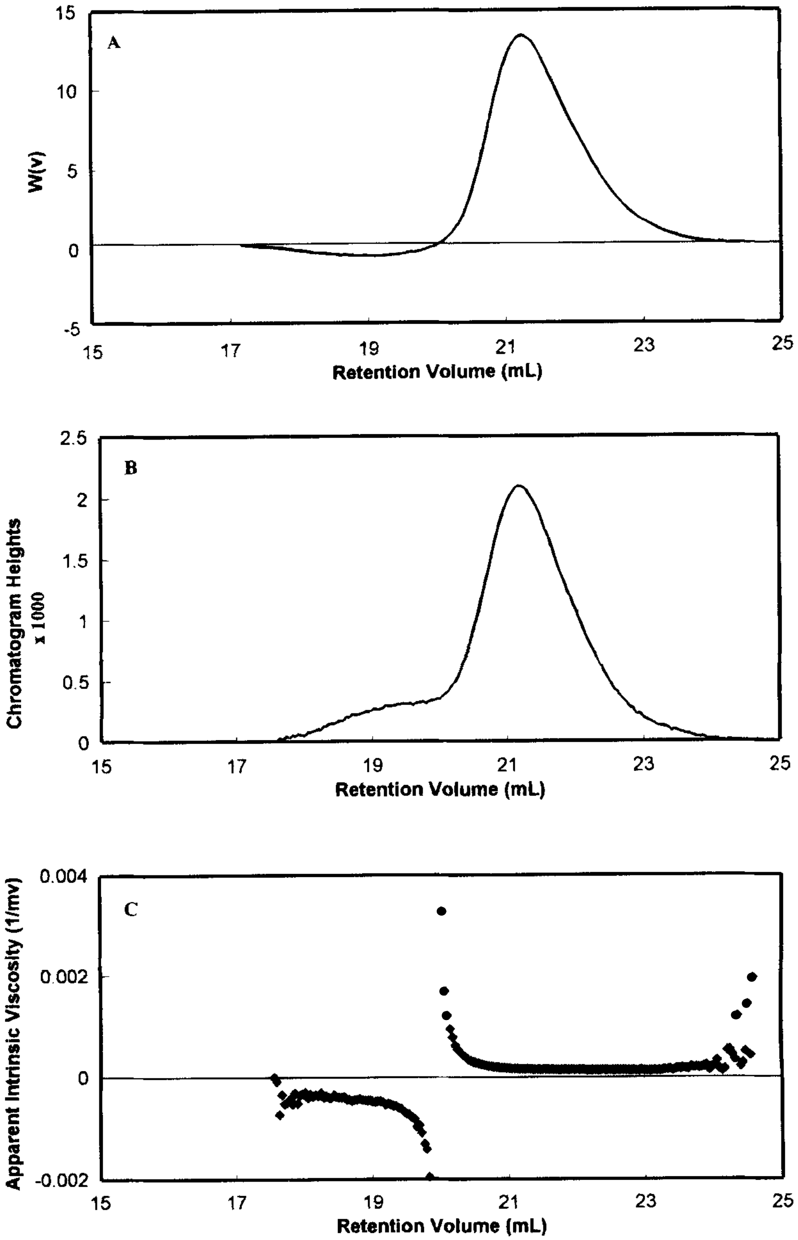

FIGURE 7 Chromatograms and apparent intrinsic viscosity obtained from DRI and DV for the PS-PDMS blend after applying the precipitation sample preparation method: a: DRI; b: DV; c: apparent intrinsic viscosity.

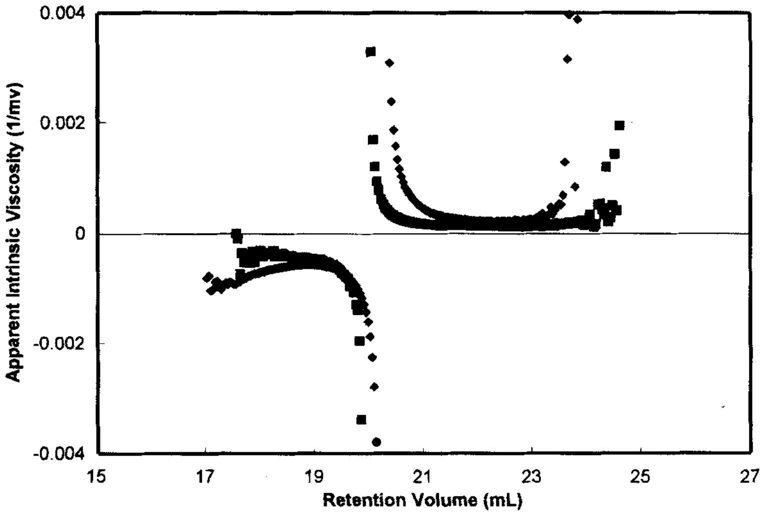

FIGURE 8 Method II: comparison of apparent intrinsic viscosities obtained for the PS-PDMS blends before and after applying the precipitation method: ◆ before precipitation; ■ after precipitation.

Method II: Local Polydispersity Detection Using Dual Detector SEC

The combination of dual detector SEC with precipitation as a sample preparation method was found to be a general, easily applied method for the detection of local polydispersity. A change in the apparent local intrinsic viscosity after precipitation indicated the presence of local polydispersity. If no change occurred, local polydispersity may or may not be important. Thus the power of this method is dependent upon precipitation conditions. The method was developed using a PS-PDMS blend.

NOMENCLATURE

M(v)	Local molecular weight
$W_i(v)$	Unnormalized retention volume-based chromatogram height
$w_{i,A}(v)$	Weight fraction of A unit of polymer blends (A+B) or copolymer (A+B) at retention volume v

$w_{i,B}(v)$	Weight fraction of B unit of polymer blends (A+B) or copolymer (A+B) at retention volume v
$[\eta](v)$	Total intrinsic viscosity of polymer sample, dL/g
$[\eta]_i(v)$	Local total intrinsic viscosity of polymer sample, dL/g
$[\eta]_{i,AP}(V)$	Apparent local intrinsic viscosity at each retention volume, [mv]-1
$\eta_{sp,i}(v)$	Specific viscosity at each retention volume

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