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Analysis method

Molar mass distributions in homopolymer blends from multimodal chromatograms obtained by Sec/Gpc with a concentration detector

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ABSTRACT

This article proposes data treatment for estimating the individual (and unimodal) molar mass distributions (MMDs) of each polymer component in a blend from multimodal concentration chromatograms obtained by size exclusion chromatography (SEC/GPC). The Differential Refractometer (DR) chromatograms are deconvoluted into linear combinations of exponentially-modified Gaussian distributions. The deconvolutions are possible if the individual peaks are not fully overlapped and if the mass fractions of the minor components are not too low. To help determine the number and approximate location of the individual peaks, the second derivative of the chromatogram is employed. For blends of chemically identical homopolymers, the deconvolution stage directly provides the mass fractions of the individual peaks. For blends of two chemically different homopolymers, the chemical composition and detector responses of the individual components must be determined, for example with the help of dual detection (UV/DR). The procedure was validated with blends of *a priori* known components.

1. Introduction

Size exclusion chromatography (SEC/GPC) is the main technique for determining the molar mass distribution (MMD) and averages ($\overline{M}_n$ and $\overline{M}_w$) of synthetic and natural polymers [1–4]. In its simplest and most common configuration, a single (concentration-sensitive) detector is employed. In this case, the technique is relative, since calibration standards are required for transforming elution volumes into molar masses. Typical concentration (or mass) detectors are differential refractometers (DR), UV spectrophotometers and evaporative light-scattering sensors. The inclusion of on-line light-scattering or specific viscosity sensors enables estimation of the local molar masses in the mid-chromatogram region. A difficulty with molar mass-sensitive detectors is their low sensitivity toward low molar masses. General difficulties with SEC are: fractionation by hydrodynamic volume (rather than by molar mass), imperfect resolution (or band broadening), eventual presence of non-exclusion (or enthalpic) separation mechanisms, concentration effects, baseline uncertainties and errors in the molar mass calibration [5].

The characterization of polymer blends is of interest, not only for the wide use of polymer mixtures, but also because, on many occasions, a major polymer is contaminated by other minor polymeric components. For example, block

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copolymers are typically contaminated by small amounts of their parent homopolymers [6,7]. Blends of chemically different polymers can be characterized by multi-detection SEC, and by combining SEC with other liquid chromatography techniques. Trathnigg et al. [8] utilized a UV and a density detector for estimating the individual MMDs in a blend of poly(methyl methacrylate) (PMMA) and poly(ethylene glycol). The proposed method is simple, but requires proper selection of detectors, and accurate calibration of their responses toward each polymer component. Busnel and Degoulet [9] analyzed a triblock polymer of polystyrene (PS), polybutadiene (PB) and poly(methyl methacrylate) by SEC with a differential refractometer and a dual UV detector fitted at 254 and 234 nm. They determined the instantaneous mass fractions of each block from the specific refractive index increments ($\partial n/\partial c$) and absorptivities of the three polymer components. Similarly, Rowland and Striegel [10] characterized a poly(acrylamide-*co*-N,N-dimethylacrylamide) and a blend of the same homopolymers with five on-line detectors: a quasi-elastic light scattering detector, a multiangle light scattering detector (MALS), a UV spectrophotometer, a viscometer and a DR. For the homopolymers blend, the MALS, UV and DR signals were employed to estimate the mass fractions of polymeric components along the molar mass, as is required for calculating their quantitative MMDs.

For blends of chemically different polymers, several investigations have combined SEC with other liquid chromatography techniques to first isolate the individual components, and then analyze each of them separately. For example, Lee and Chang [11] characterized blends of PS and PMMA by dual fractionation of SEC/interaction chromatography (IC). The stationary and mobile phases were chosen to fractionate PMMA by SEC, and PS by IC. Esser et al. [12] isolated PB from a styrene-butadiene rubber by adjusting the stationary and mobile phases at the critical point of enthalpic interaction of PB, in order to attain elution of PB as a narrow peak, and independently of its molar mass. Berek [6] employed a liquid chromatography technique under limiting conditions of desorption (LC LCD) for isolating a PS-PMMA block copolymer from its homopolymer contaminants (PS and PMMA). Later, Berek and Šišková [13], developed a sequenced 2-dimensional liquid chromatography technique for estimating the MMD of each homopolymer chain in the mentioned PS/PMMA blends and in PS-PMMA block copolymer. First, the homopolymers were isolated with the help of LC LCD, and then their MMDs were determined in a second SEC stage. Lee and Chang [14] analyzed a PS-*b*-PI-*b*-PMMA triblock copolymer contaminated by its PS and PS-*b*-PI precursors. While SEC was incapable of detecting such contamination, the contaminants were efficiently separated by IC. Rollet et al. [7] employed LC-LCD for the full separation of a PS-poly(ethyleneoxide)-PS triblock copolymer from small amounts of its parent homopolymers. Unfortunately, all the mentioned non-SEC (or enthalpic) fractionation methods are highly dependent on temperature and on the chemical nature of the stationary phase, mobile phase and blend components. Thus, the fractionations based on entropy–enthalpy combinations cannot really be considered general. They are only suitable for the particular complex polymer system, and are not applicable to blends of chemically identical macromolecules.

This work deals with the analysis of multimodal SEC chromatograms obtained with concentration detectors. The samples may be either blends of chemically identical or distinct homopolymers. For blends of chemically different homopolymers, a single concentration detector is generally incapable of detecting the instantaneous (or local) mass concentration, except for the very unlikely case of identical detector responses towards both kinds of macromolecules [4].

Evidence of multi-modality of the polymer sample is manifested by the presence of two or more maxima, shoulders, bulges or long tails on the concentration chromatogram. At least two methods have been developed for detecting the individual peaks (or modes) in multimodal chromatograms [15]. One of them is based on the ability of the second derivative of multimodal chromatograms to reveal the presence and location of the individual modes or peaks. A difficulty with this method is the high-frequency noise that must be filtered out from the raw measurement prior to calculation of the second derivative; to this effect, the Savitzky-Golay filter [16] is typically applied [15]. The second method is normally known as matched filters. It consists of convoluting the measured chromatogram with the third derivative of a given distribution (*e.g.*, a Gaussian distribution of known standard deviation), and the presence and location of an individual mode is evidenced by the point where the convoluted signal changes from negative to positive. Both methods are ineffective when the multimodal chromatograms contain important baseline oscillations, and/or when the unimodal modes (or peaks) are too close to each other [15].

In this paper, data treatment is presented for determining the mass fractions and unimodal MMDs of the individual polymer components contained in multimodal SEC chromatograms. The technique is tested on bimodal chromatograms obtained from mixtures of homopolymers of identical and different chemical nature. The work was carried out under the auspices of the IUPAC project: “Data Treatment in SEC and Other Techniques of Polymer Characterization. Correction for Band Broadening and Other Sources of Error”, Chair G. Meira, http://www.iupac.org/web/ins/2009-019-2-400.

2. Proposed data treatment

Consider the data treatment for the most common case of DR detection. (Note however, that the developed equations are easily extendable to UV detection at a single wavelength.) For blends of homopolymers of identical composition, only standard molar mass calibration is required. For blends of homopolymers with different chemical composition, the nature of the individual sample constituents must be known, together with their corresponding detector responses and molar mass calibrations.

2.1. Number of unimodal polymer components

Often, the number of polymer components in the blend is *a priori* known. If this is not the case, then the second

derivative of the multimodal chromatogram is to be determined to estimate the number and approximate location of the components or unimodal peaks. Prior to assessment of the discrete second derivatives, pre-smoothening of the chromatograms was required. To this effect, the Savitzky-Golay filter was applied with a third-order polynomial and a frame of size 11 [16].

2.2. Deconvolution of the multimodal chromatogram

Assume that the (unimodal, normalized, and discrete) chromatograms of each j-th polymer component in the blend (with $j = 1, 2, \ldots, J$) is represented by an Exponentially-Modified Gaussian distribution (EMG) $f_j(V_i)$, defined by:

$$f_j(V_i) = \left(\frac{1/\Delta V}{\sigma_j\sqrt{2\pi}} e^{-\frac{\left(V_i-\mu_j\right)^2}{2\sigma_j^2}}\right) * \left(\frac{e^{-\frac{V_i}{\tau_j}}}{\tau_j}\right), \quad (j = 1, \ldots, J) \tag{1}$$

where V_i is the discrete elution volume after discretization of the continuous signal at regular ΔV intervals; $*$ is convolution product; and (μ_j, σ_j, τ_j) are respectively, the mean, standard deviation and decay parameter of the j-th EMG [15,17]. Note that each j-th EMG is normalized, *i.e.*: $\sum_{\forall i} f_j(V_i) = 1$ with ($j = 1, \ldots, J$). Also, note that, without lost of generality, any EMG may be substituted by any other (normalized and unimodal) distribution that could better adjust the measurements.

Call $s_{DR}(V_i)$ the (multimodal, baseline corrected, and discrete) DR chromatogram. Note that this signal is proportional to the total instantaneous mass $g(V_i)$ only for blends of a single homopolymer. The normalized DR chromatogram is:

$$s(V_i) = \frac{s_{DR}(V_i)}{\sum_{\forall i} s_{DR}(V_i)} \quad \text{with} \quad \sum_{\forall i} s(V_i) = 1 \tag{2}$$

The normalized chromatogram is adjusted by a linear combination of J weighted EMGs, of parameters and weights estimated through the following optimization procedure:

$$\min_{\{\mu_1,\sigma_1,\tau_1,w_1;\cdots;\mu_J,\sigma_J,\tau_J,w_J\}} \left\| 1 - \frac{s(V_i)}{\widehat{s}(V_i)} \right\| \tag{3a}$$

with

$$\widehat{s}(V)_i = \sum_{j=1}^{J} w_j f_j(V_i) = \sum_{j=1}^{J} \widehat{s}_j(V_i) \quad \text{and} \quad \sum_{j=1}^{J} w_j = 1 \tag{3b}$$

where $\|\mathbf{x}\| = \sqrt{x_1^2 + x_2^2 + \ldots + x_j^2}$ is the 2-norm of vector $\mathbf{x}$; $\widehat{s}(V_i)$ is the estimated normalized chromatogram; w_j is the chromatogram fraction of the j-th EMG; and $\widehat{s}_j(V_i)$ ($j = 1, \ldots, J$) are the estimated chromatograms of the individual polymer components. Each $\widehat{s}_j(V_i)$ is represented by a weighted (*i.e.*: not normalized) EMG, with: $\sum_{\forall i} \widehat{s}_j(V_i) = w_j$ ($j = 1, \ldots, J$). Equations (3a,b) were solved through a hybrid numerical procedure based on a particle swarm optimization algorithm implemented with 100 particles and 4,000 generations [18,19], followed by a sequential quadratic programming procedure [20]. The optimization outputs are the EMG parameters and their weights, *i.e.*: (μ_j, σ_j, τ_j, w_j) with ($j = 1, \ldots, J$).

2.3. Normalized MMD of each unimodal polymer component

For blends of homopolymers with the same chemical composition, the weights w_j in Eq. (3b) directly represent the mass fractions of each unimodal component, and a single molar mass calibration is required for estimating the MMDs of both the individual components and the complete blend. For blends of chemically different homopolymers, the normalized MMD of each j-th blend component is estimated from its EMG distribution and its molar mass calibration represented by $M_j(V_i)$ ($\equiv M_{i,j}$) with $j = 1, \ldots, J$. In this case, the weights w_j in Eq. (3b) no longer represent the component mass fractions, and only the normalized MMDs of the individual components $f_j(M_{i,j})$ may be obtained. For blends of chemically different homopolymers, consider an extension of the data treatment for estimating the mass fractions of each polymer component, and the MMD of the total blend.

2.4. Blends of chemically different homopolymers: mass fractions and MMD of the total blend

For simplicity, assume a blend of two homopolymers: PA and PB. As we have seen, the deconvolution step approximates the normalized chromatogram by a weighted sum of EMGs, *i.e.*:

$$\widehat{s}(V_i) = \widehat{s}_A(V_i) + \widehat{s}_B(V_i) = w_A f_A(V_i) + w_B f_B(V_i) \tag{4}$$

The measured (not normalized) DR chromatogram is modeled by [4]:

$$\begin{aligned} s_{DR}(V_i) &= \left(K_{DR}\frac{\partial n_A}{\partial c}\right) g_A(V_i) + \left(K_{DR}\frac{\partial n_B}{\partial c}\right) g_B(V_i) \\ &= k_A g_A(V_i) + k_B g_B(V_i) \end{aligned} \tag{5}$$

where K_{DR} is an instrumental constant that is independent of the analyzed polymer; $\partial n_A/\partial c$, $\partial n_B/\partial c$ are the specific refractive index increments of PA and PB; $g_A(V_i)$, $g_B(V_i)$ are the instantaneous (or local) masses of PA and PB; and k_A ($= K_{DR}\frac{\partial n_A}{\partial c}$), k_B ($= K_{DR}\frac{\partial n_B}{\partial c}$) are the detector responses for PA and PB. The normalized DR chromatogram is:

$$\begin{aligned} s(V_i) = \frac{s_{DR}(V_i)}{\sum_{\forall i} s_{DR}(V_i)} &\cong \left(\frac{K_{DR}}{\sum_{\forall i} s_{DR}(V_i)}\frac{\partial n_A}{\partial c}\right) g_A(V_i) \\ &+ \left(\frac{K_{DR}}{\sum_{\forall i} s_{DR}(V_i)}\frac{\partial n_B}{\partial c}\right) g_B(V_i) \end{aligned} \tag{6}$$

By comparing Eqs (4) and (6), one obtains:

$$\widehat{s}_A(V_i) = w_A f_A(V_i) \cong \frac{K_{DR}}{\sum_{\forall i} s_{DR}(V_i)}\frac{\partial n_A}{\partial c} g_A(V_i) \tag{7a}$$

$$\widehat{s}_B(V_i) = w_B f_B(V_i) \cong \frac{K_{DR}}{\sum_{\forall i} s_{DR}(V_i)}\frac{\partial n_B}{\partial c} g_B(V_i) \tag{7b}$$

and therefore

$$\widehat{g}_A(V_i) = \frac{\sum_i s_{DR}(V_i)}{K_{DR}} \frac{w_A}{\partial n_A/\partial c} f_A(V_i) \quad (8a)$$

$$\widehat{g}_B(V_i) = \frac{\sum_i s_{DR}(V_i)}{K_{DR}} \frac{w_B}{\partial n_B/\partial c} f_B(V_i) \quad (8b)$$

Thus, the instantaneous (or local) mass fraction of PA in the detector cell is given by:

$$\widehat{\omega}_A(V_i) = \frac{\widehat{g}_A(V_i)}{\widehat{g}_A(V_i) + \widehat{g}_B(V_i)} = \frac{\frac{w_A}{\partial n_A/\partial c} f_A(V_i)}{\frac{w_A}{\partial n_A/\partial c} f_A(V_i) + \frac{w_B}{\partial n_B/\partial c} f_B(V_i)} \quad (9)$$

Also, after integration of Eqs. (8), the following expression is obtained for the estimate of the mass fraction of PA in the total blend ($\widehat{\omega}_A$):

$$\widehat{\omega}_A = \frac{\widehat{G}_A}{\widehat{G}_A + \widehat{G}_B} = \frac{\frac{w_A}{\partial n_A/\partial c}}{\frac{w_A}{\partial n_A/\partial c} + \frac{w_B}{\partial n_B/\partial c}} = \frac{\frac{w_A}{k_A}}{\frac{w_A}{k_A} + \frac{w_B}{k_B}} \quad (10)$$

where $\widehat{G}_A = \sum_i \widehat{g}_A(V_i)$, $\widehat{G}_B = \sum_i \widehat{g}_B(V_i)$, and $\widehat{G} = \widehat{G}_A + \widehat{G}_B$ are, respectively, the estimates of the total injected masses of PA, PB and blend. Equation (10) enables to calculate $\widehat{\omega}_A$ from the weights (w_A, w_B) obtained in the deconvolution step and knowledge of either the specific refractive index increments or the detector responses at given experimental conditions. More generally, the estimated normalized local mass is:

$$\frac{\widehat{g}(V_i)}{\widehat{G}} = \sum_{j=1}^{J} \omega_j f_j(V_i) = \sum_{j=1}^{J} \frac{\widehat{g}_j(V_i)}{\widehat{G}} \quad \text{with} \quad \sum_{j=1}^{J} \omega_j = 1 \quad (11)$$

where ω_j with ($j = 1, \ldots, J$) is the global mass fraction of component j. Note that for blends of homopolymers with identical chemical composition: $\widehat{s}_j(V_i) \propto \widehat{g}_j(V_i)$; and $\frac{\widehat{g}(V_i)}{\widehat{G}} = \widehat{s}(V_i)$. Therefore:

$$\frac{\widehat{g}(V_i)}{\widehat{G}} = \sum_{j=1}^{J} w_j f_j(V_i) = \sum_{j=1}^{J} \frac{\widehat{g}_j(V_i)}{\widehat{G}} \quad \text{with} \quad \sum_{j=1}^{J} w_j = 1 \quad (12)$$

In Eq (12), the ω_j mass fractions of Eq. (11) are substituted by the chromatogram mass fractions w_j obtained from Eq. (3b).

Finally, the MMD estimate of the total blend is calculated from a linear combination of the individual MMDs $f_j(M_{i,j})$, weighted by their global mass fractions ω_j, *i.e.*:

$$\frac{\widehat{g}\left(\widehat{M}_i\right)}{\widehat{G}} = \sum_{j=1}^{J} \omega_j f_j\left(\widehat{M}_{i,j}\right) \quad \text{with} \quad \sum_{j=1}^{J} \omega_j = 1 \quad (13)$$

3. Experimental examples

The following blends were analyzed: i) a PS sample containing two components with different average molar masses, each of them exhibiting broad MMDs; and ii) three mixtures of two low-dispersity standards of chemically different homopolymers. In both cases, the size exclusion chromatograph was a Waters 1525, and the eluent was tetrahydrofurane (THF) at 1 mL/min and 25 °C. For the broad PS sample, a set of seven μ-Styragel® columns (Waters HR 0.5, HR 1, HR 2, HR 3, HR 4, HR 5, HR 6) was employed, and the detector was a Waters 2414 DR. For the mixture of narrow standards, only column HR 3 was employed, and a Waters UV spectrophotometer at 254 nm was added in series with the DR. The inter-detector volume ($\delta = 0.229$ mL) was determined from the shift between the DR and UV chromatograms of a narrow standard [21]. For the molar mass calibrations, sets of nine PS standards and six PMMA standards were used (Table 1). For all the blends, the second derivatives of their smoothened bimodal chromatograms were determined to test their ability for automatic detection of the number and approximate location of the unimodal peaks. All the computer work was carried out in Matlab®.

3.1. Contamination of a high molar mass PS with a low molar mass PS prepolymer

This bimodal PS sample was obtained in a radical mini-emulsion polymerization of styrene; where the recipe included a low molar mass PS prepolymer that was added to stabilize the initial mini-emulsion [22]. The prepolymer concentration was 21% in weight with respect to the monomer. The polymerization was carried out until total monomer conversion, and the mass fraction of the main polymer component was 79%. The final sample was a mixture of a main (high molar mass) PS component and a low molar mass PS prepolymer. The SEC system included the DR and the full set of seven fractionation columns. The molar mass calibration (Fig. 1a) was obtained from the chromatograms of the PS standards after fitting a third order polynomial to the points (V_p, M_p); where V_p and M_p are, respectively, the peak retention volumes and the peak molar masses (Table 1).

Figure 1b) presents the normalized chromatogram of the initial prepolymer [$s_{prep.}(V_i)$], the normalized bimodal chromatogram of the final polymer blend [$s(V_i)$] and the second derivative of the bimodal chromatogram [$d^2s(V_i)/dV^2$]. As expected, the second derivative exhibits two local minima; with the minimum at $V_i = 50$ ml acceptably locating the minor component. The average molar masses of both the prepolymer and the final blend (see upper rows of Table 2) were calculated from the calibration dependences and the chromatograms $s_{prep.}(V_i)$ and $s(V_i)$.

Consider the results of Eqs (1–3). In Fig. 1c), it is seen that the estimated chromatogram of the total polymer [$\widehat{s}(V_i) = \widehat{s}_{main}(V_i) + \widehat{s}_{prep}(V_i)$], adequately reproduces the measurement [$s(V_i)$]. In addition, the estimated prepolymer chromatogram [$\widehat{s}_{prep}(V_i)$] adequately reproduces the rescaled prepolymer chromatogram $s_{prep.}(V_i)$. The prepolymer chromatogram was rescaled with the estimated mass fraction of 19%, a value that is close to the expected mass fraction of 21% (Table 2). Finally, Table 2 also presents the estimated average molar masses of the unimodal polymer components and total polymer, as calculated from the calibration dependence and $\widehat{s}_{main}(V_i)$, $\widehat{s}_{prep}(V_i)$ and $\widehat{s}(V_i)$. As expected, the $\overline{M}_n$ and $\overline{M}_w$ values of the prepolymer estimated from $\widehat{s}_{prep}(V_i)$ (11,100 and 30,600 g/mol,

Table 1
Specifications of the PS and PMMA standards, provided by Shodex (Showa Denco America inc.), and by Polysciences Inc., respectively. The manufacturers' specifications are based on SEC/GPC measurements.

PS Standards				PMMA Standards			
	$\overline{M}_n$	$\overline{M}_w$	M_p[a]		$\overline{M}_n$	$\overline{M}_w$	M_p[a]
PS_1	2,960	3,070	3,070	$PMMA_1$	12,300	12,900	13,100
PS_2	7,070	7,240	7,210	$PMMA_2$	–	–	27,000
PS_3	19,200	19,600	19,600	$PMMA_3$	83,200	84,900	85,100
PS_4	52,600	54,100	55,100	$PMMA_4$	–	–	127,000
PS_5	131,000	133,000	133,000	$PMMA_5$	209,700	218,600	218,600
PS_6	273,000	285,000	275,000	$PMMA_6$	347,000	361,000	386,000
PS_7	604,000	637,000	666,000				
PS_8	1,250,000	1,290,000	1,320,000				
PS_9	2,840,000	2,980,000	3,150,000				

[a] Molar mass of the chromatogram peak.

respectively) are close to their reference values obtained directly from the prepolymer chromatogram (11,900 and 28,900 g/mol). Similarly, for the total polymer, the molar mass averages estimated from $\hat{s}(V_i)$ (30,300 and 534,800 g/mol) are close to the estimates obtained from the total measured chromatogram (33,900 and 510,800 g/mol).

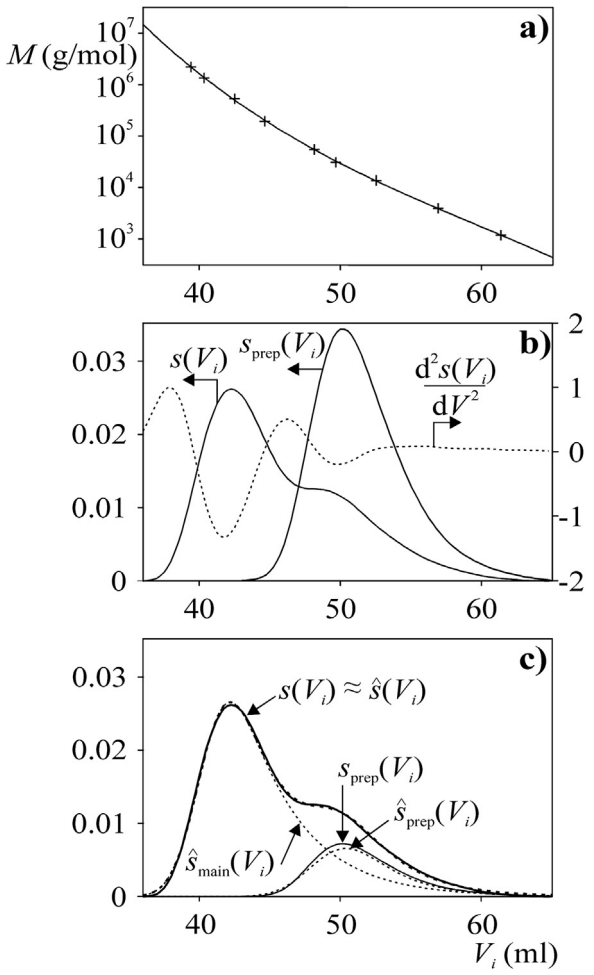

Fig. 1. Bimodal PS sample obtained by miniemulsion polymerization of styrene in presence of a low-molar-mass prepolymer. a) Molar mass calibration obtained with PS standards (Table 1). b) Normalized chromatogram of the prepolymer, $s_{prep,}(V)$; normalized chromatogram of blend, $s(V)$, and second derivative of $s(V)$. c) The measured chromatograms (in continuous lines) are compared with their estimates (in broken lines).

3.2. Blend of PS and PMMA standards

Three blends of standards PS_5 and $PMMA_5$ of nominal mass percentages $\omega_{PMMA5}/\omega_{PS5}$ = 20/80, 50/50 and 90/10 (Table 1) were analyzed,. The molar mass calibrations for PS and PMMA are presented in Fig 2a), and were obtained from the sets of standards in Table 1. The DR and UV detector responses for PS ($k_{DR,PS}$ and $k_{DR,UV}$) and for PMMA ($k_{DR,PMMA}$ and $k_{UV,PMMA}$) were determined from four independent injections of known masses of PS_5 and $PMMA_5$ (= 0.1, 0.5, 0.9, and 1.0 mg). More specifically, the responses were estimated from the slopes of the straight lines that represent the chromatogram areas [$= \sum_{\forall i} s(V_i)$] *vs.* the injected masses (Fig. 2b). For the DR, the responses for PS and PMMA were: $k_{DR,PS}$ = 9,640 mg^{-1} and $k_{DR,PMMA}$ = 5,079 mg^{-1}. The following specific refractive index increments were adopted for PS and PMMA in THF at 25 °C: $\partial n_{PS}/\partial c = 0.185\ mg^{-1}$ and $\partial n_{PMMA}/\partial c = 0.090\ mg^{-1}$ [23]. Note that, even although one should expect: $k_{DR,PS}/k_{DR,PMMA} = (\partial n_{PS}/\partial c)/(\partial n_{PMMA}/\partial c)$, in our case it resulted in: $k_{DR,PS}/k_{DR,PMMA}$ = 1.898 and $(\partial n_{PS}/\partial c)/(\partial n_{PMMA}/\partial c)$ = 2.056. For the UV detector at 254 nm, the responses for PS and PMMA were: $k_{UV,PS} = 3.845\ mg^{-1}$ and $k_{UV,PMMA} \approx 0\ mg^{-1}$, respectively. [The measurements for $k_{UV,PMMA}$ are not represented in Fig. 2b) because of the very low signals involved.]

Figure 2c) shows the normalized chromatograms of the individual standards and blends $\omega_{PMMA5}/\omega_{PS5}$ = 20/80, 50/50, and 90/10. As before, the minima of the second

Table 2
Bimodal PS sample obtained by miniemulsion polymerization of styrene in presence of an initial low-molar-mass prepolymer: average molar masses and global mass fractions (ω).

Basis of Calculation	$\widehat{\overline{M}}_n$	$\widehat{\overline{M}}_w$	$\hat{\omega}$ (%)
a) Prepolymer Chromatogram	11,900	28,900	21[a]
b) Total Blend Chromatogram	33,900	510,800	
c) Deconvoluted Total Blend Chromatogram			
PS Prepolymer	11,100	30,600	19
Main PS Component	50,500	651,800	81
Total Polymer	30,300	534,800	100

[a] *A priori* estimate from polymerization reaction.

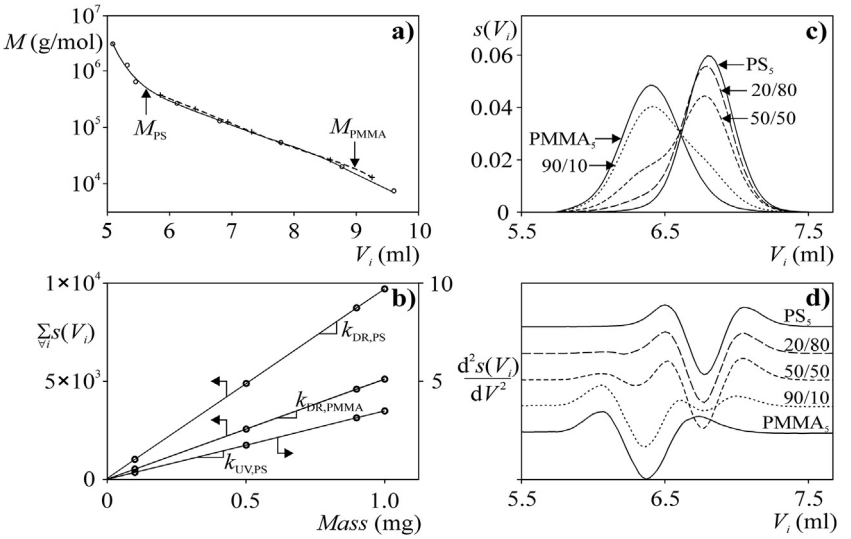

Fig. 2. Blend of standards PS_5 and $PMMA_5$. a) Individual molar mass calibrations of PS and PMMA, obtained with the standards of Table 1. b) Mass calibrations of the DR and UV detectors. (The calibration results for the UV response toward PMMA are not shown because of the extremely low signals involved, yielding: $k_{UV,PMMA} \approx 0$.) c,d) Normalized chromatograms of the investigated blends, and their second derivatives. Blends are labeled with the weight ratios of $PMMA_5$ and PS_5.

derivatives indicate the approximate location of the component peaks [Fig. 2d)].

For the individual standards and their nominal blend compositions, Table 3 presents the best (or reference) average molar masses. For the individual standards, the reference values were determined from the chromatograms of $PMMA_5$ and PS_5 [Fig. 2c)], and the molar mass calibrations in Fig. 2a), see first two rows of Table 3a). For the three blends, their reference molar mass averages were obtained from:

$$\frac{1}{\overline{M}_n} = \frac{\omega_{PS}}{\overline{M}_{n,PS}} + \frac{\omega_{PMMA}}{\overline{M}_{n,PMMA}} \tag{14a}$$

$$\overline{M}_w = \omega_{PS}\overline{M}_{w,PS} + \omega_{PMMA}\overline{M}_{w,PMMA} \tag{14b}$$

with the nominal weight fractions of Table 3, and the average values for $PMMA_5$ and PS_5 in the first two rows of Table 3.

Figure 3 and Table 4 present the results of the proposed data treatment applied to the bimodal chromatograms of Fig. 2c). For space reasons, only the graphical results for blends $\omega_{PMMA5}/\omega_{PS5} = 20/80$ and 90/10 are presented here. Figs. 3a,c) present the following results from the deconvolution step: a) normalized chromatograms of total blends [$s(V_i)$] and their estimates $\widehat{s}(V_i)$; and b) estimated chromatograms of the individual components [$\widehat{s}_{PS}(V_i)$ and $\widehat{s}_{PMMA}(V_i)$], and rescaled chromatograms of the individual standards [$s_{PS}(V_i)$ and $s_{PMMA}(V_i)$]. The chromatograms of the individual standards were rescaled according to their chromatogram fractions: ($w_{PMMA} = 0.12$, $w_{PS} = 0.88$) for blend 20/80; and ($w_{PMMA} = 0.80$, $w_{PS} = 0.20$) for blend 90/10. [As expected, the chromatogram fractions (w), differ from the global mass fractions (ω).]

Figures 3b,d) show (in continuous lines), the reference (or best) MMDs of the individual components [$g_{PS}(\log M)$ and $g_{PMMA}(\log M)$], and of the total blends [$g(\log M)$]. They were obtained as follows. First, the normalized MMDs of the individual components were obtained from the individual chromatograms of $PMMA_5$ and PS_5 (Fig. 2c), and their corresponding molar mass calibrations (Fig. 2a). Then, these normalized distributions were rescaled according to the nominal weight percentages of 20/80 and 90/10. Finally, the reference MMDs of the total blends were obtained by simple addition of the rescaled individual distributions. Figs. 3b,d) also present the estimated MMDs $\widehat{g}(\log M)$, $\widehat{g}_{PS}(\log M)$ and $\widehat{g}_{PMMA}(\log M)$ (in discontinuous lines) after application of the proposed data treatment to the bimodal chromatograms of Fig. 2c).

Table 4 presents the estimates obtained with the help of the proposed data treatment. First, the deconvolution procedure provided the normalized EMG distributions of the individual components and their chromatogram fractions (w_j). Second, the molar mass averages of the normalized EMG distributions were obtained, and their values are close to the reference values of Table 3. Third, the estimated mass percentages ($\widehat{\omega}_{PMMA}$ and $\widehat{\omega}_{PS}$) of Table 4 were calculated with Eqs (10), employing either the adopted specific refractive index increments or the experimentally-determined DR detector responses. Again,

Table 3
Blends of $PMMA_5$ and PS_5: reference average molar masses of the individual standards and their nominal blends.

	ω_{PMMA}	ω_{PS}	$\overline{M}_n$	$\overline{M}_w$
$PMMA_5$	100%	–	204,800	215,000
PS_5	–	100%	136,700	140,100
Blend 20/80	20%	80%	146,400	155,100
Blend 50/50	50%	50%	163,900	177,500
Blend 90/10	90%	10%	195,000	207,400

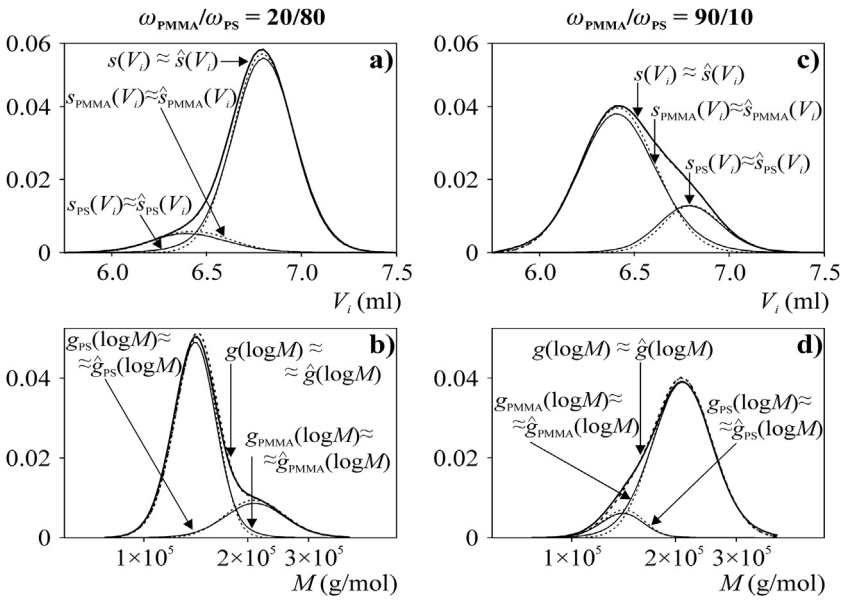

Fig. 3. Blends of $PMMA_5$ and PS_5 standards. The results of blends 20/80 and 90/10 are in columns a,b) and c,d), respectively. a,c) Measured (—) and estimated (−) chromatograms for the individual PS and PMMA components, $s_{PS}(V_i)$, $s_{PMMA}(V_i)$; and for the total blend, $s(V_i)$. b,d) Reference (—) and estimated (−) MMDs of the blend, $g(\log M)$; and of the individual PS and PMMA components, $g_{PS}(\log M)$, $g_{PMMA}(\log M)$.

the results are close to the expected nominal values of ω_{PMMA} and ω_{PS}. Finally, the molar mass averages of the total blends were estimated from the normalized EMG distributions and the global mass fractions. The resulting averages (Table 4) are close to the reference values of Table 3.

To estimate the MMD of the individual polymer components, the proposed method requires identifying the chemical nature of the individual unimodal components. For some blends, this information may be obtained by multiple detection SEC from the evolution of the local chemical composition. For a mixture of two homopolymers, the dual DR/UV detection enables determination of the local concentration and chemical composition of the eluting mixture, and this information can, in turn, be used for estimating the MMD of total polymer. Blends of PMMA and PS are well suited for dual detection because, while the DR responds to both polymers, the UV detector at 254 nm only responds to PS. In this case, the following expressions can be written for the DR and UV detector signals [$s_{DR}(V_i)$ and $s_{UV}(V_i - \delta)$], where the UV signal includes a correction for the inter-detector volume (δ):

$$s_{DR}(V_i) = \hat{g}_{DR/UV}(V_i)\{\hat{\omega}_{PS,DR/UV}(V_i)k_{DR,PS} + [1 - \hat{\omega}_{PS,DR/UV}(V_i)]k_{DR,PMMA}\} \quad (15a)$$

$$s_{UV}(V_i - \delta) = \hat{g}_{DR/UV}(V_i)\{\hat{\omega}_{PS,DR/UV}(V_i)k_{UV,PS}\} \quad (15b)$$

where $\hat{g}_{DR/UV}(V_i)$, $\hat{\omega}_{PS,DR/UV}(V_i)$, and $\hat{\omega}_{PMMA,DR/UV}(V_i) = 1 - \hat{\omega}_{PS,DR/UV}(V_i)$ are, respectively, the dual detection estimates of the local total mass, PS mass fraction and PMMA mass fraction. From Eqs (15a,b), the following expressions are derived [4]:

Table 4
Blends of $PMMA_5$ and PS_5 standards. Average molar masses and mass fractions ($\hat{\omega}$) of the individual components and of total blend, estimated with the proposed method. For the total blends, the average molar masses estimated by dual detection are also presented. The reference values are given in Table 3.

Blend	Estimation Method	Estimates of	$\widehat{M}_n$	$\widehat{M}_w$	$\hat{\omega}$ (%)
$\omega_{PMMA} = 20\%$ $\omega_{PS} = 80\%$	Proposed Method	$PMMA_5$ Component	204,800	213,700	21[a] (20)[b]
		PS_5 Component	137,300	140,300	79[a] (80)[b]
		Total Blend	147,800[a] (147,100[b])	156,000[a] (155,100[b])	–
	Dual Detection	Total Blend	146,300	153,700	–
$\omega_{PMMA} = 50\%$ $\omega_{PS} = 50\%$	Proposed Method	$PMMA_5$ Component	207,500	216,500	50[a] (48[b])
		PS_5 Component	136,800	139,900	50[a] (52[b])
		Total Blend	164,800[a] (163,400[b])	177,900[a] (176,300[b])	–
	Dual Detection	Total Blend	161,310	173,830	–
$\omega_{PMMA} = 90\%$ $\omega_{PS} = 10\%$	Proposed Method	$PMMA_5$ Component	207,800	216,800	89[a] (88[b])
		PS_5 Component	135,700	138,600	11[a] (12[b])
		Total Blend	196,200[a] (195,500[b])	207,900[a] (207,200[b])	–
	Dual Detection	Total Blend	193,400	205,900	–

[a] Value based on Eq. (10) and the literature values of the specific refractive index increments.
[b] Value based on Eq. (10) and the experimentally-determined DR responses for PS and PMMA.

$$\widehat{g}_{DR/UV}(V_i) = \frac{k_{UV,PS} - k_{UV,PMMA}}{k_{DR,PMMA}k_{UV,PS} - k_{DR,PS}k_{UV,PMMA}} s_{DR}(V_i) + \frac{k_{DR,PMMA} - k_{DR,PS}}{k_{DR,PMMA}k_{UV,PS} - k_{DR,PS}k_{UV,PMMA}} s_{UV}(V_i - \delta) \quad (16a)$$

$$\widehat{\omega}_{PS,DR/UV}(V_i) = \frac{k_{UV,PMMA} - k_{DR,PS}[s_{UV}(V_i - \delta)/s_{DR}(V_i)]}{(k_{UV,PMMA} - k_{UV,PS}) + (k_{DR,PS} - k_{DR,PMMA})[s_{UV}(V_i - \delta)/s_{DR}(V_i)]} \quad (16b)$$

Note that, while $\widehat{g}_{DR/UV}(V_i)$ is obtained from a linear combination of the signals, $\widehat{\omega}_{PS,DR/UV}$ [and $\widehat{\omega}_{PMMA,DR/UV}(V_i)$] are obtained from a nonlinear combination of the signals. Thus, while Eq. (16a) is in principle well behaved along the full chromatogram range, Eq. (16b) is potentially subject to errors at the chromatogram tails.

The estimates of the local masses of PS and PMMA [$\widehat{g}_{PS,DR/UV}(V_i)$ and $\widehat{g}_{PMMA,DR/UV}(V_i)$], are directly obtained from $\widehat{g}_{DR/UV}(V_i)$ and $\widehat{\omega}_{PS,DR/UV}(V_i)$, through:

$$\widehat{g}_{PS,DR/UV}(V_i) = \widehat{\omega}_{PS,DR/UV}(V_i) \times \widehat{g}_{DR/UV}(V_i) \quad (17a)$$

$$\widehat{g}_{PMMA,DR/UV}(V_i) = \left[1 - \widehat{\omega}_{PS,DR/UV}(V_i)\right] \times \widehat{g}_{DR/UV}(V_i) \quad (17b)$$

Then, the MMD of each component is obtained from $\widehat{g}_{PS,DR/UV}(V_i)$, $\widehat{g}_{PMMA,DR/UV}(V_i)$, and the local calibrations $M_{PS}(V_i)$ and $M_{PMMA}(V_i)$ (Fig. 2a). Finally, the MMD of the total blend is estimated by addition of the individual MMDs, *i.e.*:

$$\widehat{g}_{DR/UV}(\log M) = \widehat{g}_{PS,DR/UV}(\log M) + \widehat{g}_{PMMA,DR/UV}(\log M) \quad (18)$$

Note that Eqs (16) are also employed for analyzing copolymers with varying local composition. However, for copolymers, the local molar masses are obtained by interpolation (with the local composition) between the direct calibrations of the corresponding homopolymers [4].

The results of dual detection are presented in Fig. 4 and Table 4. Figs. 4a,d) present the DR and UV chromatograms for blends 20/80 and 90/10. At low elution volumes, the UV signal is relatively lower than the DR signal, which indicates that the mixture mainly contains PMMA; while the opposite occurs at high elution volumes. The chemical nature of the tails of the bimodal chromatograms becomes evident from Figs. 4b,e), where the local masses of the individual standards are shown rescaled with their nominal mass fractions. Similarly, Figs. 4c,f) compares the estimated local mass fractions of PS by dual detection through Eq. (16b) [$\widehat{\omega}_{PS,DR/UV}(V_i)$], with the same estimates obtained through the proposed deconvolution procedure and Eq. (9) [$\widehat{\omega}_{PS}(V_i)$]. The deconvolution estimates are based on smooth EMGs, and properly suggest a continuous variation of $\omega_{PS}(V_i)$ between 0 and 1. In contrast, errors are suspected in $\widehat{\omega}_{PS,DR/UV}(V_i)$ at the high elution volumes. These errors are corroborated when comparing the local masses of Figs. 4b,f) with their estimates by dual detection [$\widehat{g}_{PS,DR/UV}(V_i)$ and $\widehat{g}_{PMMA,DR/UV}(V_i)$] presented in Figs. 4d.h), and based on $\widehat{\omega}_{PS,DR/UV}(V_i)$. Clearly, large errors are observed in the estimated local masses of $PMMA_5$ of Figs. 4d,h), caused by errors in $\widehat{\omega}_{PS,DR/UV}(V_i)$. Possible reasons for errors in $\widehat{\omega}_{PS,DR/UV}(V_i)$ are: i) poor signal-to-noise ratios at the chromatogram tails; ii) uncertainties in the inter-detector volume; and iii) a final band broadening distortion of the UV signal compared with the DR signal, introduced by the interdetector capillary and by the (non-negligible) UV cell volume. The global MMD estimates obtained by deconvolution of the DR signal seem preferable to those obtained by dual detection. However, dual detection is important for determining the chemical nature of the individual peaks. Table 3 presents the average molar masses of the total blends, estimated by dual detection. In spite of the large errors in $\widehat{\omega}_{PS,DR/UV}(V_i)$ and in the PMMA chromatograms of Figs. 4d,h), the average molar mass estimates are all reasonably accurate. This insensitivity toward the local composition is explained by the fact that the molar mass calibrations of PS_5 and $PMMA_5$ are almost overlapped (Fig. 2a) and, therefore, any instantaneous composition produces almost identical molar masses. Clearly, this would not be the case if the courses of individual calibrations were sufficiently different.

3.3. Limitations of the proposed data treatment

The proposed data treatment was tested with other multimodal samples and fractionation columns. For example, for a mixture containing 10% in weight of a PS standard of $\overline{M}_w = 10{,}500$ g/mol, and 90% of a PS Standard of $\overline{M}_w = 16{,}500$ g/mol, the technique failed when a column with lower resolution was employed (AM GEL LINEAR, from American Polymer Standard Corporation, particle size 10 μm). However, the same mixture was successfully resolved when either: a) increasing the weight fraction of the minor component to 20% in weight, or b) increasing the column resolution by employing two Jordi columns: a GEL DVB (pore size 100 Å) and GEL DVB (pore size 1000 Å).

With DRs, the minimum detectable mass fraction strongly depends on the specific refractive index increment of the analyzed component. For example, for mixtures of PS and PMMA standards, a high resolution column enabled resolution of a mixture of 10%-wt PS and 90%-wt PMMA, but not a mixture of 90%-wt PS and 10%-wt PMMA, due to the lower PMMA signal caused by its lower specific refractive index increment.

Chromatogram widths are also important, since broad unimodal chromatograms are more difficult to resolve than narrow unimodal peaks. In addition, broad unimodal chromatograms are more difficult to fit by EMGs than narrow chromatograms of standards.

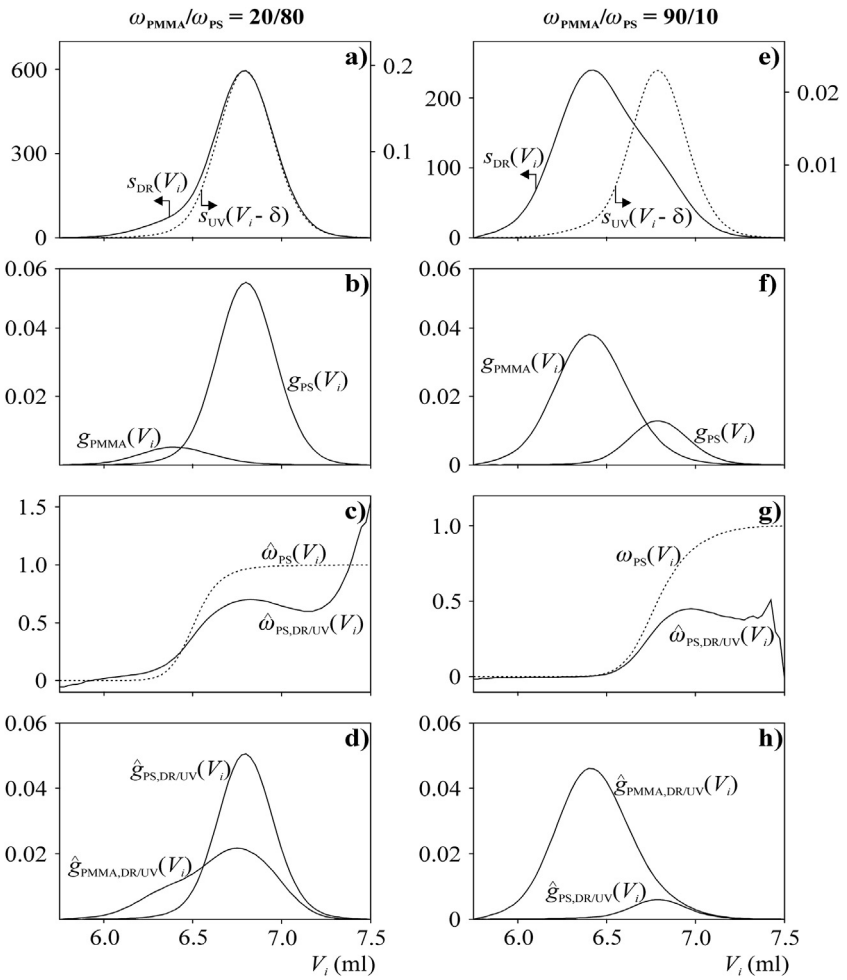

Fig. 4. Blends of $PMMA_5$ and PS_5 standards. The results for blends 20/80 and 90/10, are in columns a-d) and e-h), respectively. a,e) Measured chromatograms $s_{DR}(V_i)$ and $s_{UV}(V_i-\delta)$. b,f) Local masses of the individual PS and PMMA components, $g_{PS}(V_i)$ and $g_{PMMA}(V_i)$. c,g) Local mass fractions of PS estimated by dual detection $\hat{\omega}_{PS,DR/UV}(V_i)$, and with the proposed data treatment, $\hat{\omega}_{PS}(V_i)$. d,h) Estimated mass chromatograms of the individual PS and PMMA components, $\hat{g}_{PS,DR/UV}(V_i)$ and $\hat{g}_{PMMA,DR/UV}(V_i)$, as obtained by dual detection.

Note that, for good results, the multimodal chromatograms should preferably fall completely inside the central region of the fractionation range of the given SEC columns. In fact, samples of broad unimodal distributions with totally excluded high molar mass fractions exhibit bimodal chromatograms due to column saturation, and not due to MMD bimodality. Such apparently bimodal chromatograms contain the so-called accumulation peaks.

4. Conclusions

A simple method was proposed for determining the unimodal MMDs of the individual polymer components contained in a blend, based on the processing of multimodal concentration chromatograms. Multimodal chromatograms were fitted by linear combinations of EMGs, with adjustable parameters representing the mean, standard deviation, skewness and chromatogram fraction. EMGs are appropriate for representing typical unimodal chromatograms of a single maximum and zero slopes at the tail ends.

The proposed method was tested on a sample containing two PS components of broad MMDs, and on mixtures of narrow PS and PMMA standards. In all cases (and after a smoothing operation), the second derivative of the bimodal chromatograms adequately predicted the approximate position of the individual peaks. In addition, the global chromatograms were properly represented by weighted sums of EMGs.

For blends of homopolymers with identical chemical composition, the deconvolution operation directly provides the mass fractions of the individual polymer components (w_j), and a single molar mass calibration is required for determining the MMDs of the individual components and the total blend. For blends of two homopolymers of distinct chemical composition, the deconvolution technique enables isolation of the chromatograms of the individual polymer components. However, to estimate their normalized MMDs, the chemical nature of the individual peaks must be identified, and the individual molar mass calibrations are required. In addition, for blends of chemically different homopolymers, the DR or UV signals are not

proportional to the total concentration, and the deconvolution weights (w_j) no longer represent the total mass fractions (ω_j). To estimate the total mass fractions and MMD of the total polymer, the detector responses toward each sample component are also required.

Dual UV/DR detection is important for characterizing blends of two chemically different homopolymers. By estimating the local concentration and the local composition, it enables identification of the chemical nature of the polymer components and isolation of their individual chromatograms. Unfortunately, due to propagation of errors at the chromatogram tails, dual detection only provides acceptable estimates of the instantaneous composition in the mid-chromatogram regions, and large errors are expected in the isolated chromatograms. In contrast, in the proposed deconvolution procedure, the calculations are based on smooth analytical functions that produce smooth estimates of the local composition and the unimodal MMDs. This suggests the use of dual detection for identifying the chemical nature of the blend components, and the use of the proposed data treatment for estimating the MMDs of the individual sample components.

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