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Analysis method

Molar mass distributions in binary homopolymer blends by single-step two-dimensional liquid chromatography: Operation and data treatment

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ABSTRACT

A single-step two-dimensional liquid chromatography technique is employed for estimating the individual molar mass distributions in blends of polystyrene and poly(methyl methacrylate). It involves an initial separation of the homopolymers by liquid chromatography under limiting condition of desorption (first column), followed by their fractionation by size exclusion chromatography (second column). The technique requires a calibration stage with narrow standards for determining (for each homopolymer): a) the molar mass calibration of the complete fractionation system; and b) the band broadening function corresponding to the first column. Then, the molar mass distributions are estimated as follows: i) the polymer blend is injected into the tandem of both fractionation columns; ii) the obtained bimodal chromatogram is pre-processed to isolate the homopolymer peaks; iii) each isolated chromatogram is corrected for the band broadening caused by the first column; and iv) the molar mass distributions are estimated from the band broadening corrected chromatograms and the corresponding molar mass calibrations. The analysis is straightforward and fast, but it requires a relatively elaborate calibration process.

1. Introduction

Size exclusion chromatography (SEC) is the main technique for determining the molar mass distribution (MMD) and averages ($\overline{M}_n$ and $\overline{M}_w$) of synthetic polymers [1–5]. In its simplest and most common configuration, a single concentration-sensitive detector is employed, such as a differential refractometer (DR), a UV spectrophotometer, or an evaporative light scattering detector. Blends of different homopolymers are found in many technical applications; and block copolymers are normally contaminated by small fractions of their parent homopolymers [6,7]. The characterization of polymer blends from single concentration chromatograms is difficult when the chromatograms of the individual polymer components are partially or totally overlapped. Moreover, the MMD of global blends cannot be accurately estimated because the detector signal is not proportional to the total instantaneous concentration, and each polymer component exhibits a different molar mass calibration. (Acceptable estimates of the global MMD are only produced in the rather rare case of blends with identical detector responses and molar mass calibrations for both polymer components [3].) In our recent publication [8], a deconvolution method was proposed for estimating the individual MMDs of partially-overlapped chromatograms of binary polystyrene (PS)/poly(-methyl methacrylate) (PMMA) blends by SEC with only a DR.

Polymer blends have been characterized by multiple-detection SEC. For example, a UV- and a density detector have been used for estimating the individual MMDs in a PMMA/poly(ethylene glycol) (PEG) blend [9]. The proposed method is simple, but it requires an accurate calibration of the detector gains toward each polymer component. Busnel and Degoulet [10] analyzed a polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) triblock copolymer by SEC with a differential refractometer and a dual UV detector fitted at 254 and 234 nm; and were able to determine the instantaneous mass fractions of each block, on the basis of their

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differences in specific refractive indexes (d*n*/d*c*) and absorptivities. Similarly, Rowland and Striegel [11] characterized blends of poly(-acryl amide) and poly(dimethyl acrylamide) by SEC with quintuple detection; *i.e.*, fitted with a multi-angle light scattering (MALS), a quasi-elastic light scattering, a differential viscometer, a UV spectrophotometer, and a DR. The global MMD and the chemical heterogeneity distribution were obtained from the blend chromatograms of the MALS, DR, and UV sensors. Some limitations of multi-detection SEC are: i) the low signal-to-noise ratio at the chromatogram tails; ii) the high sensitivity toward errors in the inter-detector volumes; iii) distortions introduced by band broadening (BB) in the inter-detector capillaries; and iv) uncertainty in the response factors and/or detector gains.

Several hyphenated liquid chromatography methods have been developed for the analysis of polymer blends, that first isolate the individual components by composition, and then analyze each of them separately; *e.g.*: [6,7,12–17]. Lee and Chang [12] characterized blends of PS and PMMA by 2-dimensional interaction chromatography/SEC. The stationary and mobile phases and the temperature along the column were chosen such that PMMA was fractionated by size exclusion, while PS was fractionated by interaction chromatography. Esser et al. [13] separated a styrene-butadiene rubber (SBR) from polybutadiene (PB) by employing stationary and mobile phases at the critical point of absorption of PB; thus enabling isolation of the PB fraction as a narrow peak, independent of molar mass. Lee and Chang [16] successfully employed interaction chromatography for analyzing a polystyrene-*b*-polyisoprene-*b*-poly(methyl methacrylate) triblock copolymer contaminated by its polystyrene and polystyrene-*b*-polyisoprene precursors. Rollet et al. [7] employed a liquid chromatography technique under limiting conditions of desorption (LC-LCD) for separating the homopolymer contaminants from a polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene triblock copolymer. More recently, Lee et al. [17] characterized a PS-*b*-PMMA sample by a 2-dimensional liquid chromatography technique. In the first dimension, solvent-gradient reverse-phase liquid chromatography enabled separation of the homopolymer precursors in two steps: first, the PMMA was removed with a C18 silica column; and then the PS was removed with a bare silica column. In the second dimension, the three isolated components were analyzed by SEC, to determine their MMDs.

Principles of the LC-LCD technique were first introduced by Berek [6] for the separation of the parent homopolymers (PS and PMMA) that contaminated PS-PMMA block copolymer. In LC-LCD, an adsorption-active column is packed with porous particles. The separation of a binary polymer blend is based on the barrier effect that a low molar mass substance exerts on only one of the polymeric components. The eluent promotes free, exclusion based elution of both polymers from the column packing. A narrow zone of liquid, which promotes adsorption of only one blend component (*e.g.*, a properly-chosen solvent mixture) is injected immediately or a few minutes before the polymer blend. This zone acts as a pore-permeating, slowly eluting barrier, impermeable to the adsorbing macromolecules. As a result, one blend component elutes slowly behind barrier while the non-adsorbing macromolecules are freely eluted in the exclusion mode. In this way the polymers with distinct adsorptivities on the column packing can be efficiently base-line separated. For separation of ternary polymer systems, two distinct barriers are to be used. Each of them selectively decelerates one polymer. More details on LC-LCD and related separation techniques can be consulted elsewhere [14].

Berek [6] utilized LC-LCD for isolating a PS/PMMA block copolymers from their parent homopolymers. To this effect, the sample blend was injected into a silica gel column together with two properly-chosen solvent barriers for selectively decelerating the block copolymer and PMMA, but without affecting PS elution. Later, Berek and Šišková [14,15] introduced the sequential 2-dimensional liquid chromatography technique (S2D-LC) for comprehensive characterization the MMDs of complex, multi-component polymer systems. The technique was successfully employed for analyzing PS/PMMA blends containing a minor component (either PS or PMMA); and for separating the PS and PMMA parent homopolymers that contaminated a PS-*b*-PMMA copolymer samples. The S2D-LC technique consisted of several stages. In the first stage, the components of complex polymer system were separated in an LC-LCD column with help of the above described coupled entropy-enthalpy mechanism; and in the following stages the components separated by LC-LCD were one-by-one, sequentially forwarded into a SEC column to determine their MMD. This technique is further reviewed in the following section.

In this work, the individual MMDs of binary PS/PMMA blends are analyzed through a modification of the original S2D-LC technique [14,15] that we shall call single-step two dimensional liquid chromatography (SS2D-LC). In the new SS2D-LC approach, both peaks eluting from the LC-LCD column are directly forwarded into

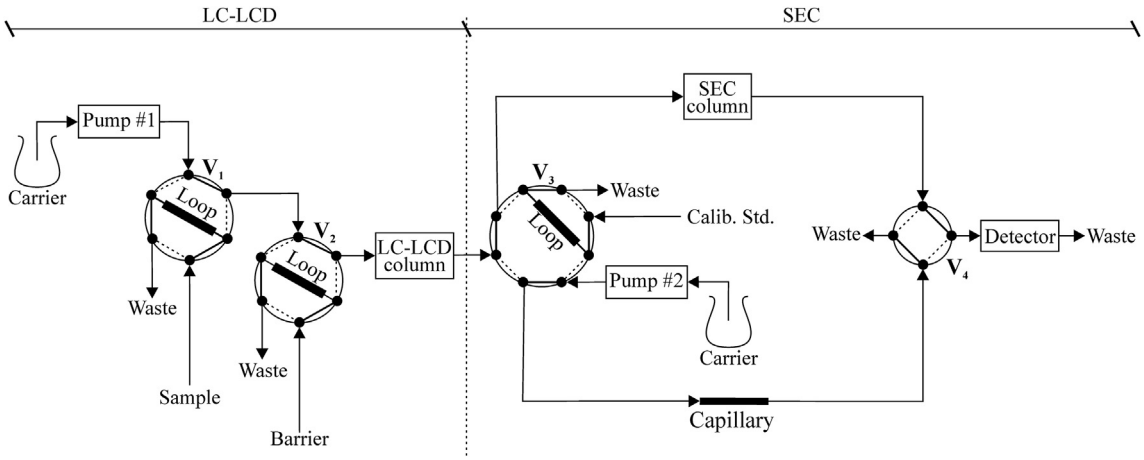

Fig. 1. Setup of the proposed SS2D-LC system. The following operation modes were employed: a) SEC mode: V_3/SEC column/V_4/Detector; b) LC-LCD mode: V_1/V_2/LC-LCD column/V_3/Capillary/V_4/Detector; and c) LC-LCD/SEC mode: V_1/V_2/LC-LCD column/V_3/SEC column/V_4/Detector.

Table 1
Peak molar masses, M_p, of the employed calibration standards as provided by the manufacturers: Pressure Chemical Comp. for the PS standards, and Röhm GmbH and Co. for the PMMA standards.

PS standards		PMMA standards	
	M_p (g/mol)		M_p (g/mol)
PS_1	17,500	$PMMA_1$	16,000
PS_2	37,000	$PMMA_2$	31,000
PS_3	100,000	$PMMA_3$	103,000
PS_4	233,000	$PMMA_4$	294,000
PS_5	612,000	$PMMA_5$	613,000

the SEC column to determine their MMDs. The calibration stage requires a set of narrow standards for each homopolymer that are used for estimating: a) the molar mass calibration of each homopolymer in the series of LC-LCD and SEC columns; and b) the non-uniform Band Broadening Function (BBF) introduced by the first LC-LCD column onto each homopolymer. For the blend analysis, the bimodal chromatogram obtained at the output of the SEC column is first pre-processed for isolating the individual homopolymer peaks, and then each peak is corrected for the BBFs introduced by the LC-LCD column. Finally, the MMD of each homopolymer is estimated from the corrected individual chromatograms with help of corresponding molar mass calibrations. The results are compared to those obtained by emulating the original sequential method [14,15].

2. Review of the S2D-LC technique

Fig. 1 illustrates an experimental setup proposed for the SS2D-LC technique, which is similar to the setups described in Refs. [14,15] for the original S2D-LC technique. The six-port valve V_1 is used to inject the polymer sample, and the six-port valve V_2 is used to inject the solvent barriers (around 1 or 2 min before the sample injection). The eight-port valve V_3 and the four-port valve V_4 are used to select either LC-LCD mode (*i.e.*, with only the LC-LCD column), or LC-LCD/SEC mode (*i.e.*, with the series of both LC-LCD and SEC columns). Additionally, valve V_3 is used to inject the calibration standards directly into the SEC column. Pump #1 is used to introduce the solvent barrier and samples into the LC-LCD fractionation column, while Pump #2 is used to: (i) stabilize the SEC column while working in LC-LCD mode; (ii) operate in pure SEC mode for standards injected *via* valve V_3; and (iii) generate a pressure drop along the capillary that emulates the SEC column back-pressure.

Berek [14] employed a three-step procedure for estimating the MMD of any given polymer component (*e.g.*, PS) by S2D-LC. First, the molar mass calibration of the SEC column alone, $\log M^{PS}_{SEC}(V_i)$, is determined from a set of narrow PS standards directly injected in SEC mode through valve V_3. Second, in LC-LCD mode, the barrier is injected *via* valve V_2 immediately or 1–2 min before the PS/PMMA blend (or the block copolymer sample) is injected *via* valve V_1; and the following is determined from the isolated PS peak, $s^{PS}_{LC-LCD}(V_i)$: the peak volume, V_p^{PS}, and the elution volume range, $[V_0^{PS} - V_f^{PS}]$. Third, in LC-LCD/SEC mode, the barrier and polymer blend are once again injected through valves V_2 and V_1, respectively. After separation of both homopolymers in the LC-LCD column, valve V_3 is operated at V_0^{PS} and V_f^{PS}, to transfer the isolated PS peak into the SEC column, in order to obtain the LC-LCD/SEC chromatogram of the PS component, $s^{PS}_{LC-LCD/SEC}(V_i)$. Finally, the MMD of the PS component is estimated from $s^{PS}_{LC-LCD/SEC}(V_i + V_p^{PS})$ and $\log M^{PS}_{SEC}(V_i)$. This method assumes that the entire LC-LCD peak of each homopolymer is separately transferred into the SEC column, and that the SEC data processing starts when the apex of the isolated (PS or PMMA) peak (V_p^{PS} and V_p^{PMMA}, respectively) enters into the SEC column [14,15]. Unfortunately, the procedure is subject to errors due to: a) the relatively broad LC-LCD chromatograms that are transferred into the SEC column (compared to direct narrow pulse injections in SEC mode); and b) imperfect synchronization between the LC-LCD/SEC chromatogram and the SEC molar mass calibration, $\log M^{PS}_{SEC}(V_i)$, that induces bias into the average molar masses.

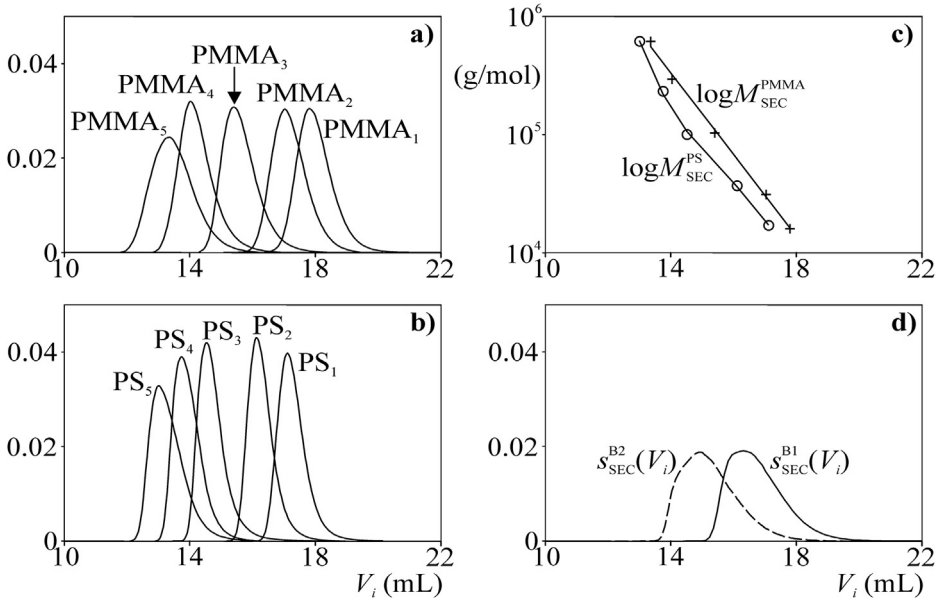

Fig. 2. SEC mode analysis. a), b) Chromatograms of the PMMA and PS calibration standards. c) Molar mass calibrations of the SEC column for PMMA and PS. d) Chromatograms of blends B_1 and B_2.

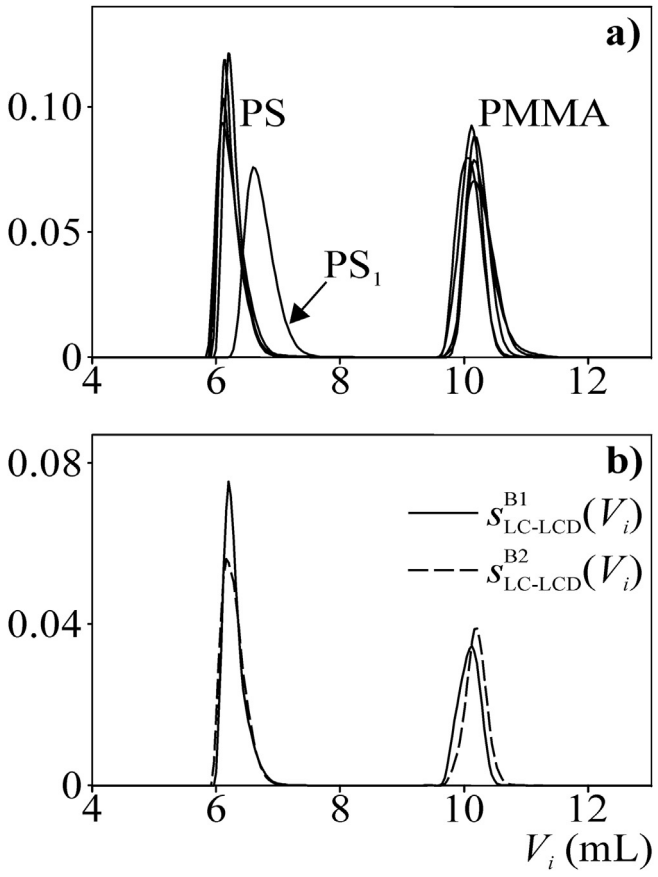

Fig. 3. LC-LCD mode analysis. a) Chromatograms of the individual (PMMA and PS) calibration standards; and b) Chromatograms of blends B_1 and B_2.

3. Experimental work

The setup of Fig. 1 was here employed with the following equipment: two pumps P102 from Watrex Prague Ltd.; an evaporative light scattering detector model 1000 from PL-Agilent Technologies; a LC-LCD column packed with bare silica gel Kromasil 60 Å (300 mm × 7.5 mm) from Eka Chemical; and 2 SEC columns AM PL gel (300 mm × 7.5 mm, pore size 10 μm) from American Polymer Standard. The carrier eluent was a 70/30 wt% solution of tetrahydrofuran and toluene at 1 mL/min. The barrier was a 30/70 wt% solution of tetrahydrofuran and toluene; and it enabled to decelerate PMMA in the first LC-LCD column, while not affecting PS elution.

Table 1 presents the main characteristics of the employed (PS and PMMA) calibration standards. The analyzed blends (B_1 and B_2) consisted of 50:50 wt% mixtures of standards PS_2-$PMMA_2$ and PS_3-$PMMA_3$, respectively. Each of the 10 standards and each of the 2 blends were injected as follows: in SEC mode through valve V_3; in LC-LCD mode through valve V_1; and in LC-LCD/SEC mode through valve V_1. In the experiments of modes LC-LCD and LC-LCD/SEC, 1 mL of solvent barrier was injected through valve V_2 2 min before injection of the standard or blend. Figs. 2 and 3 present the sets of chromatograms obtained in modes SEC and LC-LCD, respectively; while Fig. 4 presents the sets of chromatograms obtained in LC-LCD/SEC mode.

Fig. 2a and b shows the SEC chromatograms of the PMMA and PS standards, $s^{PMMA}_{SEC}(V_i)$ and $s^{PS}_{SEC}(V_i)$, respectively, obtained in SEC mode. From these chromatograms, the SEC calibrations for PMMA and PS [$\log M^{PMMA}_{SEC}(V_i)$ and $\log M^{PS}_{SEC}(V_i)$] of Fig. 2c were obtained by fitting a third order polynomial onto points (V_p, M_p), where V_p and M_p respectively represent the peak volumes and peak molar masses (Table 1). Fig. 2d presents the chromatograms of blends B_1 and B_2 [$s^{B1}_{SEC}(V_i)$ and $s^{B2}_{SEC}(V_i)$]. Since both homopolymer components in the blends elute in similar retention volume ranges, normal SEC with a single DR is incapable of producing accurate estimates of their individual MMDs [8].

Fig. 3a shows the LC-LCD chromatograms of the PMMA and PS standards, $s^{PMMA}_{LC-LCD}(V_i)$ and $s^{PS}_{LC-LCD}(V_i)$. As expected, quite different elution rates are observed, with PMMA eluting later, due to the deceleration effect of the adsorption-promoting solvent barrier. Also, all PS standards elute in a similar elution volume range, except

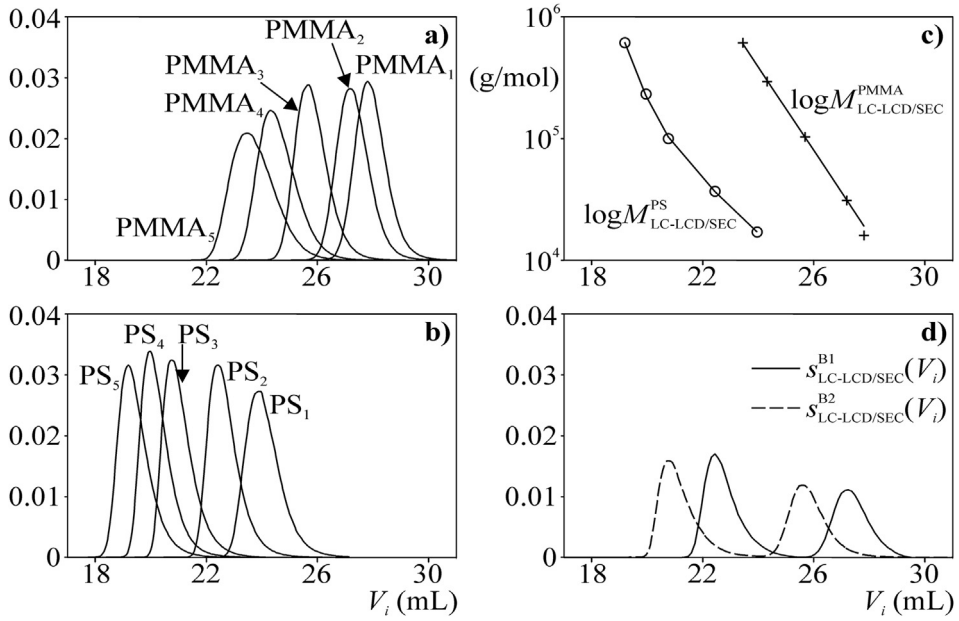

Fig. 4. LC-LCD/SEC mode analysis. a), b) Chromatograms of the PMMA and PS calibration standards; c) Molar mass calibrations for PMMA and PS; and d) LC-LCD/SEC chromatograms of blends B_1 and B_2.

for the lowest molar mass standard (PS_1) that was retained by an extra 30 s with respect to the others. This is because the LC-LCD column packing exhibits narrow pore sizes and most PS samples are pore excluded, except for samples of too small hydrodynamic volume.

Fig. 3b shows the LC-LCD chromatograms of blends B_1 and B_2 [$s^{B1}_{LC-LCD}(V_i)$ and $s^{B2}_{LC-LCD}(V_i)$, respectively]. As expected, the PS and PMMA peaks were efficiently separated, and show a negligible dependence on the molar mass.

Note that if fractionation in LC-LCD mode were strictly by chemical composition, then the chromatograms of Fig. 3 would consist of two separate impulses (or Delta functions), one for each homopolymer. Also note that the chromatograms of Fig. 3 represent the spurious (and non-uniform) BBFs introduced by the LC-LCD column and the capillary installed before the concentration detector (see Fig. 1). The steep onsets of most PS peaks in Fig. 3a suggest that they were pore excluded in the LC-LCD column. In contrast, the lowest molar mass standard PS_1 shows some fractionation by an entropic mechanism. Finally, note that all PMMA peaks largely differ from Delta functions. In summary, these unwanted effects suggest a probable lack of efficiency of the LC-LCD column, which is here modeled as an equivalent non-uniform BBF.

Fig. 4a,b shows the LC-LCD/SEC chromatograms of the calibration standards, [$s^{PMMA}_{LC-LCD/SEC}(V_i)$ and $s^{PS}_{LC-LCD/SEC}(V_i)$]; and Fig. 4d shows the corresponding blend chromatograms [$s^{B1}_{LC-LCD/SEC}(V_i)$ and $s^{B2}_{LC-LCD/SEC}(V_i)$]. In the blends, the homopolymers are first separated by composition in the LC-LCD column, and then by molar mass in the SEC column. Fig. 4a,b enable to determine the molar mass calibrations for each homopolymer in the 2 columns of the LC-LCD/SEC mode, *i.e.*: $\log M^{PMMA}_{LC-LCD/SEC}(V_i)$ and $\log M^{PS}_{LC-LCD/SEC}(V_i)$. Such calibrations are presented in Fig. 4c, and as far as the authors are aware, they have never been reported before. Compared to the SEC calibrations of Fig. 2c, the global molar mass calibrations in the LC-LCD/SEC mode are shifted toward higher elution volumes, and are considerably more separated from each other, due to fractionation in the LC-LCD column. Moreover, the shift between the PS and PMMA calibrations in Fig. 4c is so large that chromatograms of most blends will exhibit baseline separated peaks, and therefore they can be directly processed without requiring independent injections for both homopolymers. Fig. 4d confirms that the PS and PMMA species exhibit baseline separated LC-LCD/SEC chromatograms.

4. Proposed data treatment

The aim of the work is to estimate the MMDs of the individual homopolymers present in a PS/PMMA blend that is analyzed by SS2D-LC. Note that the LC-LCD/SEC mode is mainly affected by two independent sources of errors: 1) lack of efficiency of the LC-LCD column for producing extremely narrow peaks of PS and PMMA; and 2) the (relatively large) BB introduced by the SEC column. The present data processing method is designed to only compensate for error #1). The correction for BB in the SEC column is not here considered, although it could be implemented as a final stage of the data processing.

The proposed data treatment requires an initial calibration stage that is based on the results of Figs. 2a,b and 4a-c. The following assumptions are adopted: 1) the LC-LCD column fractionates by chemical composition, and not by molar mass (this is strictly valid for high enough molar masses); and 2) in the LC-LCD mode, all the BB is concentrated in the LC-LCD column (while in reality, it also includes the contributions by valve V_1, valve V_2, and the interconnection capillaries).

The calculation procedure involves the following steps: i) for each analyzed homopolymer, estimate the BBF due to the LC-LCD column; ii) correct the isolated homopolymer peaks of the LC-LCD/SEC chromatogram for the effects of BB in the LC-LCD column; and c) calculate the individual MMDs with the global calibrations of Fig. 4c. (When the effect of BB in the LC-LCD column is not corrected for, then overestimated global dispersities [$\overline{M}_w/\overline{M}_n$] are obtained.)

For each homopolymer h (= PS, PMMA), the non-uniform BBF introduced by the LC-LCD column #1 is estimated by adjustment to the following exponentially-modified Gaussian function (EMG) [18,19]:

$$g^h_1(V_i,V_j)=\left[\frac{\Delta V}{\sigma^h_1(V_j)\sqrt{2\pi}}e^{-\frac{(V_i-V_j)^2}{2\,\sigma^h_1(V_j)^2}}\right]*\left[\frac{e^{-\frac{V_i}{\tau^h_1(V_j)}}}{\tau^h_1(V_j)/\Delta V}\right],(\mathrm{h}=\mathrm{PS,PMMA}) \quad (1)$$

where $g^h_1(V_i,V_j)$ is the BBF of homopolymer h; and $(-)^*(-)$ represents a convolution product between a Gaussian function of mean volume V_j and standard deviation $\sigma^h_1(V_j)$, and an exponential function of decay $\tau^h_1(V_j)$. The BBF of each h homopolymer is assumed non-uniform because the chromatograms of Fig. 3 show some dependence with the average molar masses. For computational reasons, $g^h_1(V_i,V_j)$ was discretized at regular volume intervals, ΔV.

Unfortunately, the chromatograms of Fig. 3 are not representative of the BBF due to column #1 alone, because they include the BB introduced by the capillary shown in Fig. 1. For that reason, an alternative procedure is employed to find $g^h_1(V_i,V_j)$, that is based on comparing the chromatograms of the narrow standards in direct SEC mode (Fig. 2a,b), with the corresponding chromatograms of the same standards in the LC-LCD/SEC mode (Fig. 4a,b). (In LC-LCD/SEC mode, the chromatograms are shifted and broadened with respect to the direct SEC chromatograms.)

Call $s^{h,c}_{LC-LCD/SEC}(V_i)$ any LC-LCD/SEC chromatogram of homopolymer h (h: PS, PMMA) corrected by the BB caused by the LC-LCD column. Note that (for each homopolymer h), the shape of $s^{h,c}_{LC-LCD/SEC}(V_i)$ is expected to coincide with the shape of the direct SEC chromatograms $s^h_{SEC}(V_i)$, but to differ in their average elution volumes. Thus, one can write:

$$s^{h,c}_{LC-LCD/SEC}(V_i)=s^h_{SEC}\left(V_i-\delta^h\right);(\mathrm{h}=\mathrm{PS,PMMA}) \quad (2)$$

where δ^h represents the difference between the average elution volumes of $s^{h,c}_{LC-LCD/SEC}(V_i)$ and $s^h_{SEC}(V_i)$. For simplicity, we shall represent $s^h_{SEC}(V_i-\delta^h)$ by $s^h_{SEC,\delta}(V_i)$.

The non-uniform BBF $g^h_1(V_i,V_j)$ broadens any hypothetical BB-free chromatogram $s^{h,c}_{LC-LCD/SEC}(V_i)$ into $s^h_{LC-LCD/SEC}(V_i)$. Such interrelationship is described in vectorial notation by Refs. [20–22]:

$$\mathbf{s}^h_{LC-LCD/SEC}=\mathbf{G}^h_1\mathbf{s}^{h,c}_{LC-LCD/SEC}=\mathbf{G}^h_1\mathbf{s}^h_{SEC,\delta};\quad (h=\mathrm{PS},\ \mathrm{PMMA}) \quad (3)$$

where vectors $\mathbf{s}^h_{LC-LCD/SEC}$, $\mathbf{s}^{h,c}_{LC-LCD/SEC}$, and $\mathbf{s}^h_{SEC,\delta}$ contain the ordinates of chromatograms $s^h_{LC-LCD/SEC}(V_i)$, $s^{h,c}_{LC-LCD/SEC}(V_i)$, and $s^h_{SEC}(V_i-\delta^h)$, respectively; and matrix $\mathbf{G}^h_1$ is built from the set of uniform BBF's of fixed average elution volumes V_j. The first equality of Eq. (3) indicates that the BB-corrected chromatogram $s^{h,c}_{LC-LCD/SEC}(V_i)$ may be estimated from the measurements $s^h_{LC-LCD/SEC}(V_i)$ and the knowledge of the BBF given by $\mathbf{G}^h_1$. The second equality of Eq. (3) is employed to estimate the evolution of

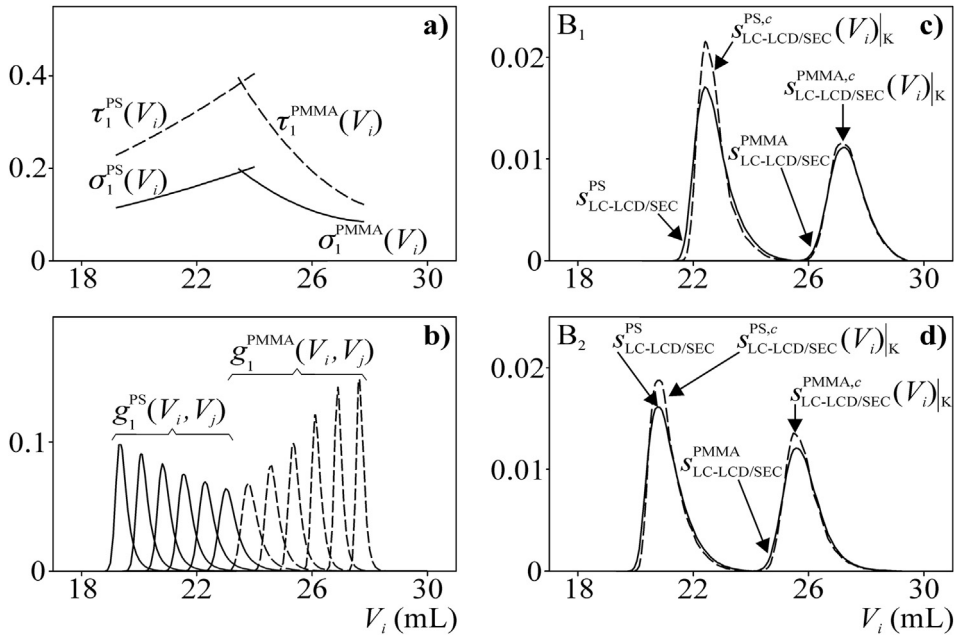

Fig. 5. Data processing of blends B_1 and B_2 by SS2D-LC. a,b) Evolution of the BBF parameters and resulting BBFs. c,d) Isolated LC-LCD/SEC chromatograms of blends B_1 and B_2 [$s^{PS}_{LC-LCD/SEC}(V_i)$ and $s^{PMMA}_{LC-LCD/SEC}(V_i)$, respectively] and corresponding BB-corrected chromatograms [$s^{PS,c}_{LC-LCD/SEC}(V_i)\big|_K$ and $s^{PMMA,c}_{LC-LCD/SEC}(V_i)\big|_K$].

the BBF parameters, $\sigma_1^h(V_j)$ and $\tau_1^h(V_j)$, by solving the following optimization problem:

$$\min_{\substack{a_\sigma,\ b_\sigma,\ c_\sigma \\ a_\tau,\ b_\tau,\ c_\tau}} \sum_{n=1}^{N^h} \| \mathbf{s}^h_{LC-LCD/SEC}|_n - \mathbf{G}_1^h\ \mathbf{s}^h_{SEC,\delta}|_n \|, \quad (h = PS, PMMA) \tag{4a}$$

with:

$$\sigma_1^h(V_j) = a_\sigma \left[(V_j - b_\sigma)^2 + c_\sigma^2\right], \quad (a_\sigma > 0) \quad (h = PS, PMMA) \tag{4b}$$

$$\tau_1^h(V_j) = a_\tau \left[(V_j - b_\tau)^2 + c_\tau^2\right], \quad (a_\tau > 0) \quad (h = PS, PMMA) \tag{4c}$$

where $\|.\|$ represents the 2-norm of a vector, and $\mathbf{s}^h_{LC-LCD/SEC}|_n$ and $\mathbf{s}^h_{SEC,\delta}|_n$ (n = 1, ., N^h) are respectively the LC-LCD/SEC and SEC chromatograms of the N^h standards of homopolymer h. In Eqs. (4b),(4c), second-order polynomials were adopted for the evolution of the BBF parameters.

In SS2D-LC, the first column isolates the individual homopolymers, and the second fractionates them according to molar mass. As expected, the chromatograms of the PS/PMMA mixtures [$s_{LC\text{-}LCD/SEC}(V_i)$] are bimodal (Fig. 4d), with each mode corresponding to an isolated homopolymer. The following 3-steps calculation procedure is proposed to obtain the MMD of each homopolymer in the blend: 1) isolate the individual chromatograms $s^{PS}_{LC-LCD/SEC}(V_i)$ and $s^{PMMA}_{LC-LCD/SEC}(V_i)$ from the total measured chromatogram $s_{LC\text{-}LCD/SEC}(V_i)$; 2) estimate the BB-corrected chromatograms $s^{PS,c}_{LC-LCD/SEC}(V_i)$ and $s^{PMMA,c}_{LC-LCD/SEC}(V_i)$ by numerical inversion of Eq. (3); and 3) estimate the MMD of each component by combining $s^{PS,c}_{LC-LCD/SEC}(V_i)$ and $s^{PMMA,c}_{LC-LCD/SEC}(V_i)$ with the global molar mass calibrations, $\log M^{PS}_{LC-LCD/SEC}(V_i)$ and $\log M^{PMMA}_{LC-LCD/SEC}(V_i)$.

5. Results

The described data treatment was applied onto blends B_1 and B_2. First, the BBFs due to the LC-LCD column were determined through Eqs. (4a), (4b) and (4c), yielding the parameter functions of Fig. 5a, and the final BBFs of Fig. 5b. Standard PS_1 was discarded for the estimation of the BBF $g_1^{PS}(V_i,V_j)$, since it may exhibit fractionation by molar mass in the LC-LCD column (see Fig. 3a). Fig. 5c,d presents the $s^{PS}_{LC-LCD/SEC}(V_i)$ and $s^{PMMA}_{LC-LCD/SEC}(V_i)$ chromatograms of blends B_1 and B_2. The numerical inversion of Eq. (3) was solved by application of the iterative procedure that was originally proposed by Ishige et al. [23]; and is here implemented through:

$$s^{h,c}_{LC-LCD/SEC}(V_i)\Big|_k = \frac{s^h_{LC-LCD/SEC}(V_i)}{\sum_{j=1}^{J} g_1^h(V_i,V_j)\ s^{h,c}_{LC-LCD/SEC}(V_i)\Big|_{k-1}}\ s^{h,c}_{LC-LCD/SEC}(V_i)\Big|_{k-1}; \quad (h = PS, PMMA); \quad (k = 1, 2, \ldots, K) \tag{5}$$

with $s^{h,c}_{LC-LCD/SEC}(V_i)\big|_0 = s^h_{LC-LCD/SEC}(V_i)$. The total number of iterations is limited to a relatively low value (K < 10), in order to avoid spurious oscillations in the final results. Finally, the MMD of

Table 2
Weight-average molar masses [$\overline{M}_w$] and dispersities [$\overline{M}_w/\overline{M}_n$] of the homopolymer components of blends B_1 and B_2 (*i.e.*: standards PS_2, PS_3, $PMMA_2$ and $PMMA_3$); as estimated by: a) the new SS2D-LC technique; b) standard SEC (reference values); and c) emulation of the original S2D-LC technique [15].

Blend	Blend Comp.	New SS2D-LC		Standard SEC		Original S2D-LC	
		$\overline{M}_w$ (g/mol)	$\overline{M}_w/\overline{M}_n$ (−)	$\overline{M}_w$ (g/mol)	$\overline{M}_w/\overline{M}_n$ (−)	$\overline{M}_w$ (g/mol)	$\overline{M}_w/\overline{M}_n$ (−)
B_1	$PMMA_2$	29,556	1.24	28,356	1.22	27,582	1.27
	PS_2	33,048	1.07	33,098	1.11	28,936	1.34
B_2	$PMMA_3$	100,800	1.27	99,250	1.23	101,710	1.33
	PS_3	87,834	1.15	95,900	1.15	85,226	1.22

each component was obtained by combining $s^{h,c}_{LC-LCD/SEC}(V_i)\big|_K$ with the corresponding molar mass calibration of Fig. 4c. Table 2 presents the weight-average molar masses and dispersities of each homopolymer in blends B_1 and B_2 (*i.e.*: of standards PS_2, PS_3, $PMMA_2$ and $PMMA_3$), as obtained by the proposed SS2D-LC technique.

For comparison purposes, the averages and dispersities of each homopolymer in blends B_1 and B_2 were also estimated by direct standard SEC, and by emulating the original S2D-LC technique [15]. The standard SEC estimates were adopted as reference values, and were obtained from the chromatograms and calibrations of Fig. 2a–c. The estimates of the original S2D-LC technique [15] were obtained by first isolating homopolymer chromatograms of Fig. 5c,d; then determining the peak volumes of the PS and PMMA fractions in the LC-LCD chromatograms, V_p^{PS} and V_p^{PMMA} (Fig. 3b); and finally calculating the MMDs and averages from the calibrations of Fig. 2c and the shifted chromatograms, $s^{PS}_{LC-LCD/SEC}(V_i + V_p^{PS})$ and $s^{PMMA}_{LC-LCD/SEC}(V_i + V_p^{PMMA})$.

The $\overline{M}_w$ estimates by the modified and the original S2D-LC techniques are close to the SEC reference values (Table 2). However, while the global dispersities estimated by the new SS2D-LC technique are close to the reference values, the global dispersities according to [15] result overestimated, since they do not include correction for the BBs introduced in the LC-LCD column (Table 2).

6. Conclusions

A new LC technique was proposed for analyzing binary homopolymer blends. It is called Single Step Two-dimensional Liquid Chromatography, SS2D-LC. Compared to the original proposal [6,15], it involves a simplified operation, and produces more accurate MMD estimates of the individual homopolymer components. The method was evaluated with blends of PS and PMMA standards. It requires an elaborate calibration for estimating (for each homopolymer) the BBF introduced by the LC-LCD column, and the molar mass calibration in LC-LCD/SEC mode. However, after calibration, a blend analysis requires a single injection in LC-LCD/SEC mode, and a relatively straightforward data treatment. This represents an advantage with respect to the original S2D-LC technique that requires two injections for the same purpose: one for measuring the LC-LCD chromatogram, and another for determining the MMD of each polymer component [6,15]. Furthermore, the new technique compensates for the BBF in the LC-LCD column and avoids synchronization errors potentially introduced in the original (manual and sequential) procedure.

The SS2D-LC technique is straightforward when the LC-LCD/SEC chromatogram exhibits two baseline-separated homopolymer peaks. If however such peaks were partially-overlapped, then the deconvolution method by Clementi et al. [8] could be applied to isolate the homopolymer chromatograms, prior to estimating their individual MMDs.

The new calculation procedure corrects for the BBs introduced by the LC-LCD column onto each homopolymer, and the effect of such correction is to narrow the final MMDs. In the presented experiments, the SEC column exhibited a relatively poor fractionation efficiency, and its BB effect was not corrected for. For that reason, the molar mass dispersities *via* the new method were only a little lower than the dispersities obtained *via* the original method [6,15]. Clearly, the effect of BB-correction in the LC-LCD column would have been more noticeable if a high-resolution SEC column had been employed. The described technique can be extended to the analysis of other homopolymer blends, but this would require identification of effective solvent barriers to ensure adequate fractionation by composition in the LC-LCD column. Unfortunately, not all polymer blends can be separated by LC-LCD. (To be separated, polymers must exhibit different adsorptivities in the LC-LCD column, and also be soluble in solvents of distinct polarities.)

The analysis of homopolymer blends is based on the assumption that no fractionation by molar mass is introduced in the LC-LCD column. This was almost verified in the described analyses, except perhaps for the smaller molecules (of small hydrodynamic volumes). If fractionation by molar mass in the LC-LCD column were non negligible, then a different operation strategy and data treatment would be required.

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