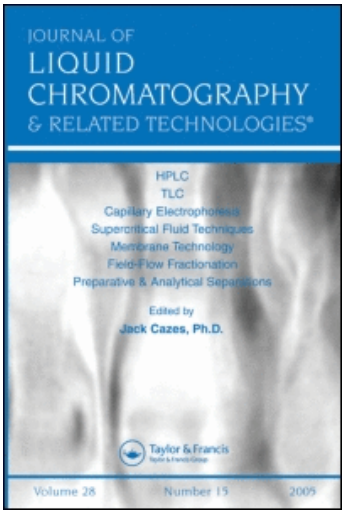

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CORRECTIONS FOR INSTRUMENTAL AND SECONDARY BROADENING IN THE CHROMATOGRAPHIC ANALYSIS OF LINEAR COPOLYMERS

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ABSTRACT

The effects of instrumental broadening and of polymer/solvent/packing interactions (secondary broadening) are separately investigated in the context of chromatography experiments, for the characterization of linear copolymers with two types of repeating units. The problems associated to the estimation of: a) the joint molecular weight distribution - chemical composition distribution (MWD-CCD) through orthogonal chromatography; and of b) the average MWD - average CCD through standard size exclusion chromatography (SEC) with dual detection are considered. The main difficulty with the secondary broadening correction, is the calibration for this effect. In the case of standard SEC with dual detection, a simple solution was found to the instrumental broadening problem, that involves a direct extension of the calibration and deconvolution techniques developed for linear homopolymers and mass detectors.

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INTRODUCTION

The more important characteristics related to the molecular architecture of a linear copolymer are: a) chemical nature of the repeating units; b) molecular weight distribution (MWD); c) chemical composition distribution (CCD); d) sequence length distribution; and e) stereo-regularity distribution.

Many publications have appeared in relation to the joint distribution of molecular weights and chemical composition in copolymers. Review papers on copolymer characterization are referenced in (1-3), and theoretical expressions for the expected joint distributions according to the polymerization mechanisms involved have been developed (4-8). The CCD is an important characteristic determining the physical properties of a polymer, but relatively few correlations have been established in this sense, e.g.: (9).

SEC is presently the most important analytical tool for the molecular characterization of copolymers. This is because standard dual detection (absorption spectrophotometry and differential refractometry) allows the determination of the instantaneous mass and average composition at each retention time (10-16). However, SEC is incapable of measuring the composition distribution at each retention time, and to this effect other techniques responding to composition such as cross fractionation and thin layer chromatography may be employed (17-21). A promising technique called "cross" or "orthogonal" chromatography (22,23), allows in prin-

ciple the estimation of the complete joint MWD-CCD. Two liquid chromatographs are utilized: one fractionating on the basis of molecular size and the other on the basis of composition; but so far it does not provide acceptable quantitative information.

There are many problems associated to SEC of copolymers, particularly when accurate determinations are required. The most important limitations are listed below.

1) Even in ideal SEC, separation is produced according to molecular size and not molecular weight. Therefore, in copolymers (and unless all repeating units exhibit the same partial molar volume), a distribution of molecular weights will be present in the detector cell. For this reason, copolymers are considered as "complex polymers" from the chromatographic point of view (24). The closely related problem of the calibration (i.e., the assignment of a certain molecular weight average at every retention volume) is as yet not wholly solved, in spite of the many papers that have dealt with this matter (24-36). For example, even if an "absolute" molecular weight detector such as a low-angle light scattering photometer is utilized, the accurate calculation of the instantaneous weight average molecular weight is impossible unless the complete joint MWD-CCD is measured. This is so because some of the constants required for the calculation (the refractive indexes and the specific refractive index increments) are, in general, different for each of the comonomers.

2) The instrumental broadening process (due to axial dispersion in the columns, parabollic flows in the capillaries, finite injection and detection cell volumes, etc.) is unavoidable, and is the main cause of imperfect resolution in SEC. The logaritmic nature of the calibration curve determines that the resolution capacity decreases as the molecular weight is increased. Instrumental spreading is reasonably well corrected in the case of mass detectors and linear homopolymers (37-41).

3) The presence of secondary mechanisms in SEC such as adsorption, partition and ionic inclusion (42), may severely distort the chromatogram shape. For homopolymers or strictly alternating copolymers, the effect is a chromatogram time shift with no peak broadening.

4) Another unwanted phenomena, which may or may not be related to secondary broadening, is the presence of solvation volumes around the polymer molecules. The problem is aggravated when solvation per unit volume is different for each comonomer. It does not depend on the instrument itself, and will not be hereafter considered.

In this paper, instrumental and secondary broadening are investigated in the context of chromatographic copolymer analysis. We shall restrict ourselves to the simplest case of linear copolymers with two repeating units types, where the sequence length distribution and the stereo-regularity distribution are not of interest.

REPRESENTATIONS OF THE JOINT DISTRIBUTION

Consider a copolymer with repeating units A and B, of molecular weights M_A and M_B, respectively. Every type of molecular species in the sample is characterized by: M: molecular weight; n_A, n_B: number of repetitive units of A and B, respectively; n: total number of repeating units; w_A: weight fraction of A in the molecular species; g: total mass associated to the molecular type; and g_A, g_B: masses associated with A and B, respectively. The following is verified:

$$M = n_A M_A + n_B M_B \tag{1}$$

$$n = n_A + n_B \tag{2}$$

$$w_A = \frac{n_A M_A}{M} \quad ; \quad (0 \leq w_A \leq 1) \tag{3}$$

$$g = g_A + g_B = w_A g + (1 - w_A) g \tag{4}$$

Note that g_A and g_B may be derived from the knowledge of g, n_A, n_B, M_A and M_B.

SEC fractionates according to hydrodynamic volume v. Call v_A, v_B the hydrodynamic volumes of each repetitive unit of A and B, respectively. For every value of v, a whole distribution of molecular weights with averages: $\bar{M}_n$, $\bar{M}_v$, $\bar{M}_w$, $\bar{M}_z$ is associated. Hamielec and Ouano (43) determined that an "universal" molecular weight calibration for complex polymers involves the function $[\eta]\bar{M}_n$ vs. v, where $[\eta]$ is the intrinsic viscosity. For this reason, it is rather unfortunate that a universal on-line analyzer

for $\bar{M}_n$ is not available. Under certain circumstances however, a signal proportional to the number of molecules may be obtained (e.g., if a strong chromophore is present in the initiator portion of the polymer chain). As a first approximation, one can write:

$$v = n_A v_A + n_B v_B \tag{5}$$

Complete Joint Distribution

From the point of view of the mathematical models (e.g., 4-8), possibly the most "natural" representation of the joint MWD-CCD is through the function $g(n_A, n_B)$. An illustrative example is provided by Fig. 1. However, no direct way of measuring such a distribution is available; and for this reason other representations which lend themselves more to the existing instrumentation are preferable. Consider, for example $g(n_A, M)$, and note the following:

i) All variables are discrete; and if a very large number of species are present in the sample, the resulting discrete function is difficult to represent. Alternatively, "continuous" surfaces such as that of Fig. 2 are preferable, where the original species are replaced by fictitious components appearing at constant intervals of n_A and M. The transformations are in general irreversible, in the sense that the "true" discrete distribution is irrecuperable from the derived continuous surface. Continuizations of discrete distributions are here performed with the criterion that the

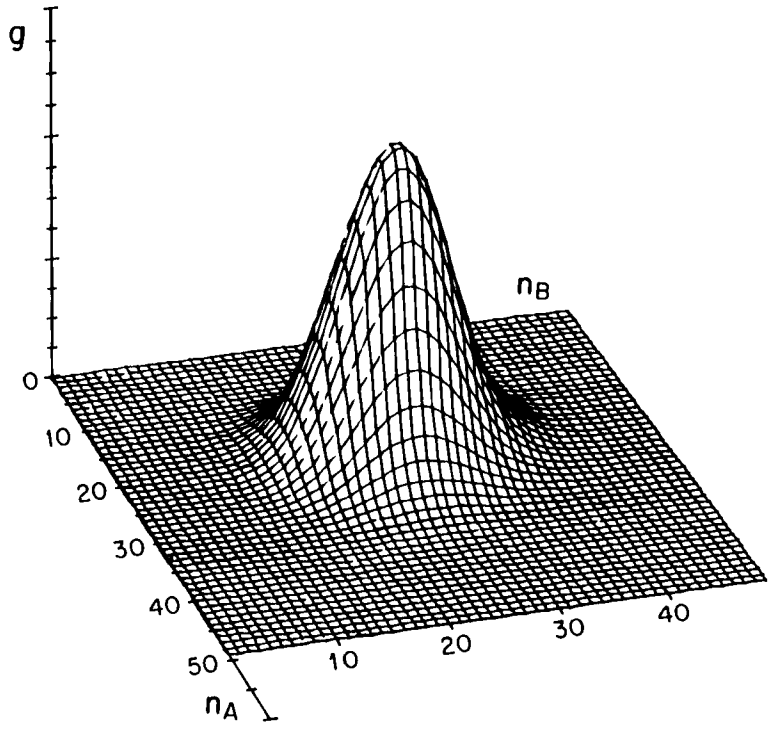

FIGURE 1: A bivariate Poisson MWD-CCD, where A=styrene and B=butadiene.

volume determined by the continuous surface and any "base" $\Delta n_A \times \Delta M$ on the n_A-M plane, is proportional to the total mass of the molecular species contained within such a base. Consequently, the total volume under the surface is proportional to the sample mass.

ii) Species on the M axis correspond to homopolymer B, while the straight line $M=n_A M_A$ represents homopolymer A. From eqn. (3), the inequality $n_A M_A \leq M$ is verified, and there is a

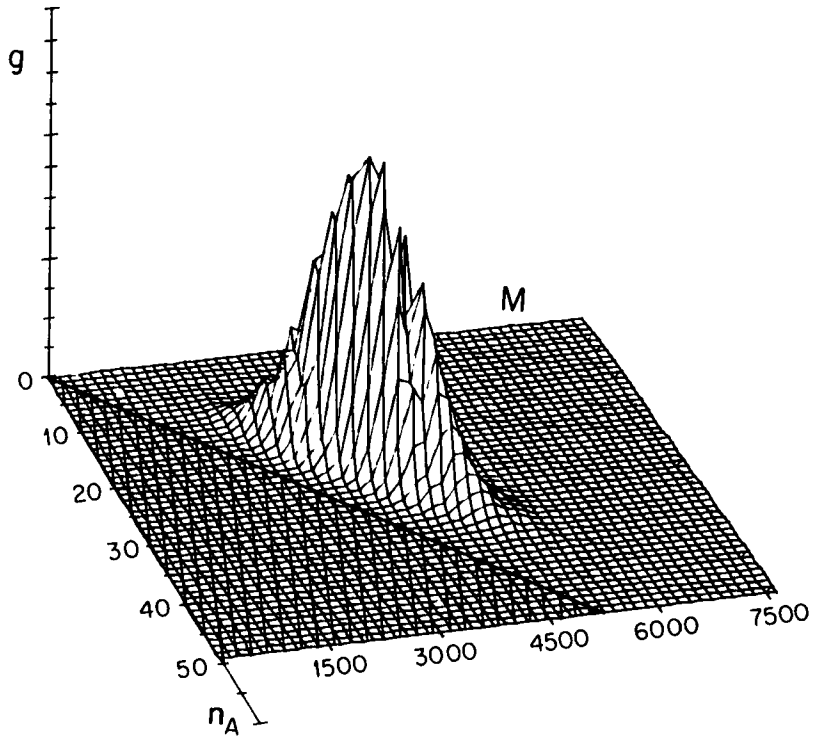

FIGURE 2: Alternative representation of the distribution in Fig. 1.

region (shown shaded in Fig. 2) where the distribution is not possible.

iii) In the special case of copolymers with constant composition in all of its molecular species (e.g.: an exactly alternating copolymer), the three-dimensional surface is reduced to a line, as in Fig. 3.

iv) From the masses associated to each of the comonomers, the derived distributions $g_A(n_A,M)$ and $g_B(n_A,M)$ may be defined.

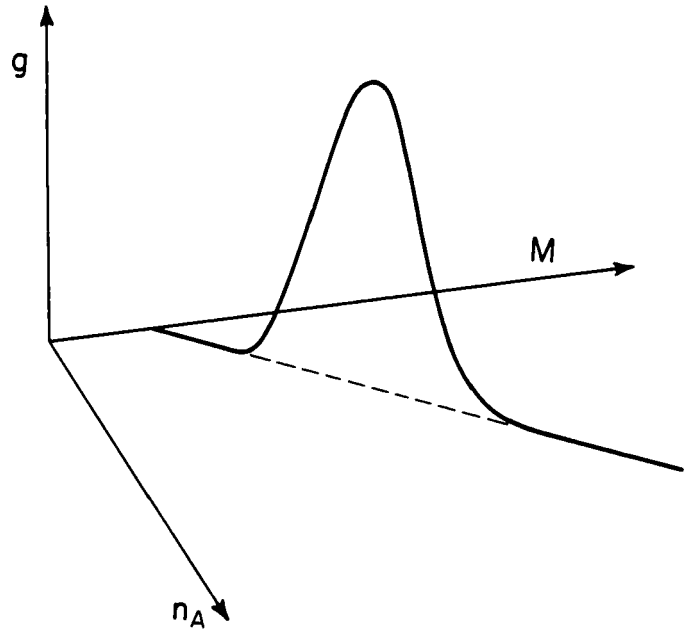

FIGURE 3: MWD-CCD of a copolymer with a strictly uniform composition.

From $g(n_A,n_B)$, the joint distribution $\underline{g(n_A,v)}$ is obtained. Note the following:

i) In the special case where both repeating units have the same partial molar volume, i.e.:

$$M_A/v_A = M_B/v_B \qquad (6)$$

then $M \propto v$, and $g(n_A,v)$ will have the same shape as $g(n_A,M)$.

ii) $g(n_A,v)$ may be in principle estimated from ideal orthogonal chromatography, with the first chromatograph fractionating according to v, and the second according to n_A.

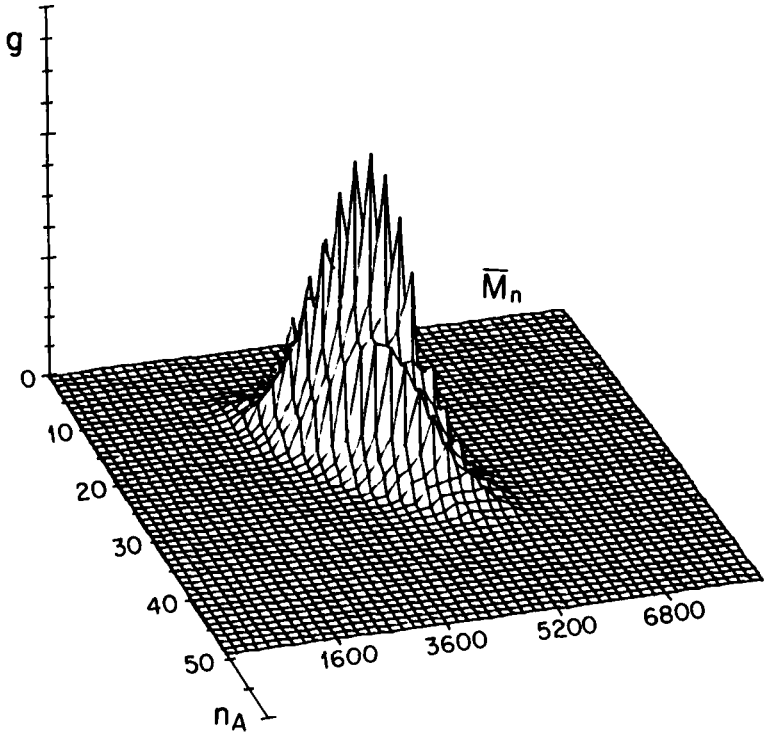

FIGURE 4: Average MWD-CCD obtained form Fig. 1; with M_A=104.15 g/mol, M_B=54.09 g/mol, v_A=115 cm^3/mol and v_B=87 cm^3/mol.

iii) A distribution of molecular weights is in general associated to each value of v. If an ideal on-line molecular weight detector were available, a generic molecular weight average $\overline{M}$ could be determined. Also, after an appropriate transformation, the surface $g(n_A,v)$ provides $g(n_A,\overline{M})$. We shall call this last function the average MWD-CCD. For example, the distribution in Fig. 4 was derived from the MWD-CCD of Fig. 1, with the intermediate calculation of $g(n_A,v)$.

Average Molecular Weight Distribution - Average Composition Distribution

Call G the mass associated to a copolymer fraction of a given molecular weight M, and G_A the total mass of comonomer A in that fraction, i.e.:

$$G(M) = \sum_{n_A} g(n_A,M) \tag{7}$$

$$G_A(M) = \sum_{n_A} g_A(n_A,M) \tag{8}$$

The average weight fraction of A for a given M, is

$$p_A(M) = \frac{G_A(M)}{G(M)} \tag{9}$$

In can be easily shown that for a fixed M, $p_A(M)$ is also the mean value of the function $g(w_A,M)$. The global composition of the whole copolymer sample is:

$$\bar{p}_A = \frac{\sum_M G_A(M)}{\sum_M G(M)} \tag{10}$$

The pair of functions $G(M)$, $p_A(M)$ we shall call the MWD-average CCD. Also, from the average MWD-CCD $g(n_A,\bar{M})$, the average MWD-average CCD is obtained:

$$G(\bar{M}) = \sum_{n_A} g(n_A,\bar{M}) \tag{11}$$

$$p_A(\bar{M}) = \frac{\sum_{n_A} g_A(n_A,\bar{M})}{G(\bar{M})} \tag{12}$$

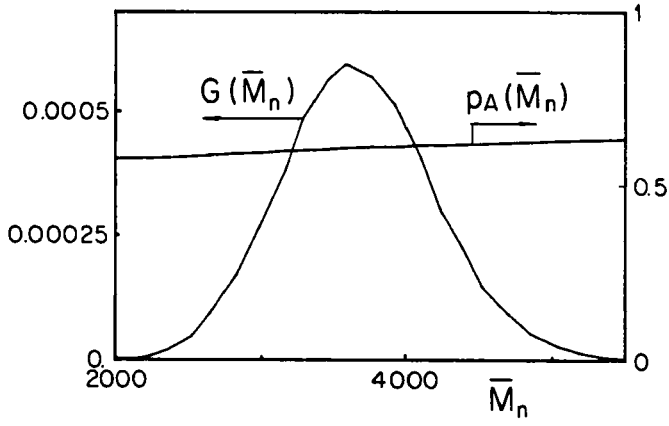

FIGURE 5: Average MWD-average CCD obtained from Fig. 1.

Fig. 5 represents the average MWD-average CCD corresponding to Figs. 1 and 4.

Calculations under Ideal Chromatographic Conditions

Assume ideal SEC, in the sense that size fractionation is the only separation mechanism. Also assume standard dual detection with a differential refractometer and a UV/vis spectrophotometer with a signal proportional to the total mass of comonomer A. The detector equations are (44):

$$\Delta n_i = [\nu_A p_{Ai} + \nu_B (1 - p_{Ai})] G_i \quad (13)$$

$$A_i = \varepsilon p_{Ai} G_i \quad (14)$$

where: Δn_i is the measured refractive index difference; A_i is the measured spectrophotometer response; ν_A, ν_B are the known

specific refractive index increments for homopolymers A and B respectively; and ε is the known absorption coefficient for homopolymer A. From the last two equations:

$$p_{Ai} = \frac{\nu_B \, (A_i/\Delta n_i)}{k_A + (\nu_B - \nu_A)(A_i/\Delta n_i)} \tag{15}$$

$$G_i = \frac{\Delta n_i}{\nu_B} + \frac{(\nu_B - \nu_A)\, A}{k_A \, \nu_B} \tag{16}$$

From eqns. (15,16) and after calibration, $G_i(\bar{M})$ and $p_{Ai}(\bar{M})$ may be readily derived. A propagation of errors study (44), indicates that p_{Ai} is bound to be contaminated by errors at the high and low molecular weight limits of the polymer sample.

Assume now ideal orthogonal chromatography, in the sense that fractionation is based on size in the first chromatograph, and on composition in the second. With standard dual detection in each chromatograph and after calibration, the first instrument would allow the calculation of $G_i(\bar{M})$ and $p_{Ai}(\bar{M})$, while the second the set of functions $g_i(n_A)$, for each $\bar{M}_i$. In this last case, g_i replaces G_i in eqn. (16); and n_A may be obtained from $(p_{A_i} \, g_i)/M_A$, after calculation of p_{A_i} through eqn. (15).

SECONDARY BROADENING ONLY

Secondary broadening distortion is a consequence of the composition distribution in copolymers. Assume: a) ideal orthogonal chromatography, except for the presence of secondary broadening in the first chromatograph; and b) that an absolute mass detector is available.

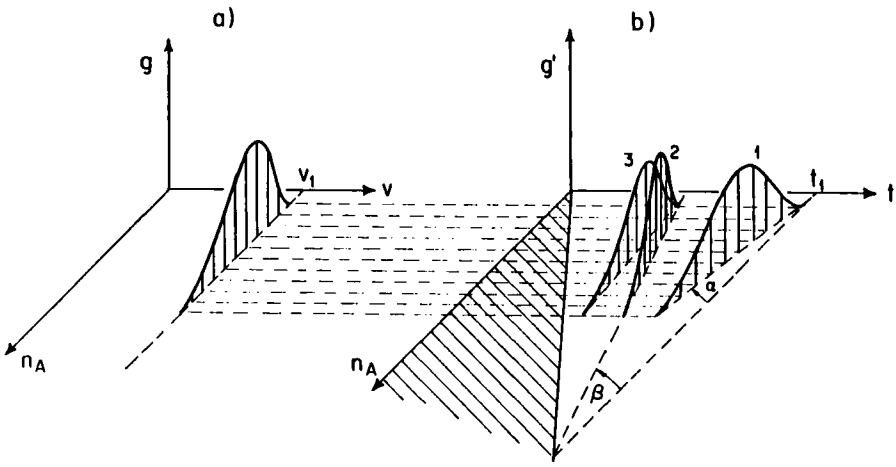

FIGURE 6: a) Hypothetical monodisperse MWD-CCD; and b) corresponding measurement, assuming secondary broadening.

Consider the hypothetical MWD-CCD of Fig. 6.a, which is strictly monodispense in hydrodynamic volume. Assume first that comonomer A is repelled by the column packing while no interactions occur with comonomer B. The measurement may look as curve 1 in Fig. 6.b. Each of the original points are translated in the direction of the t-axis, with a displacement proportional to the contents of A. The curve projection on plane n_A-v is rotated by an angle α about $(0,v_1)$, that corresponds to pure homopolymer B of hydrodynamic volume v_1. The curve heights must be appropriately reduced, to compensate for the "stretching" introduced by the translation. If comonomer B alone were repelled by the packing, a rotation by an angle β would be produced (curve 2) about the point corresponding to homopolymer A, at ($n_A=v_1/v_A$, $t=t_1$). If both comonomers simultaneously interacted with the packing, the measurement

would look as curve 3, that results from the addition of the individual translations. Clearly, if a comonomer had been adsorbed rather than repelled, a rotation towards higher retention times would have been produced.

Assume strictly monodisperse A and B homopolymers, of known hydrodynamic volumes. Also consider homologous calibration standards from the point of view of hydrodynamic volume, but inert with reference to secondary mechanisms. From the shifts in retention times with respect to the ideal values, the secondary broadening calibration, i.e. the pair of functions $\alpha(v)$ and $\beta(v)$ could be determined. As a first approximation, α and β may be considered constant for all v.

To correct a measurement $g'(n_A,v)$ of a polydisperse distribution for secondary spreading, one would require to perform the appropriate translations-rotations at each hydrodynamic volume. To represent the resulting continuous surface $g(n_A,v)$, the heights must be appropriately modified, to generate a uniform density of points in the plane n_A-v.

Consider the problems associated to the correction for secondary broadening in the estimation of the average MWD-average CCD, through standard SEC with dual detection. Due to the sampling of continuouis signals, the true distributions are represented by a set of relatively few hypothetical molecular species equally spaced along the v axis. As first approximation, one could consider that:

i) each of the hypothetical monodisperse molecular species has a constant composition p_{A_i}; and

ii) each species is shifted for secondary broadening by an amount:

$$\delta v_i = p_{A_i} \delta v_{i,A} + (1 - p_{A_i}) \delta v_{i,B} \qquad (17)$$

where $\delta v_{i,A}$ and $\delta v_{i,B}$ are the positive or negative shifts introduced by monodisperse A and B homopolymers of hydrodynamic volume v_i; that may be obtained from a calibration at two hydrodynamic volumes, and assuming linear variations of the shifts along v.

Eqn. (17) indicates how a distribution $G_i(v_i)$, $p_{A_i}(v_i)$ is distorted into $G'(v_i+\delta v_i)$, $p'_{A_i}(v_i+\delta v_i)$. Its inversion, followed by a continuization of the resulting distributions would allow, in principle, to correct for the unwanted process. Such operation is not simple and provides only an approximation to the real solution because: a) only the average values of the composition distribution are utilized; and b) the estimation of G and p_A is coupled to the secondary broadening correction.

INSTRUMENTAL BROADENING ONLY

In orthogonal chromatography, call t the elution time in the first chromatograph, and consider the estimation of $g(n_A,t)$. Assume the system exhibits instrumental broadening in the first chromatograph, but is otherwise ideal. Call $h(t,\tau)$ the non-uniform spreading function, where τ is the mean elution time.

According to the principle of "universal peak broadening calibration" (45) and for mass detectors, the spreading process depends on hydrodynamic volume only, and it is independent of composition. Thus, all copolymer species of different compositions but of the same value of τ, produce the same broadening $h(t)$. Assume for simplicity, the existence of an absolute mass detector allowing the direct measurement of $g'(n_A,t)$, that exhibits instrumental spreading in the direction of the t-axis. Tung's equation (46) may be rewritten as follows:

$$g'(n_A,t) = \int_{-\infty}^{\infty} h(t,\tau)\, g(n_A,\tau)\, d\tau \qquad (18)$$

where $g(n_A,t)$ is the corrected joint distribution, from which $g(n_A,v)$ may be obtained. To correct for instrumental broadening, a numerical deconvolution technique (40,41,47), could be repeatedly applied at different levels of n_A.

Consider the estimation of $G(t)$ and $p_A(t)$ through standard SEC with dual detection. Two solution paths seem possible. Path No. 1 involves: a) correction of the raw measurements $\Delta n'(t)$ and $A'(t)$ for instrumental spreading through:

$$\Delta' n(t) = \int_{-\infty}^{\infty} h_{\Delta n}(t,\tau)\, \Delta n(\tau)\, d\tau \qquad (19)$$

$$A'(t) = \int_{-\infty}^{\infty} h_A(t,\tau)\, A(\tau)\, d\tau \qquad (20)$$

and; b) calculation of the derived variables $G(t)$ and $p_A(t)$ through eqns. (15,16). Alternatively, in path No. 2, one would: a) calculate $G'(t)$ and $p'_A(t)$ from the raw measurements; and b)

correct those derived variables for instrumental broadening with:

$$G'(t) = \int_{-\infty}^{\infty} h_G(t,\tau)\, G(\tau)\, d\tau \qquad (21)$$

$$p_A'(t) = \int_{-\infty}^{\infty} h_{p_A}(t,\tau)\, p_A(\tau)\, d\tau \qquad (22)$$

An error propagation analysis is required to determine the best solution, but path No. 1 seems "a priori" preferable.

Finally, consider the way of estimating the broadening functions $g_{\Delta n}$, g_A and g_G. Assume that strictly monodisperse copolymers in both hydrodynamic volume and molecular weight were available. In this case, p_{A_i} is some arbitrary but constant value; and from eqns. (13,14), it follows that Δn_i and A_i are both proportional to the mass G_i. For this reason, and calling $h_{PS}(t,\tau)$ the spreading calibration obtained through normal techniques with a mass detector and narrow polystyrene standards (38,39,48), one can write:

$$h_{\Delta n}(t,\tau) = h_A(t,\tau) = h_G(t,\tau) = h_{PS}(t,\tau) \qquad (23)$$

Thus, correction for instrumental broadening with dual detection may involve two independent deconvolutions [eqns. (19,20)], with the spreading functions obtained in standard fashion.

CONCLUDING REMARKS

If one is not interested in the microstructure, the molecular arquitecture of a linear copolymer with two repeating units types

may be adequately described by a 3-dimensional surface (the complete MWD-CCD), or by two functions with a common independent variable (the average MWD-average CCD).

Through standard SEC, only the average MWD-average CCD may be estimated. So far, an accurate analytical technique for the determination of the complete MWD-CCD is not available. However, it has been herein assumed that orthogonal chromatography will eventually provide the necessary information for such a task.

While instrumental broadening is unavoidable in chromatographic experiments, the broadening due to secondary fractionation mechanisms may be negligible (e.g.: a styrene-butadiene copolymer analyzed with a styrene-based column packing). When the average composition is identical for all polymer species (as in alternating or azeotrope copolymers), then secondary broadening introduces pure time shifts but no peak distortion.

The analysis for secondary and instrumental broadening was simplified as follows:

1) Each broadening process was independently investigated, and the principle of superposition was assumed. This reasonable hypothesis, may however involve some kind of iterative procedure when the correction for the combined effect of both processes is required.

2) For orthogonal chromatography, both spreading phenomena were attributed to chromatograph N° 1 only. The previous ideas may be extended to include both instruments, however.

3) In several situations, independent mass and composition detectors were assumed to be available. In practice, standard dual detection would be utilized, and the calculation of g vs. n_A for every M, or of the pair G(M), $p_A(M)$ would be coupled to the spreading corrections.

The correction for secondary broadening is complicated because its calibration requires the synthesis of a well-characterized homologous series of linear homo- and copolymers. In relation to the MWD-CCD, it involves rotations and translations of the measured surface. For the average MWD-average CCD, a procedure requiring the translation and rescaling of the hypothetical species associated to the distribution was suggested.

The calibration for instrumental spreading in standard SEC with standard dual detection presents the difficulty that the measured signals are not proportional to the eluting mass. However, it may be easily shown that the spreading associated to each of the sensors is identical to the spreading obtained for linear homopolymers with mass detectors. The correction for instrumental broadening is relatively simple, because it involves the independent deconvolution of each signal.

If an on-line light scattering photometer were included, the estimation of $\bar{M}w(t)$ could be performed after obtention of the corrected distributions $g(n_A,t)$ or $G(t)$, $p_A(t)$. Presently, UV-vis multidiode array spectrophotometers are available for liquid chromatography. These detectors seem ideal for accurate composition

measurements, and may eventually replace single wavelength sensors.

Currently, simulated examples of the suggested correction techniques are being developed. These shall be the subject of a later communication.

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