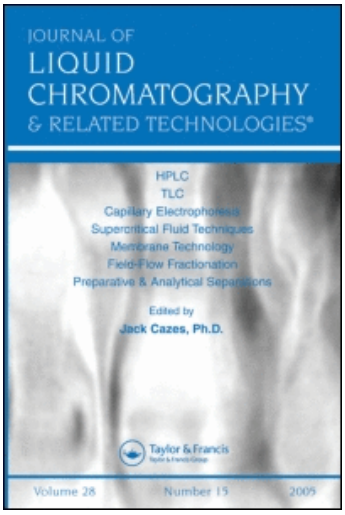

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Size Exclusion Chromatography (SEC) of Complex Polymers-Methods of Correction for Imperfect Resolution

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SIZE EXCLUSION CHROMATOGRAPHY (SEC) OF COMPLEX POLYMERS-METHODS OF CORRECTION FOR IMPERFECT RESOLUTION

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ABSTRACT

Herein is reported a review and extension of recently published methods of correction for imperfect resolution (inadequate peak separation and or excessive peak broadening) for the SEC of linear homo and uniform copolymers and complex polymers such as polymers with long chain branching and nonuniform copolymers. Emphasis is placed on analytical correction methods and absolute detector systems such as the low angle laser light scattering photometer and viscometer in series with a mass detector. Analytical correction methods and absolute detector systems play a vital role in the SEC characterization of complex polymers.

INTRODUCTION

The equilibrium theories of SEC of polymers show that peak separation is proportional to total pore volume[1], and transport theories show that the principal cause of peak broadening is pore dispersion[2]. When peak separation is inadequate and/or peak broadening is excessive, corrections for imperfect resolution should be made on the average molecular weights, intrinsic viscosity and, in some circumstances, on the molecular weight distribution itself. If the distribution is broad, corrections for imperfect resolution would probably change the shape very little. For narrow MWD samples the change in shape can be appreciable and these narrow distributions should be corrected. There is a misconception in the literature that a broad distribution needs no correction for its molecular weight averages and intrinsic viscosity. This is definitely not true. The misconception arose in the early days of GPC when corrections to broad and narrow chromatogram shapes were compared. Corrections for imperfect resolution are significant when the magnitude of the corrections to $\bar{M}_n$ and $\bar{M}_w$ exceed about 5%. Transport theories[2] of SEC have shown that under the usual range of operation of chromatographs with polymers, the separation mechanism can be in three regimes, equilibrium, transition and diffusion-controlled.

With increase in mobile phase flow rate, increase in solute size in solution and increase in packing particle size and pore depth, the chromatograms for single species change from Gaussian shape to those which are skewed towards longer retention volume as one moves from the equilibrium regime to the diffusion-controlled regime. Correction methods may have to consider skewed single species chromatograms if accurate molecular weight data is to be obtained by SEC. With the recent advent of micropackings (packing particles with a diameter of about 10 microns) with their greatly reduced pore lengths and consequent greatly reduced peak broadening, it was believed by some that corrections for imperfect resolution would be insignificant. This is indeed not the case. To reduce pressure drop across columns packed with micropackings and to reduce analysis time, the total pore volumes were greatly reduced. As a consequence, peak separation is also greatly reduced. Polystyrene standards of molecular weights 4000 and 2×10^6 are often separated in a retention volume range of as small as 12 cc. Corrections for imperfect resolution are often not insignificant with micropackings.

Complex polymers are those for which a unique relationship between size in the mobile phase and molecular weight does not exist. Examples include polymers with long chain branching, synthesized by free radical polymerization. The polymer product contains some linear chains and chains with various numbers of long branches. Polymer molecules with the same size in solution will have different molecular weights from such a mixture. For a copolymer with composition drift, the same problem arises. The size of a copolymer molecule in solution depends on molecular weight and chain composition and sequence length distribution.

The theoretical basis for methods of correction for imperfect resolution are now developed.

THEORY

The integral equation which follows is the starting point for all rigorous methods of correction for imperfect resolution.

$$F(v) = \int_0^\infty W(y)\, G(v,y)dy \qquad (1)$$

F(v) is the detector response at retention volume V. G(v,y) is the normalized detector response for a single species with mean retention volume y. W(y)dy is the area of the detector response for a single species with mean retention volume y. Species with the same mean retention volume may, in certain circumstances, have different molecular weights or compositions as with polymers with long chain branching and copolymers with composition drift. The use of equation (1) with such complex polymer mixtures would imply that polymers with the same mean retention volume or hydrodynamic volume

in solution would have the same single-species chromatogram shape. Tung[3] was the first to apply equation (1) to correct GPC chromatograms for peak broadening. He solved the integral equation numerically for the corrected chromatogram or corrected detector response, W(y). This chromatogram was then integrated to obtain the corrected molecular weight averages. The normalized detector signal for the single species with mean retention volume y, G(v,y) or, as it will henceforth be called, the instrumental spreading function, was assumed to be Gaussian in shape. Tung and Runyon[4] were the first to investigate the hypothesis that polymer solutes of different chemistry, but having the same mean retention volume or size in the mobile phase, have the same single species chromatogram shape. Their limited data for polystyrene, polyvinylchloride and polybutadiene were in agreement with the hypothesis. This concept of universal peak broadening is not unreasonable, as one would expect that polymer solute molecules of the same size in the mobile phase would have the same available pore volume and diffusion coefficients would not differ greatly. The hypothesis would more likely be valid in the equilibrium regime of SEC separations. Many numerical methods have been proposed for the solution of the integral equation over the years. Among the best of these are those developed by Chang and Huang[5] and Ishige, Lee, and Hamielec[6]. The first analytical solution of the integral equation was reported by Hamielec and Ray[7]. This solution which employs a uniform Gaussian spreading function follows. Uniform means that the shape parameters (in the case of the Gaussian distribution, the variance) are independent of mean retention volume y or size of the polymer solute in the mobile phase. In this instance, equation (1) becomes a convolution integral as shown in equation (2).

$$F(v) = \int_0^\infty W(y)\, G(v-y)dy \tag{2}$$

Taking LaPlace transformations of the convolution integral one obtains

$$\bar{F}(s) = \bar{W}(s)\bar{G}(s) \tag{3}$$

where

$$\bar{F}(s) = \int_0^\infty F(v)\exp(-sv)dv \tag{3a}$$

and so on. For a mass detector, the molecular weight averages and intrinsic viscosity are given by

$$\bar{M}_K\ (uc) = \left(\int_0^\infty F(v)M(v)^{K-1}dv\right)\left(\int_0^\infty F(v)M(v)^{K-2}dv\right)^{-1} \tag{4a}$$

$$[\bar{\eta}]\ (uc) = \left(\bar{K}\int_0^\infty F(v)M(v)^{a}dv\right)\left(\int_0^\infty F(v)dv\right)^{-1} \tag{4b}$$

where M(v) is the molecular weight at retention volume v and $\bar{M}_K(uc)$ is the K^{th} molecular weight average of the whole polymer uncorrected for imperfect

resolution. $[\bar{\eta}](uc)$ is the whole polymer intrinsic viscosity uncorrected for imperfect resolution and $\bar{K}$ and a are Mark-Houwink constants for linear polymer. These definitions would not be appropriate for polymers with long chain branching and for copolymers with composition drift. In these cases, even with perfect resolution, the detector cell contains polymer molecules of the same size but possibly very different molecular weights. The appropriate definitions in these cases follow.

$$\bar{M}_K(uc) = \left[\int_0^\infty F(v)\bar{M}_K(v)^{K-1}dv\right]\left[\int_0^\infty F(v)\bar{M}_K(v)^{K-2}dv\right]^{-1} \tag{5a}$$

$$[\bar{\eta}](uc) = \left[\int_0^\infty F(v)\ [\bar{\eta}]\ (v)dv\right]\left[\int_0^\infty F(v)dv\right]^{-1} \tag{5b}$$

where K=1, for the number-average molecular weight average

K=2, the weight-average

K=3, the Z-average

K=4, the Z+1-average and so on

and $\bar{M}_K(v)$ and $[\bar{\eta}](v)$ are the K^{th} molecular weight average and intrinsic viscosity of the detector cell contents at retention volume V when the resolution is perfect. It is now assumed that the following relationships between molecular weight averages and intrinsic viscosity and retention volume, v, hold.

$$\bar{M}_K(v) = D_{1K}\exp(-D_{2K}V) \tag{6a}$$

$$[\bar{\eta}](v) = \bar{D}_1\exp(-\bar{D}_2V) \tag{6b}$$

where D_{1K}, D_{2K} and $\bar{D}_1$ and $\bar{D}_2$ are positive constants.
Introducting these molecular weights and intrinsic viscosity calibration curves into equations (5a) and (5b) one obtains

$$\bar{M}_K(uc) = D_{1K}\,\bar{F}\left[(K-1)D_{2K}\right]/\bar{F}\left[(K-2)D_{2K}\right] \tag{7a}$$

$$[\bar{\eta}](uc) = \bar{D}_1\,\bar{F}\,(\bar{D}_2) \tag{7b}$$

In a similar manner one may write

$$\bar{M}_K(c) = D_{1K}\,\bar{W}\left[(K-1)D_{2K}\right]/\bar{W}\left[(K-2)D_{2K}\right] \tag{7c}$$

$$[\bar{\eta}](c) = \bar{D}_1\bar{W}\,(\bar{D}_2) \tag{7d}$$

for the quantities corrected for imperfect resolution. Substituting equations (7) into equation (3) one obtains

$$\frac{\bar{M}_K(c)}{\bar{M}_K(uc)} = \frac{\bar{G}\left[(K-2)D_{2K}\right]}{\bar{G}\left[(K-1)D_{2K}\right]} \tag{8a}$$

$$\frac{[\bar{n}](c)}{[\bar{n}](uc)} = \frac{1}{\bar{G}(\bar{D}_2)} \tag{8b}$$

It is clear that the correction factors for imperfect resolution depend on the calibration curve slope (D_{2K} and $\bar{D}_2$), the shape of the instrumental spreading function and upon the molecular weight average (K). To take the development of correction factors further one must assume a form for the instrumental spreading function. At this stage it is assumed that it is Gaussian as follows:

$$G(v-y) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-(v-y)^2/2\sigma^2\right) \tag{9}$$

The La Place transformation follows

$$\bar{G}(s) = \exp\left(\frac{s^2\sigma^2}{2}\right) \tag{9a}$$

The correction equations now take on the form

$$\frac{\bar{M}_K(c)}{\bar{M}_K(uc)} = \exp\left((3-2K)(D_{2K}\sigma)^2/2\right) \tag{10a}$$

$$\frac{[\bar{n}](c)}{[\bar{n}](uc)} = \exp\left(-(\bar{D}_2\sigma)^2/2\right) \tag{10b}$$

For the particular case of a linear polymer where under conditions of perfect resolution, all the polymer solute in the detector cell has the same molecular weight, equation (6a) reduces to

$$M(v) = D_1 \exp(-D_2 v) \tag{11}$$

and, in equations (10a) and (10b), $D_{2K} = D_2$ for all K and $\bar{D}_2 = aD_2$ where a is the Mark-Houwink exponent. For the case of complex polymers such as polymers with long chain branching and copolymers with composition drift, the contents of the detector cell may be polydisperse in molecular weight and one then must contend with one calibration curve for each molecular weight average and another for the intrinsic viscosity. This analytical solution can be generalized to include nonlinear molecular weight calibration curves which can be fit with a sum of exponential terms[8]. Another generalization was proposed by Provder and Rosen[9]. They suggested the use of a general instrumental shape function used by statisticians, the Gram-Charlier series. This function is given by

$$G(v) = \phi(v) + \sum_{n=3}^{\infty} (-1)^n \frac{An}{n!} \frac{\phi^n(v)}{\sqrt{1/\sigma^n}} \tag{12}$$

where $\phi(v)$ is a Gaussian distribution and $\phi^n(v)$ denotes its n^{th} order derivatives. The term n=3 corrects for chromatogram skewing. Shape parameters with

n > 4 are of little practical interest in SEC as the number of parameters is then excessive and calibration becomes difficult with little or any added benefit in terms of molecular weight accuracy. With the Gaussian instrumental spreading function corrected for skewing, the corrections for imperfect resolution now become

$$\frac{\bar{M}_K(c)}{\bar{M}_K(uc)} = \exp\left(\frac{(3-2K)(D_{2K}\sigma)^2}{2}\right)\frac{\{1-(K-2)^3 SK_K\}}{\{1-(K-1)^3 SK_K\}} \qquad (13a)$$

$$\frac{[\bar{\eta}](c)}{[\bar{\eta}](uc)} = \exp\left(\frac{-(\bar{D}_2\sigma)^2}{2}\right)\frac{1}{\{1-\overline{SK}\}} \qquad (13b)$$

where $SK_K = (D_{2K}\sigma)^3 A_{3/6}$

Again, these correction equations have been generalized to include the situation where polymer molecules in the detector cell have the same size but different molecular weights. The next major contribution was proposed by Yau et al[16]. They solved the integral equation (equation (1)) in a unique manner and derived correction equations for imperfect resolution for the contents of the detector cell rather than for the whole polymer. They presented solutions for $\bar{M}_N(v)$ and $\bar{M}_W(v)$ for polymer in the detector cell under the restriction that polymer molecules with the same mean retention volume or size in the mobile phase have the same molecular weight. A generalization of their treatment to include higher molecular weight averages and intrinsic viscosity but with the same restriction gives the following solutions:

$$\frac{\bar{M}_K(v,uc)}{M(v)} = \frac{F(v-(K-1)D_2(v)\sigma(v)^2)}{F(v-(K-2)D_2\sigma(v)^2)} \exp\left((2K-3)(D_2(v)\sigma(v))^2/2\right) \qquad (14a)$$

$$\frac{[\bar{\eta}](v,uc)}{[\bar{\eta}](v)} = \frac{F(v-aD_2(v)\sigma(v)^2)}{F(v)} \exp\left(aD_2(v)\sigma(v)^2/2\right) \qquad (14b)$$

where $\bar{M}_K(v,uc)$ is the K^{th} molecular weight average of the contents of the detector cell at retention volume V. The use of absolute detector system such as a low angle laser light scattering photometer in series with a mass detector would give a measure of $\bar{M}_2(v,uc)$. A viscometer detector in series with a mass detector would provide a measure of $[\bar{\eta}](v,uc)$. Equations (14a) and (14b) were derived assuming constant D_2 and σ when integrating in the detector cell. The contributions from neighboring species falls off rapidly and one can therefore set $D_2 = D_2(v)$ and $\sigma = \sigma(v)$ with negligible error. In other words, these equations apply for the more general situation where the molecular weight calibration curve is non-linear and where the peak broadening parameter σ changes with molecular weight or retention volume. Equations (14a) and (14b)

are now generalized to include the SEC of complex polymers where, even under conditions of perfect resolution, polymer molecules in the detector cell having the same size in the mobile phase may have very different molecular weights. The generalized equations follow:

$$\frac{\bar{M}_K(v,uc)}{\bar{M}_K(v)} = \frac{F(v - (K-1)D_{2K}(v)\sigma(v)^2)}{F(v - (K-2)D_{2K}(v)\sigma(v)^2)} \exp\left(\frac{(2K-3)(D_{2K}(v)\sigma(v))^2}{2} \right) \quad (15a)$$

$$\frac{[\bar{\eta}](v,uc)}{[\bar{\eta}](v)} = \frac{F(v - \bar{D}_2(v)\sigma(v)^2)}{F(v)} \exp\left((\bar{D}_2(v)\sigma(v))^2/_2 \right) \quad (15b)$$

For complex polymers there is an infinite number of molecular weight calibration curves. We shall concern ourselves with those which are of some practical interest. To illustrate the use of the equations, a multiple absolute detector system which includes a low angle laser light scattering photometer, a viscometer, and a mass detector will be considered later in the section on applications. Another important development in the treatment of complex polymers was the generalization of the universal molecular weight calibration curve by Hamielec and Ouano[10]. When dealing with complex polymers, the universal calibration curve is a plot of $[\bar{\eta}](v)\,\bar{M}_N(v)$ versus retention volume. An online viscometer gives a measure of $[\bar{\eta}](v,uc)$ and, of course, $[\bar{\eta}](v)$ is the correct intrinsic viscosity to use with the universal calibration curve.

APPLICATIONS OF RESOLUTION CORRECTION FACTORS

Non-complex Polymers (linear polymers, uniform copolymers, and specially synthesized polymers with long chain branching).

Noncomplex polymers have a unique size - molecular weight relationship and these are considered first. For polymers of this type equations (10a), (10b), (13a), (13b), (14a) and (14b) are appropriate. A number of detector systems will now be considered.

Single Mass Detector

Equations (13a) and (13b) with $D_{2K} = D_2$ and $SK_K = SK$ for all K values and $\bar{D}_2 = aD_2$, where a is the Mark-Houwink exponent, should be used in this instance. The peak broadening parameters σ and SK can be determined using narrow or broad MWD standards if the molecular weight calibration curve is known. D_2 can be considered the slope of the molecular weight calibration curve at the peak position of the chromatogram. If skewing of single-species chromatograms can be neglected (SK=0), two broad MWD standards may be used along with equations (13a) and (13b) and the universal molecular weight calibration curve based on polystyrene to obtain the peak broadening parameter

σ and the molecular weight calibration curve for the polymer in question[11]. Once the peak broadening parameters have been measured, equations (13a) and (13b) may be used to correct the average molecular weights and intrinsic viscosity for imperfect resolution of other polymer samples being analyzed by SEC. Universal calibration of peak broadening parameters may find use here[4].

Low Angle Laser Light Scattering Photometer and Mass Detector

Equations (10a) and (14a) should be used in this instance. The detector system measures $\bar{M}_W(v,uc)$. This local weight average molecular weight can be integrated to obtain the true $\bar{M}_W(t)$ of the whole polymer using equation (16). Hence, the term absolute detector.

$$\bar{M}_W(t) = \int_0^\infty F_N(v)\, \bar{M}_W(v,uc)dv \qquad (16)$$

where $F_N(v)$ is the normalized mass detector response.

In applying equation (10a), $\bar{M}_W(c)$ is set equal to $\bar{M}_W(t)$ and again $D_{2K} = D_2$ for all K. The normalized mass detector response $F_N(v)$ and the molecular weight calibration curve can be used to determine $\bar{M}_W(uc)$ using equation (5a). Equation (10a) can then be solved to determine an average σ for the whole chromatogram. One can get more detailed information on the variation of σ with retention volume or molecular weight through the use of equation (14a). For the case K=2, the left side of equation (14a) is known and one can therefore solve for σ as a function of retention volume. If the molecular weight calibration curve is not known, but the universal molecular weight calibration curve based on polystyrene is, one can use the following approach. Equation (14a) can be rewritten as follows:

$$\frac{\bar{M}_W(v,uc)}{\alpha\, f(v)^\beta} = \frac{F(v - D_2(v)\sigma(v)^2)}{F(v)} \exp\left(\frac{(D_2(v)\sigma(v))^2}{2} \right) \qquad (17)$$

where $\alpha = (1/\bar{K})^{\frac{1}{1+a}}$ and $\beta = \frac{1}{1+a}$

and $\bar{K}$ and a are the Mark-Houwink constants for the polymer in question and the universal calibration curve is given in equation (18).

$$[\bar{\eta}](v)\, M(v) = f(v) \qquad (18)$$

We now have unknowns α, β and the few constants required to describe the variation of σ with retention volume. $D_2(v)$ is a function of v and the two parameters α and β. Equation (17) at an appropriate number of retention volumes can be used to solve for these unknowns. We have thus determined

the molecular weight calibration curve, the peak broadening parameters, and the Mark-Houwink constants simultaneously. A similar application of the Chromatix KMX-6 detector was recently suggested by McConnell[12].

Viscometer and Mass Detector

Equations (10b) and (4b) should be used in this instance. The detector system measure $[\bar{\eta}](v,uc)$. This local intrinsic viscosity can be integrated to obtain the true intrinsic viscosity of the whole polymer $[\bar{\eta}](t)$ using equation (19).

$$[\bar{\eta}](t) = \int_0^\infty F_N(v)[\bar{\eta}](v,uc)dv \qquad (19)$$

Hence, the term absolute detector is used. In applying equation (10b), $[\eta](c)$ is set equal to $[\eta](t)$ and $D_2 = aD_2$. The mass detector response along with the molecular weight calibration curve and Mark-Houwink constants can be integrated to determine $[\bar{\eta}](uc)$. Equation (10b) can then be solved for an average σ for the whole chromatogram. One can get more detailed information on the variation of σ with retention volume or molecular weight through the use of equation (14b). If the molecular weight calibration curve is known, the universal calibration curve can be used to determine $[\bar{\eta}](v)$. Equation (14b) would then permit the determination of the variation of σ with retention volume. If the molecular weight calibration curve is not known, the following approach may be used. Equation (14b) may be rewritten as follows:

$$\frac{[\bar{\eta}](v,uc)}{\alpha f(v)^\beta} = \frac{F(v-aD_2(v)\sigma(v)^2)}{F(v)} \exp\left(\frac{(aD_2(v)\sigma(v))^2}{2}\right) \qquad (20)$$

where $\alpha = (\frac{1}{K})^{\frac{1}{1+a}}$ and $\beta = \frac{a}{1+a}$

We now have unknowns $\bar{K}$, a and the few constants required to describe the variation of σ with retention volume. The universal calibration curve is again given by equation (18). Equation (20) at an appropriate number of retention volumes can be solved for these unknowns. We have thus determined the molecular weight calibration curve, the peak broadening parameters and the Mark-Houwink constants simultaneously.

Complex Polymers (polymers with long chain branching and copolymers with composition drift).

Complex polymers do not have a unique size - molecular weight relationship and even under conditions of perfect resolution, when all of the polymer solute molecules in the detector cell have the same size in the mobile phase,

these can be a wide range of molecular weights at the same retention volume. This gives rise to an infinite number of molecular weight calibration curves. For practical purposes we will limit our consideration to the following calibration curves, $\bar{M}_N(v)$, $\bar{M}_W(v)$, $\bar{M}_Z(v)$, $\bar{M}_{Z+1}(v)$, and $[\bar{\eta}](v)$ versus retention volume. For polymers of this type, equations (13a), (13b), (15a), and (15b) should be employed. A number of detector systems will now be employed.

Single Mass Detector

Methods of treating polymers with long chain branching using a single mass detector have been published by Drott and Mendelson[13], Ram and Miltz[14] and more recently by Foster, Hamielec and MacRury[15]. These indirect methods were developed because of the unavailability of a suitable viscometer detector. These methods require a measure of the whole polymer intrinsic viscosity. The method proposed by Foster, et al, uses C^{13} NMR to provide the absolute number of long chain branches per 1000 carbon atoms for high pressure, low density polyethylene to calibrate SEC and thus permit it to give a measure of long chain branching frequency.

Low Angle Laser Light Scattering Photometer and Mass Detector

Equations (13a) and (15a) with K=2 should be applied here. The detector system provides a measure of $\bar{M}_W(v,uc)$ and integration using equation (16) gives the true $\bar{M}_W(t)$ of the whole polymer. Let us suppose that the molecular weight calibration curve is nonlinear and of the form

$$\ln \bar{M}_W(v) = f(v, C_i) \tag{21}$$

where C_i are fitting parameters.

$D_{22}(v)$ in equation (15a) may be determined by finding the first derivative of equation (21) at v. Applying the principle of universal peak broadening one could determine $\sigma(v)$ using narrow MWD polystyrene standards. The fitting parameters in equation (21) C_i may then be determined solving equation (15a) at a sufficient number of retention volumes. The other possibility is to solve for both C_i and $\sigma(v)$ using solutions of equation (15a).

Viscometer and Mass Detector

Equations (13b), (15a), and (15b) should be used with this detector system which provides a measure of $[\bar{\eta}](v,uc)$. Integration using equation (19) provides the true whole polymer intrinsic viscosity, $[\bar{\eta}](t)$. Again, we express the intrinsic viscosity calibration curve in some nonlinear form as follows

$$[\bar{\eta}](v) = f(v, \alpha_i) \tag{22}$$

where α_i are fitting parameters. In principle, equation (15b) may be solved at a sufficient number of retention volumes to give α_i and $\sigma(v)$. Once α_i are

known, one can use the universal molecular weight calibration curve given in equation (23) to provide $\bar{M}_N(v)$[10].

$$[\bar{\eta}](v)\ \bar{M}_N(v) = f(v) \tag{23}$$

The following integration gives the true number-average molecular $\bar{M}_N(t)$.

$$\bar{M}_N(t) = \left(\int_0^\infty F_N(v)\ \bar{M}_N^{-1}(v,uc)dv \right)^{-1} \tag{24}$$

$\bar{M}_N(v,uc)$ is calculated using equation (15a).

In principle, the viscometer detector provides more information than the light scattering detector and can be used with nonuniform copolymers. The detectors provide independent information and should be used simultaneously, particularly when analyzing polymers with long chain branching.

CONCLUDING REMARKS

The advent of absolute detector systems such as the Chromatix KMX6 and viscometers which may be used online with SEC has provided powerful tools for the molecular weight characterization of complex polymers systems such as polymers with long chain branching and nonuniform copolymers. The mathematics of chromatogram interpretation which include corrections for imperfect resolution are now highly developed and appropriate for absolute detector systems. It is certain that in the near future those new tools will provide unique and valuable information on the molecular architecture of complex polymers.

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