

CHARACTERIZATION OF COMPLEX POLYMER SYSTEMS BY SIZE EXCLUSION
CHROMATOGRAPHY - HOMOPOLYMERS WITH LONG CHAIN BRANCHING AND
COPOLYMERS WITH COMPOSITION DRIFT

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Abstract - Problems associated with the characterization by size exclusion chromatography (SEC) of complex polymers, polymers for which a unique relationship between size and molecular weight does not exist, are considered. An attempt is made to develop a general methodology for the SEC of these polymers. This includes generalized universal molecular weight calibration, corrections for imperfect resolution and the use of multidetector systems, including low angle laser light scattering photometry, viscometry and UV and IR spectrophotometry. Included are examples of the estimation of branching frequency and sequence length across the SEC chromatograms of branched homopolymers and copolymers.

INTRODUCTION

SEC separates flexible polymer molecules according to hydrodynamic volume and this forms the basis of universal calibration ($\ln[\eta]M$ versus retention volume (Ref. 1)). For simple polymers, polymers for which a unique relationship between hydrodynamic volume and molecular weight exists, the use of universal calibration is clear. Under ideal conditions of perfect resolution, polymer solute molecules in the detector cell have the same hydrodynamic volume and the same molecular weight. Of course, under actual conditions of imperfect resolution, the detector cell contents vary in size and molecular weight. The practical application of universal calibration requires that certain conditions be met. For example, interactions such as polymer solute/packing interactions must be minimal, so that the separation is truly on the basis of hydrodynamic volume. The product of intrinsic viscosity and molecular weight is proportional to hydrodynamic volume at infinite dilution. Polymer solute concentrations often employed in SEC particularly for higher molecular weight solutes in good solvents can result in significant coil size reduction (Ref. 2). Extrapolations to infinite dilution may be necessary at the high molecular weight end of the calibration curve to obtain accurate molecular weight measurements.

With complex polymers, polymers for which a unique relationship between hydrodynamic volume and molecular weight does not exist, and under ideal conditions of perfect resolution, polymer solute molecules in the detector cell have the same hydrodynamic volume, but possibly, quite different molecular weights. The universal calibration curve, as originally proposed (Ref. 1), does not apply and must be generalized for complex polymers (Ref. 3). A typical example of a complex polymer is low density polyethylene synthesized at high pressures via free radical polymerization. The mechanism of synthesis clearly shows that, at intermediate and high levels of conversion, the whole polymer produced contains linear chains with a distribution of molecular weights, as well as chains containing one or more long branches. Clearly, the hydrodynamic volume is not a unique function of molecular weight for such a mixture of polymer chains.

GENERALIZATION OF UNIVERSAL CALIBRATION

It is assumed that polymer solute concentrations are sufficiently low to permit infinite dilution relationships to be applied with the effect of solute concentration on coil size negligible (Ref. 2). At this point, it is assumed that perfect resolution is closely approached so that polymer solute molecules in the detector cell have the same hydrodynamic volume. The necessary account for imperfect resolution will be made later. Consider that the detector cell contains a complex polymer at some retention volume, v . A common property for the components in the detector cell is the hydrodynamic volume. Hence, one may write

$$J_1(v) = J_2(v) = \dots = J_1(v) = J_{PS}(v) \quad (1)$$

where $J_i(v) = [\eta]_i M_i$, and subscript PS stands for polystyrene. The intrinsic viscosity of the mixture, $[\eta](v)$, is given by

$$[\eta](v) = \sum_i W_i(v) [\eta]_i(v) = \sum_i \left(\frac{W_i(v)}{M_i(v)} \right) J_i(v) = J_i(v) / \bar{M}_N(v) \quad (2)$$

It is clear that the generalization of universal calibration for complex polymers is given by (Ref. 3).

$$[\eta](v) \bar{M}_N(v) = [\eta]_{PS}(v) M_{PS}(v) \quad (3)$$

It is now appropriate to define equivalent quantities for the actual case where resolution is imperfect. $[\eta](v,uc)$, $\bar{M}_N(v,uc)$, $\bar{M}_W(v,uc)$ and, in general, $\bar{M}_k(v,uc)$ are intrinsic viscosity, number, weight and K^{th} molecular weight averages of the detector cell contents not corrected for imperfect resolution. It is these polymer properties which are measured with online detectors, such as viscometer and laser light scattering photometer. The equivalent properties for the whole polymer may be found by integration, as follows.

$$[\eta](c) = \int_0^{\infty} F_N(v) [\eta](v,uc) dv \quad (4)$$

$$\bar{M}_W(c) = \int_0^{\infty} F_N(v) \bar{M}_W(v,uc) dv \quad (5)$$

$$\bar{M}_N(c) = \left(\int_0^{\infty} F_N(v) \bar{M}_N^{-1}(v,uc) dv \right)^{-1} \quad (6)$$

where the argument 'c' stands for 'corrected for imperfect resolution'. A measurement of $[\eta](v,uc)$ by viscometry, correction for imperfect resolution to give $[\eta](v)$ and then application of generalized universal calibration permits calculation of $\bar{M}_N(v)$. An inverse correction for imperfect resolution will then give $\bar{M}_N(v,uc)$. Corrections for imperfect resolution are derived later. An online viscometer and light scattering detector can, in principle, provide \bar{M}_N , \bar{M}_W , and $[\eta]$ for the contents of the detector cell and hence, calibration curves for these same quantities. Complex polymers, in fact, have an infinite number of calibration curves for molecular weight averages. We now address the question of estimation of the molecular weight distribution $W(M,v)$ of the contents of the detector cell. Assuming a unimodal distribution, one could calculate $W(M,v,uc)$ with an appropriate inverse correction for imperfect resolution. The molecular weight distribution of the whole polymer is then given by

$$W(M,c) = \int_0^{\infty} F_N(v) W(M,v,uc) dv \quad (7)$$

In eqns. (4) to (7), $F_N(v)$ is the normalized mass concentration detector response. The polydispersity, $\bar{M}_W(v)/\bar{M}_N(v)$ gives a measure of the deviation from simple polymer behaviour. A value of unity implies simple behaviour, whereas values greater than unity may be due to long chain branching or copolymer composition variations, for example. Techniques to estimate long chain branching frequency and copolymer composition will be discussed later.

ANALYSIS OF IMPERFECT RESOLUTION

Tung's integral equation, which follows, is the starting point for all rigorous methods of correction for imperfect resolution.

$$F(v) = \int_0^{\infty} W(y) G(v,y) dy \quad (8)$$

$F(v)$ is the detector response or chromatogram at retention volume, v . The kernel $G(v,y)$ is called the instrumental spreading function and 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 in the range, $y-y+dy$. $W(y)$ may be considered the detector response or chromatogram for the whole polymer sample corrected for peak

broadening. The practical application of the integral equation requires that single species act independently and, in particular, that $G(v,y)$ is independent of the concentration and size distribution of solute in the whole polymer sample injected. In addition, species with the same mean retention volume may, in certain circumstances, have significantly different instrumental spreading functions. This might arise with complex polymers, especially where copolymer composition variations and long chain branching frequency variations are appreciable. In these instances, eqn. (8) would be replaced with an equivalent multiple integral form. To date, no progress has been made in this direction and therefore, it will be assumed that $G(v,y)$ is the same for species with the same mean retention volume in the derivation of corrections for imperfect resolution. We now define a distribution function $W(v,y)$, where $W(v,y)dvdy$ is the area under the detector response in the retention volume range, $v-v+dv$ due to polymer solute with mean retention volume in the range, $y-y+dy$. This function has the following properties.

$$W(v,y) = W(y)G(v,y) \quad (9)$$

$$\int_0^{\infty} W(v,y) dy = F(v) \quad (10)$$

$$\int_0^{\infty} W(v,y) dv = W(y) \quad (11)$$

It is clear from eqn. (11) that a knowledge of $W(v,y)$ permits a direct integration to obtain $W(y)$. An online detector which could measure $W(v,y)$ would provide an instrumental measurement of $W(y)$, the detector response corrected for imperfect resolution. This possibility will be discussed later. We now consider the special case where $G(v,y)$ is Gaussian, with a variance which depends on mean retention volume, y . For this situation, eqn. (8) takes the form

$$F(v) = 1/\sqrt{2\pi\sigma(v)^2} \int_0^{\infty} W(y) \exp\{-(v-y)^2/2\sigma(v)^2\} dy \quad (8a)$$

The use of $\sigma(v)$ rather than $\sigma(y)$ is an approximation which should be valid when peak broadening is not excessive. The distribution of molecular sizes in the detector cell now takes the form

$$W(v,y) = (W(y)/\sqrt{2\pi\sigma(v)^2}) \exp\{-(v-y)^2/2\sigma(v)^2\} \quad (9a)$$

$\bar{M}_W(v,uc)$ is now calculated as follows for a mass concentration detector

$$\begin{aligned} \bar{M}_W(v,uc) &= \int_0^{\infty} \bar{M}_W(y) W(v,y) dy / \int_0^{\infty} W(v,y) dy \\ &= \frac{\bar{M}_W(v) \exp((D_{22}(v)\sigma(v))^2/2)}{F(v)/\sqrt{2\pi\sigma(v)^2}} \int_0^{\infty} W(y) \exp\left\{-\frac{((v-D_{22}(v)\sigma(v))^2 - y)^2}{2\sigma(v)^2}\right\} dy \end{aligned} \quad (12)$$

Comparing integrals in eqn. (8) and (12), it is clear that

$$\frac{\bar{M}_W(v,uc)}{\bar{M}_W(v)} = \frac{F(v-D_{22}(v)\sigma(v)^2)}{F(v)} \exp((D_{22}(v)\sigma(v))^2/2) \quad (13)$$

where $D_{22}(v)$ is defined in general as

$$\bar{M}_K(y) = D_{1K}(v) \exp(-D_{2K}(v)y) \quad (14)$$

where $K=1$ refers to the number average molecular weight; $K=2$, the weight average molecular weight; and so on. If desired, K could take on non-integer values and represent non-integer molecular weight averages. For the special case of simple polymers, $\bar{M}_K(y) = M(y)$ and only one molecular weight calibration curve need be considered. Nonlinearities in the molecular weight calibration curves are accounted for using local linearization with eqn. (14). Corrections for imperfect resolution for other molecular weight averages and intrinsic viscosity may be derived in a similar manner and these follow.

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

$$\frac{[\eta](v, uc)}{[\eta](v)} = \frac{F(v - D_2(v)\sigma(v)^2)}{F(v)} \exp\{(D_2(v)\sigma(v))^2/2\} \quad (16)$$

where $D_2(v)$ is defined as

$$[\eta](y) = D_1(v) \exp(-D_2(v)y) \quad (17)$$

For simple polymers, the infinite number of calibration curves for molecular weight averages given by eqn. (14) collapses into one molecular weight calibration curve. Corrections for imperfect resolution for the whole polymer samples are given by

$$\bar{M}_K(c) = \int_0^\infty F(v) \bar{M}_K^{K-1}(v, uc) dv / \int_0^\infty F(v) \bar{M}_K^{K-2}(v, uc) dv \quad (18)$$

$$[\eta](c) = \int_0^\infty F(v) [\eta](v, uc) dv / \int_0^\infty F(v) dv \quad (19)$$

These equations, which correct for imperfect resolution, will now be applied for different online detector systems.

Online molecular weight detection

Consider the online measurement of $\bar{M}_W(v, uc)$ by low angle laser light scattering photometry. An application of eqn. (13) will be made for SEC operating with micropacking (packing particles of, say, 5-15 microns) and with macropacking (say, 30-60 microns). This is to illustrate the use of eqn. (13) and to compare corrections for imperfect resolution for these two packing systems, which have considerably different peak separation and peak broadening. To make this comparison, a whole polymer sample with a most probable distribution will be considered.

$$W(M) = (M/\bar{M}_N^2) \exp(-M/\bar{M}_N) \quad (20)$$

with $\bar{M}_N = 2 \times 10^5$ and $\bar{M}_W = 4 \times 10^5$.

For convenience, it is assumed that D_{12} and D_{22} in eqn. (14) are independent of retention volume, v , and that σ^2 also is independent of v . The associated chromatogram is given by

$$W(v) = \frac{D_{22} D_{12}^2}{\bar{M}_N} \exp\{-2D_{22}v\} \exp\left\{-\left(\frac{D_{12}}{\bar{M}_N}\right) \exp(-D_{22}v)\right\} \quad (21)$$

Relatively small corrections for peak broadening are considered and for our broad MWD, one can set $F(v) \approx W(v)$ with small error. The parameters in these equations employed for micro- and macropackings and the corrections obtained across the chromatogram, as well as the whole polymer ($\bar{M}_W(c)/\bar{M}_W(uc)$) correction, are shown in Table 1.

Several interesting observations can be made. Firstly, the corrections to \bar{M}_W across the chromatogram are substantial at both the high and low molecular weight ends of the distribution being about 25% and 15% even though the \bar{M}_W correction to the whole polymer is only about 3%, indicating a column set with very good resolution. The conclusion is clear - when taking \bar{M}_W measurements across the chromatogram, corrections for imperfect resolution are imperative if an accurate molecular weight calibration curve is to be obtained. This is true even for SEC operation with very high resolution involving either micro- or macropackings. Corrections for imperfect resolution near the peaks of the chromatograms are quite small and, in many circumstances, may be neglected.

Measurement of the peak broadening parameter ($\sigma(v)^2$). This will be illustrated initially with polystyrene, where almost monodisperse MWD standards are available and of course, it is

TABLE 1. Corrections for imperfect resolution for micro- and macropackings - weight-average molecular weights across the chromatogram with $\bar{M}_W(c)/\bar{M}_W(uc) = 0.969$.

Micropacking			Macropacking		
$D_{12} = 2.15 \times 10^{10}$			$D_{12} = 1.768 \times 10^8$		
$D_{22} = 0.357 \text{ ml}^{-1}$			$D_{22} = 0.0862 \text{ ml}^{-1}$		
$\sigma = 0.7 \text{ ml}$			$\sigma = 2.9 \text{ ml}$		
$D_{22\sigma} = 0.25$			$D_{22\sigma} = 0.25$		
$D_{22\sigma^2} = 0.175 \text{ ml}$			$D_{22\sigma^2} = 0.725$		

v(ml)	F(v) x 10 ³	$\bar{M}_W(v,uc)/\bar{M}_W(v)$	v(ml)	F(v) x 10 ³	$\bar{M}_W(v,uc)/\bar{M}_W(v)$
27	16.0	0.745	56	3.6	0.740
28	64.0	0.853	60	14.4	0.846
29	136.3	0.937	64	31.2	0.930
30	186.6	1.002	68	44.1	0.995
31	187.7	1.005	72	46.1	1.041
32	152.1	1.084	76	38.9	1.077
33	105.9	1.109	80	28.2	1.105
34	66.4	1.127	84	18.4	1.122
35	38.6	1.139	88	11.1	1.134
36	21.3	1.153	92	6.3	1.147

a simple polymer. The molecular weight calibration curve is constructed, using peak retention volumes and then local slopes ($D_2(v)$) are found. For a simple polymer, $\bar{M}_W(v)$ may be set equal to $M(v)$, the single molecular weight calibration curve which we have already constructed. Measurements of $\bar{M}_W(v,uc)$ across the chromatogram of a broad MWD polystyrene permit one to estimate $\sigma(v)^2$ via eqn. (15) with $K=2$.

In certain circumstances, it may be justified to use $\sigma(v)^2$ measured for polystyrenes for other polymers. This is the principle of universal peak broadening calibration which has some experimental as well as theoretical justification (Ref. 8). One might argue that, since at a given retention volume, polymer solute molecules have the same hydrodynamic volume and available pore volume, their diffusion coefficients and diffusion paths and thus, $\sigma(v)^2$ would not differ greatly, even though their chemical compositions and structure do. To date, insufficient experimental examination of this universal principle of peak broadening has been done to permit comment on its reliability. However, in the absence of $\sigma(v)^2$ values for a particular polymer, it is recommended that polystyrene values be employed when corrections for imperfect resolution are not too large (say, $\bar{M}_W(c)/\bar{M}_W(uc) > 0.9$).

Let us now consider a polymer for which normally narrow MWD standards are not available. In this regard, it is convenient to refer to dextrans and the excellent work done by Basedow et al (Ref. 9). These workers obtained narrow MWD dextran standards by fractionation and did a comprehensive investigation of the effect of molecular weight and SEC operating variables on $\sigma(v)^2$. Values of $\sigma(v)^2$ measured by Basedow et al (Ref. 9) and by Kim et al (Ref. 10), using the KMX6 low angle laser light scattering photometer, are in reasonable agreement, illustrating the great utility of online light scattering measurements in giving an almost complete calibration for peak broadening with the use of a single broad MWD standard. The refractive index increment (dn/dc) was also measured across the chromatogram to correct for variations possibly due to molecular weight dependence at the low molecular weight end and variations in polymer solute composition and structure which often only appear evident after fractionation.

Online viscosity detection

An online measurement of intrinsic viscosity gives a measure of $[\eta](v,uc)$. It is of interest to compare the magnitudes of imperfect resolution corrections for \bar{M}_W and $[\eta]$. Using the data in Table 1 for macropacking, one can show, using eqn. (16), that at a retention volume, $v = 56$, $[\eta](v,uc)/[\eta](v) = 0.809$ when a Mark-Houwink exponent, $a = 0.706$ is used. The correction for intrinsic viscosity is somewhat lower but certainly significant (19% versus 26%). The variation of the correction factor over the chromatogram should be similar to that for \bar{M}_W .

Given $D_2(v)$ and $\sigma(v)^2$, one can employ the universal calibration curve to obtain $\bar{M}_N(v)$ and with an inverse correction for imperfect resolution, find $\bar{M}_N(v,uc)$ and then, with use of eqn. (18), $\bar{M}_N(c)$ for the whole polymer. The use of online viscosity detection to estimate long chain branching frequency across the chromatogram will be considered later.

Online molecular weight distribution detection

The starting point for such a measurement would be the distribution function, $W(v,y)$. The exact form of this function depends on $W(y)$ and thus, is generally unknown. However, a reasonable approximation is suggested by the fact that often $F(v)$, for many polymer samples, is close to Gaussian in form. It can readily be shown that for constant σ^2 and Gaussian $F(v)$, $W(y)$ and $W(v,y)$ are also Gaussian. For reasonable magnitudes of peak broadening, the size distribution of polymer solute in the detector cell would be unimodal and quite narrow, even though $W(y)$ were bimodal. The following suggested form for $W(v,y)$ should be quite a good approximation over a wide range of SEC operating conditions.

$$W(v,y) = (F(v)/\sqrt{2\pi\bar{\sigma}(v)^2}) \exp\{-(y-\bar{y}(v))^2/2\bar{\sigma}(v)^2\} \quad (22)$$

where $F(v)$ is the detector response and also a normalization factor, following eqn. (10). $\bar{y}(v)$ is the mean of the mean retention volume, y and $\bar{\sigma}(v)^2$ is the variance of $W(v,y)$ at retention volume, v . In principle, online measurements of $\bar{M}_N(v,uc)$ and $\bar{M}_W(v,uc)$ by viscometry and light scattering photometry would permit one to estimate $\bar{y}(v)$ and $\bar{\sigma}(v)^2$, using the following equations.

$$\bar{M}_N(v,uc) = \int_0^\infty W(v,y) dy / \int_0^\infty W(v,y) \bar{M}_N^{-1}(y) dy \quad (23)$$

$$\bar{M}_W(v,uc) = \int_0^\infty W(v,y) \bar{M}_W(y) dy / \int_0^\infty W(v,y) dy \quad (24)$$

For simple polymers, $\bar{M}_N(y) = \bar{M}_W(y) = M(y)$, the unique molecular weight calibration curve. In some instances, a single measurement of, say $\bar{M}_W(v,uc)$, may do, as experience suggests that, for cases where peak broadening is not excessive, $\bar{y}(v) \approx v$. Once, the parameters in $W(v,y)$ are known, a direct integration of $W(v,y)$, according to eqn. (11) or the use of eqn. (27), gives the detector response corrected for peak broadening.

Analytical solution for the molecular weight distribution of whole polymer

When suitable online detectors for the measurement of the parameters of $W(v,y)$ are not available, one can solve for them analytically in terms of $\sigma(v)^2$, the variance of the instrumental spreading function. With this approach, the left-hand sides of eqns. (23) and (24) are given by eqn. (15) with, say, $K = 1$ and 2. The result follows (Ref. 6).

$$\bar{y}(v) = v + 1/D_2(v) \ln\{F(v + D_2(v)\sigma(v)^2)/F(v - D_2(v)\sigma(v)^2)F(v + D_2(v)\sigma(v)^2)\} \quad (25)$$

$$\bar{\sigma}(v)^2 = \sigma(v)^2 + 1/D_2(v)^2 \ln\{F(v - D_2(v)\sigma(v)^2)F(v + D_2(v)\sigma(v)^2)/F(v)^2\} \quad (26)$$

It can be readily shown, with a Taylor series expansion accurate to second order, that

$$\bar{y}(v) = v + \sigma(v)^2 F^1(v)/F(v) \quad (25a)$$

$$\bar{\sigma}(v)^2 = \sigma(v)^2 + \sigma(v)^4 \{F^{11}(v)/F(v) - (F^1(v)/F(v))^2\} \quad (26a)$$

The expansion properly eliminates the dependence on $D_2(v)$. For computational reasons, it is easier to employ eqns. (25) and (26) with any convenient $D_2(v)$. A knowledge of $\sigma(v)^2$, the variance of the Gaussian instrumental spreading function, permits one to find $W(y)$ by a simple direct integration, using eqn. (11) or the use of eqn. (27), for cases where peak broadening is not excessive.

$$W(v) = F(v)(\sigma(v)/\bar{\sigma}(v)) \exp\{-(v-\bar{y}(v))^2/2\bar{\sigma}(v)^2\} \quad (27)$$

An example of the use of this analytical approach to determine $W(v)$ is shown in Fig. 1.

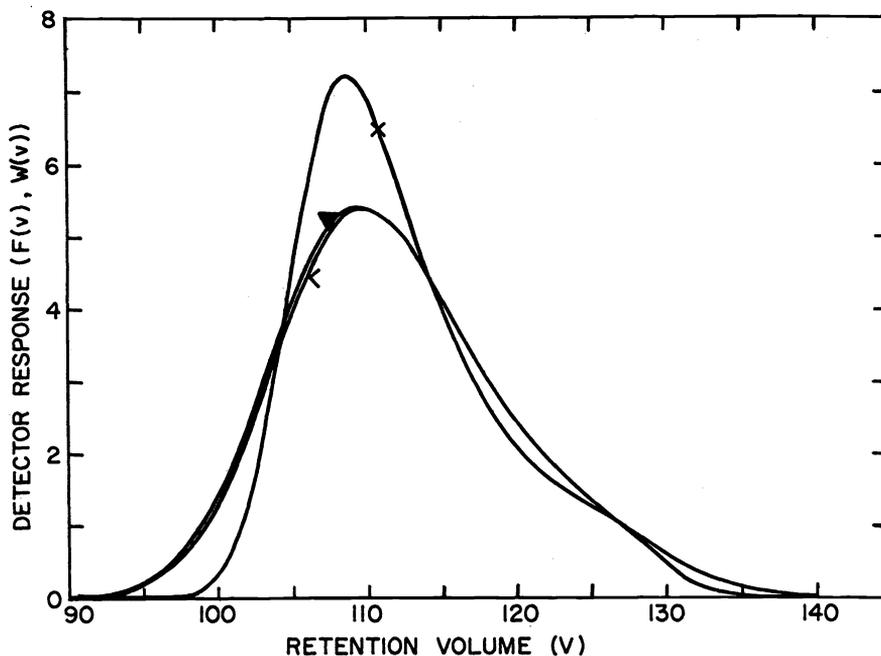


FIGURE 1. ANALYTICAL SOLUTION OF TUNG'S INTEGRAL EQUATION - APPLICATION OF EQU. (27).

	$\sigma^2(v)$ (ML ²)	V (ML)
X W(V) FROM EQU. (27)	16	90 - 10
▼ F(V)	17	102
< W(V) REBROADENED	18	104-125
	16.7	128
	16.2	130
	16.0	132-147

Analytical solution for molecular weight averages of whole polymer

Molecular weight averages and intrinsic viscosity of the whole polymer corrected for imperfect resolution may be obtained by a single direct integration, according to eqns. (18) and (19). The local intrinsic viscosity and molecular weight averages are given by eqns. (15) and (16). For the special case where the molecular weight calibration curve slope, D_{2K} and intrinsic viscosity curve slope $D_2(v)$ and $\sigma(v)^2$ are independent of retention volume, v , eqns. (18) and (19) reduce to the well-known correction equations

$$\bar{M}_K(c) = \bar{M}_K(uc) \exp((3 - 2K)(D_{2K}\sigma)^2/2) \quad (18a)$$

$$[\eta](c) = [\eta](uc) \exp(-(D_2\sigma)^2/2) \quad (19a)$$

For the special case of a simple polymer, D_2 can be set equal to aD_2 , where a is the Mark-Houwink exponent and D_2 is now the slope of the unique molecular weight calibration curve. Also, $D_{2K} = D_2$ in this instance. An example of the use of these solutions with variable D_2 and σ^2 follows for a simple polymer. The nonlinear molecular weight calibration curve which was used, follows

$$\ln M = 27.43 - 0.1922v + 6.62 \times 10^{-4} v^2 \quad (28)$$

The $\sigma(v)^2$ employed are given in the caption of Fig. 1. Molecular weight averages corrected for imperfect resolution obtained via $W(v)$ and by direct integration of $\bar{M}_K(v,uc)$ for $K=1, 2$ and 3, agree within 1%.

LONG CHAIN BRANCHING FREQUENCY MEASUREMENT

The use of online viscosity detection and indirect methods of estimation of intrinsic viscosity across the chromatogram to determine long chain branching frequency of polymer solute having the same hydrodynamic volume will now be discussed. The basis of the measurement is a comparison of the intrinsic viscosities of branched and linear molecules and then the use of the Zimm-Stockmayer branching models (Ref. 12) with some additional information provided for the whole polymer, either by NMR or by a kinetic model which describes branching development. Some data are provided for high pressure, low density polyethylene (HP-LDPE) and poly(vinyl acetate), both commercially important polymers produced by free-radical synthesis. It is useful to briefly discuss the mechanism of synthesis and the development of long chain branching. Long branches are formed mainly by transfer to polymer and the average branch length is the same as the average main chain length produced at some point in time. The rate of formation of the random trifunctional branch points is proportional to the mass of polymer. As a consequence, linear chains are produced at low conversions and the branching frequency (average number of long branches per polymer molecule or say, per 1000 carbon atoms) accelerates with conversion. The polymer product is clearly a complex polymer containing some linear chains (mainly at the low molecular weight end of the distribution) and chains with one or more long branches of varying length. In the production of LDPE, the polymerization temperature generally rises with conversion and as a consequence, the average long branch length will be smaller than the average main chain length.

Online viscosity and molecular weight detection

In principle, an online viscometer can provide a measurement of $[\eta](v,uc)$ and then a correction for imperfect resolution $[\eta](v)$, the intrinsic viscosity of a mixture of branched and linear molecules having the same hydrodynamic volume. The universal molecular weight calibration curve will then give us $\bar{M}_N(v)$ of this mixture of linear and branched chains. Zimm-Stockmayer model for random trifunctional long chain branching follows.

$$([\eta]_b/[\eta]_l)^{1/\epsilon} = ((1 + \bar{B}_N/7)^{1/2} + 4\bar{B}_N/9)^{-1/2} \quad (29)$$

where subscripts b and l represent branched and linear chains of the same molecular weight and \bar{B}_N is the number average number of long chain branches per polymer molecule. For star polymers, a value of $\epsilon = 0.5$ has been obtained (Refs. 13 and 14) and studies of model comb polymers indicate a value of 1.5 (Ref. 15). For random LCB, an ϵ value between 0.7 and 1.3 might be expected. To determine the branching factor ϵ , Foster et al (Ref. 16) studied a large group of HP-LDPE resins by ^{13}C NMR and SEC and found that $\epsilon = 0.75$ gave best agreement for long chain branching frequency for the whole polymers. A value of $\epsilon = 1.0$ was found for poly(vinyl acetate) by comparing SEC measurements with the predictions of a kinetic model (Ref. 16). The applicability of eqn. (29) for the estimation of $\bar{B}_N(v)$ across the chromatogram requires some discussion. The polymer solute in the detector cell is a mixture of linear and branched chains with different branch lengths and branching frequencies. Eqn. (29) applies when branched chains all have the same structure and the comparison is made for linear and branched chains of the same molecular weight. The application of eqn. (29) across the SEC chromatogram is therefore questionable. Errors associated with its application may be partly accounted for by calibrating the SEC with standards having known branching frequencies. The estimation of $\epsilon = 0.75$ for HP-LDPE is in fact this short of calibration. The additional measurement of $\bar{M}_w(v,uc)$ and $\bar{M}_w(v)$ may provide added insight. The polydispersity $PD(v) = \bar{M}_w(v)/\bar{M}_n(v)$ for polymer solute of the same hydrodynamic volume is now known. When $PD(v) = 1.0$, then $\bar{B}_N(v)$ must be zero. It should be possible to develop a useful relationship between $\bar{B}_N(v)$ and $PD(v)$.

Indirect measurement of intrinsic viscosity across the chromatogram

To date, a commercial online micro viscometer is not available and thus, indirect methods have been developed (Refs. 16, 17 and 18). The following polynomial expression may be used to give the variation of intrinsic viscosity across the chromatogram.

$$\ln([\eta](v)) = \ln K + a \ln \bar{M}_N(v) + b (\ln \bar{M}_N(v))^2 + c (\ln \bar{M}_N(v))^3 \quad (30)$$

where K and a are Mark-Houwink constants for the corresponding linear polymer. The constants b and c correct for long chain branching which occurs at higher molecular weights. Polymer chains below some \bar{M}_{N_L} are likely linear and thus, c in eqn. (30) may be replaced with

$$c = -b/\epsilon nM_L \quad (30a)$$

For HP-LDPE, the value normally found for M_L is between 5,000 and 10,000 (Refs. 18 and 19). To determine b and c for a polymer sample, one must first measure, say, \bar{M}_N and $[\eta]$ for the whole polymer. The SEC chromatogram obtained with a mass concentration detector is then integrated using the following procedures. Use an efficient two-variable search routine to find c and b . Guess c and b to give $[\eta](v)$ and $\bar{M}_N(v)$ with the universal molecular weight calibration curve. Apply inverse corrections for imperfect resolution to obtain $[\eta](v,uc)$ and $\bar{M}_N(v,uc)$ and then integrate using $F_N(v)$ to obtain $[\eta](c)$ and $\bar{M}_N(c)$ for the whole polymer. These values are compared with those measured offline and the iterative process is repeated to convergence. Once a suitable value for M_L is found for the polymer type in question, only the whole polymer intrinsic viscosity need be measured offline for a new polymer sample. An application of this indirect procedure to estimate viscosities and then $\bar{M}_N(v)$, $\bar{B}_N(v)$ and $\bar{\lambda}_N(v)$ across the SEC chromatogram are shown in Figs. 2 and 3. $\bar{\lambda}_N(v)$ is the number average number of long branches per 1000 carbon atoms and is given by

$$\bar{\lambda}_N(v) = 1000 M_R \bar{B}_N(v) / \bar{M}_N(v) \quad (31)$$

where M_R is the molecular weight of the repeat unit. \bar{B}_N , the number average number of long branches per polymer molecule in the whole polymer sample is found by integration

$$\bar{B}_N = \bar{M}_N(c) \int_0^{\infty} (W(v) \bar{B}_N(v) / \bar{M}_N(v)) dv \quad (32a)$$

$$\bar{\lambda}_N = 1000 \bar{M}_R \bar{B}_N / \bar{M}_N \quad (32b)$$

Fig. 2 compares whole polymer $\bar{\lambda}_N$ values for HP-LDPE samples A, B and C, measured by ^{13}C NMR and by SEC for different values of ϵ , the branching structure factor. It appears that the three values for ϵ , found to give agreement with NMR, average 0.75 with a relatively small variance. Fig. 3 shows the variation of $\bar{B}_N(v)$ across the chromatogram for a poly(vinyl acetate) sample. As expected, the branching frequency is greater at the higher molecular weight end in agreement with synthesis kinetics.

In certain applications of this indirect method of finding the variation of intrinsic viscosity across the chromatogram, it may not be convenient to construct the universal molecular weight calibration curve using polystyrene standards. It may then be preferable to construct the universal curve using linear samples of the branched polymer which is to be characterized. The molecular weight calibration curve for the linear polymer could be obtained by broad MWD standard calibration methods (Ref. 11), or better still, using online light scattering. The general procedure to follow in the basic indirect method remains the same.

ANALYSIS OF RANDOM COPOLYMERS

The characterization of copolymers by SEC involves two aspects: the measurement of compositional variations across the chromatogram and the measurement of the molecular weight distribution. A copolymer with uniform composition is a simple polymer involving one molecular weight calibration curve which can be obtained by a variety of methods (Refs. 4 and 11). A copolymer with non-uniform composition is a complex polymer with its hydrodynamic volume now a function of composition and sequence length distribution, as well as molecular weight. Under conditions of perfect resolution, the SEC detector cell may now contain polymer molecules having the same hydrodynamic volume but different molecular weights, compositions and sequence length distributions. With copolymers, one may in addition have a very difficult problem with the interpretation of detector responses, particularly with UV-spectrophotometers. Detectors which are usually used for SEC copolymer measurements include differential refractometer and UV and IR spectrophotometers, with usually two detectors in series. A recent comprehensive investigation of the use of these detector types for the SEC analysis of the styrene/acrylonitrile random copolymers (SAN) has been reported by Garcia et al (Refs. 20 and 21). The application of UV spectrophotometers to the analysis of styrene containing copolymers has been extensively reported in the literature. Unfortunately, hypochromic effects and band shifts, which result in deviations from Beer's law, have limited the applications of UV detectors as mass concentration or composition detectors in SEC. To investigate these non-ideal effects more closely, Garcia et al synthesized a large number of SAN copolymers over wide ranges of monomer conversion and composition drift and analyzed them in the infrared, near infrared, visible and ultraviolet regions of the electromagnetic spectrum. IR measurements were done with a Beckman IR-S spectrophotometer using either films or solutions. THF, DMF and CHCl_3 were the solvents normally used. Near IR spectra were measured with a Beckman DK-A spectrometer using CHCl_3 as solvent. Specific refractive index increments and UV absorption were measured with a Waters R-403 differential refractometer and

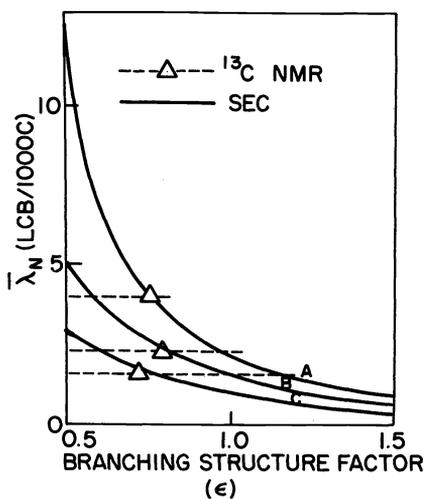


Fig. 2. Effect of the branching structure factor (ϵ) on the whole polymer long chain frequency ($\bar{\lambda}_N$) calculated for three HP-LDPE resins, A, B and C, by SEC. (Ref.16)

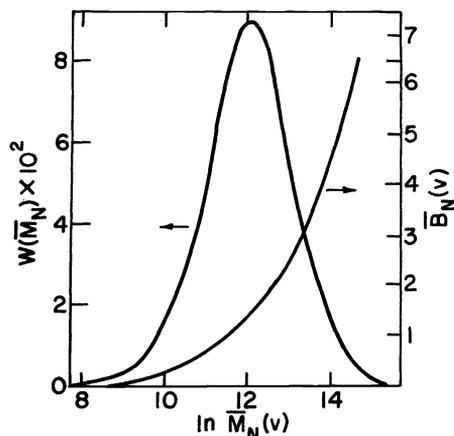


Fig. 3. Molecular weight distribution and number average number of long chain branches per polymer molecule, ($\bar{B}_N(v)$) as a function of $\ln \bar{M}_N(v)$ for a Poly(vinyl acetate) sample. ($\bar{M}_N = 92,000$, $\bar{B}_N = 0.78$, $\bar{\lambda}_N = 0.75$ for $\epsilon=1.0$) (Ref.16)

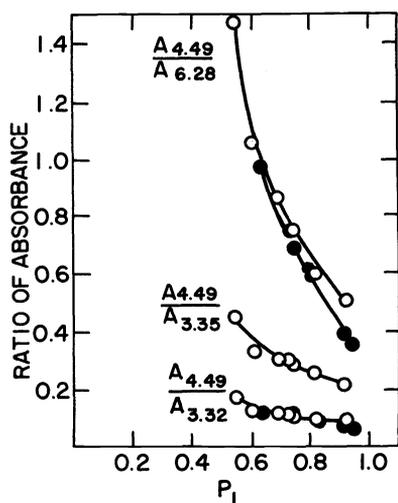


Fig. 4. Infrared absorption ratios for low conversion and homogeneous (o) and high conversion and heterogeneous (●) SAN copolymers versus styrene mole fraction in copolymer.

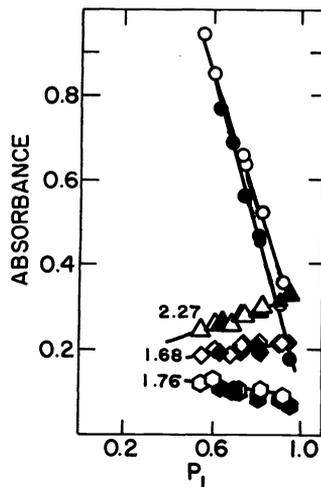


Fig. 5. Near infrared absorbance for low conversion and homogeneous (o, Δ , \diamond , \circ) and high conversion and heterogeneous (●, \blacktriangle , \blacklozenge , \bullet) SAN copolymers versus styrene mole fraction in copolymer.

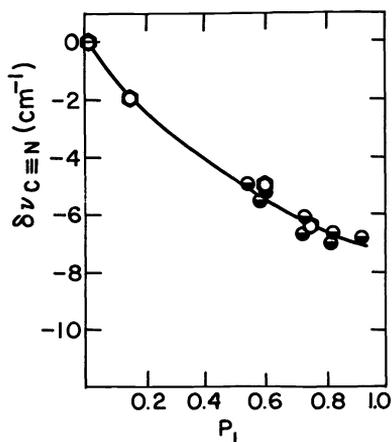


Fig. 6. Infrared shifts of $-C \equiv N$ stretching band versus styrene mole fraction in SAN copolymer (\odot) literature data (Ref. 24) and \circ present data (Ref. 20 & 21).

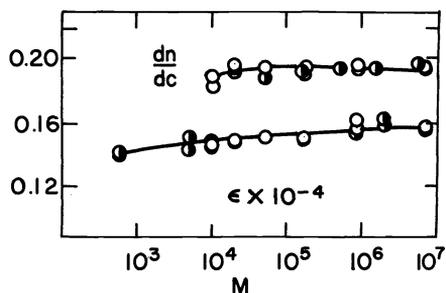


Fig. 7. Specific refractive index increments and extinction coefficients of narrow MWD anionic polystyrene (in THF at 25°C) versus molecular weight (dn/dc : \circ literature data (Ref. 25) and \odot present data (Ref. 20 & 21). (ϵ : present data (Ref. 20 & 21) \circ - Waters dual wavelength UV spectrophotometer, \bullet Beckman Model 25 UV/VIS spectrophotometer)

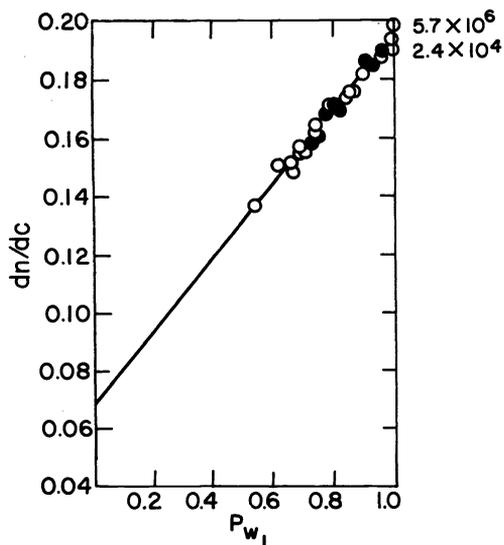


Fig. 8. Specific refractive index increments for low conversion (\circ) and high conversion (\bullet) SAN copolymers versus styrene weight fraction in copolymer (molecular weight range for polystyrene samples is indicated).

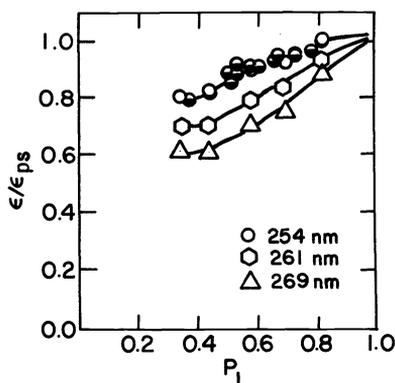


Fig. 9. Normalized extinction coefficients for SAN copolymers (in THF at 25°C) at different wavelengths versus styrene mole fraction in SAN copolymer (\circ - literature data (Ref. 23) and all remaining points are present data (Ref. 20 & 21).

a Waters 440 dual wavelength UV spectrophotometer. All measurements were done at room temperature.

Infrared and near infrared spectroscopy

The application of IR spectroscopy to the analysis of SAN copolymers in solution has two limitations: low solubility of high AN copolymers and often inadequate sensitivity of IR at SEC solute concentration levels. This latter problem is more limiting when the characteristic absorption bands have medium or weak intensities (typically $-C \equiv N$ stretching). Of particular interest are the bands greater than $3.7 \mu\text{m}$, some of which can be detected in a variety of solvents and provide information on the AN/St ratio. The bands at 13 and $14 \mu\text{m}$ are very strong and amenable to detection at SEC concentration levels. These bands contain information on the styrene concentration and molecular structure (Ref. 22). Fig. 4 shows the absorption behaviour of SAN copolymers obtained at low conversions (uniform or homogeneous in composition) and high conversions (non-uniform or heterogeneous in composition). Clearly, the $-C \equiv N$ stretching band is sensitive to the changes in molecular structure induced by the changes in synthesis environment during the course of copolymerization. The effects seem to be greater at lower AN levels in the copolymer. These observations are consistent with the near IR measurements at $2.83 \mu\text{m}$ (see Fig. 5) and show that AN placements in the chain appear to induce isotactic placements in the styrene sequences. In the case of $-C \equiv N$ stretching, not only are changes in intensity observed with increasing AN content in the chains, but also shifts in the position of the band and these also can be correlated with changes in composition (Ref. 20). Fig. 6 shows the band shifts observed for low conversion copolymers. Other absorption bands up to $12.5 \mu\text{m}$ are not as sensitive to the copolymer composition and can be used for mass concentration detection. The absorption bands beyond $12.5 \mu\text{m}$ require more analysis before a definite statement can be made about their sensitivity and information content.

Refractive index and UV spectroscopy

Narrow MWD anionic polystyrene standards were used to quantify the effect of molecular weight on refractive index increment and extinction coefficient in THF (see Fig 7). Specific refractive indices of SAN copolymers were also investigated as a function of copolymer composition (see Fig. 8). All data fall on a straight line within experimental error, indicating that the assumption of additivity appears to be valid. The scatter in the data can be attributed to errors in molecular weight and copolymer composition measurements. As a first step in the analysis of the UV absorption behaviour of SAN copolymers, the effects of tacticity and molecular weight on the extinction coefficients of well-characterized polystyrene samples were investigated. It was found that the A_{254}/A_{269} ratio increases with the fraction of isotactic sequences for homopolystyrene. This was found using isotactic, syndiotactic and atactic polystyrenes. The presence of small levels of AN in SAN copolymers also causes an increase in the A_{254}/A_{269} ratio, suggesting that the presence of AN in the chain increases the formation of isotactic styrene sequences during synthesis. This was confirmed by $^1\text{H NMR}$ measurements (Ref. 20). The extinction coefficients of SAN copolymers do not follow Beer's law, as is shown in Fig. 9. However, assuming that the deviations are due to microstructure differences, the extinction coefficient was found to be highly correlated with the number average length of the styrene sequences. Table 2 shows correlations for three wavelengths.

Table 2. Correlations between molar extinction coefficients and number average styrene sequence length (N_S) in THF at 25°C .

Wavelengths	Correlation	Correlation coefficient
254 nm	$\epsilon/\epsilon_{\text{PS}} = 1 - 0.1831/N_S$	-0.952
261 nm	$\epsilon/\epsilon_{\text{PS}} = 1 - 0.3081/N_S$	-0.995
269 nm	$\epsilon/\epsilon_{\text{PS}} = 1 - 0.4075/N_S$	-0.985

With THF as solvent, it was observed that the tacticity of the styrene sequences did not affect the extinction coefficient significantly. With other solvents, however, the extinction coefficient changed significantly with the tacticity of the styrene sequences. A recommended SEC detector system for SAN copolymer characterization might include a differential refractometer and a UV spectrophotometer which simultaneously measures absorbance at two wavelengths, 254 nm and 269 nm. Working equations for this detector system follow.

$$A(254) = \epsilon_{\text{PS}}(254)(1 - 0.1831/N_S)CP_{W_1} \quad (33)$$

$$A(269) = \epsilon_{\text{PS}}(269)(1 - 0.4075/N_S)CP_{W_1} \quad (34)$$

$$\Delta RI = (dn/dc)_1 C P_{W_1} + (dn/dc)_2 C (1 - P_{W_1}) \quad (35)$$

where $\epsilon_{PS}(254)$ and $\epsilon_{PS}(269)$ are extinction coefficients for polystyrene at 254 nm and 269 nm, and $(dn/dc)_1$ and $(dn/dc)_2$ are refractive index increments for styrene and AN. These are known quantities found by calibration. The absorbances $A(254)$, $A(269)$ and refractive index ΔRI are measured across the chromatogram by an online, dual wavelength UV spectrophotometer and a differential refractometer. One then has three equations to solve for the mass concentration of the copolymer, C , the weight fraction of styrene in the copolymer, P_{W_1} , and the number average styrene sequence length, N_S . Thus, in order to correct the extinction coefficient for compositional variations, a sequence length measurement across the chromatogram has been made possible through calibration of the UV spectrophotometer with NMR. This study has shown that the absorption spectra of SAN copolymers reflect the structure of the polymer chains, especially the masses of the constituent atoms and the intramolecular forces acting between them. It is, therefore, expected that some level of interaction between responses due to mass and those due to configuration and other environmental factors will always be present to some extent. Therefore, the linearity and additivity of the spectrophotometer response should always be verified. The use of these interactions for the elucidation of polymer microstructure appears to be very promising and further research in this area is called for. The use of multiple wavelength detectors, multiple detectors or stop-flow techniques are most appropriate for microstructure analysis in SEC. Of all the detectors investigated, the differential refractometer and the UV spectrophotometer are the most sensitive for SAN copolymers. The IR and near IR spectra, although very sensitive to the microstructure, do not have sufficient sensitivity for dilute solutions used with SEC. Modern instrumentation should be used to investigate further the potential of these two regions, particularly the near IR, where very little work has been done to date. Interesting investigations with other copolymers may be found elsewhere (Refs. 26 to 50).

Online viscosity detection

In principle, an online measurement of intrinsic viscosity across the chromatogram and the universal calibration curve permits one to estimate $M_N(v)$ and the $M_N(c)$ for the whole copolymer by integration. Again, if the polymer is simple, $M_N(v)$ will equal $M(v)$ the unique molecular weight calibration curve and then it is possible, by integration, to find all the molecular weight averages after properly correcting for imperfect resolution. For a simple polymer, an online light scattering measurement can provide $M_W(v,uc)$ and integration $M_W(c)$. However, when the polymer is complex, the measurement of $M_W(v,uc)$ and $M_W(c)$ by light scattering is not straightforward.

Indirect measurement of molecular weight distribution and averages

The availability of Mark-Houwink constants for linear copolymers as a function of microstructure (Ref. 49) permits one to use the following approximate but useful procedure. A dual detector system, as suggested above, gives a measure of composition and number average average sequence length across the chromatogram. The appropriate Mark-Houwink constants may then be used with the universal molecular weight calibration curve to estimate $M(v)$, a sort of effective molecular weight calibration curve. $M(v)$ may then be used to calculate all of the desired molecular weight averages after appropriate corrections for imperfect resolution. This approach may be considered exact for homogeneous copolymers and approximate for heterogeneous copolymers.

A novel approach to the characterization of copolymers by SEC is being developed by Balke and co-workers (Refs. 38 and 52). The method, referred to as orthogonal chromatography, first fractionates the copolymer molecules on the basis of size and then cuts containing copolymer solute of the same hydrodynamic volume are fractionated on the basis of composition. This method should permit a more complete characterization than one based on size separation alone.

CONCLUDING REMARKS

Problems associated with the characterization of complex polymers, such as homopolymers with random long chain branching and heterogeneous copolymers, have been discussed. A methodology for the interpretation of detector responses which includes corrections for imperfect resolution for complex polymers has been suggested, and a few applications to polymers with random long chain branching and copolymers with composition drift given. This methodology should prove useful in future studies of complex polymer systems.

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