

A New Method for Determining Molecular Weight Distributions of Copolymers

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Synopsis

Measurement of the molecular weight distributions of copolymers by size exclusion chromatography (SEC) presents problems because the elution volume of any species may depend on its composition as well as its molecular weight. Also, the response of the usual concentration detectors may also be influenced by the copolymer composition as well as its concentration. These problems arise when the copolymer composition may vary with molecular size. Conventional SEC techniques are suitable for copolymers with invariant compositions. This article describes and illustrates a method for measuring molecular weight distributions of copolymers. In many cases, the variation of copolymer composition with molecular weight can also be determined. The technique uses three detectors: (a) an evaporative detector (ED) to measure the concentration, Δc , of the eluting species; (b) a differential refractive index detector (DRI) to measure the refractive index difference, Δn , between the solution and solvent at any given elution volume; and (c) a low-angle laser light scattering (LALLS) detector that measures the corresponding molecular weight of the eluting solutes. This latter measurement is possible because the appropriate values of $\Delta n/\Delta c$ are available from the outputs of the other two detectors. For LALLS measurements of molecular weight all the species in the detector cell at any instant must have the same composition or, at least not have $\Delta n/\Delta c$ that varies with composition. The method is illustrated with data from ethylene-propylene and ethylene-propylene-diene copolymers.

INTRODUCTION

Measurement of the molecular weight distributions of copolymers presents particular problems that have not been solved heretofore. Size exclusion chromatography (SEC) analyses require corresponding measurements of the concentrations and sizes of polymeric species that elute with given solvent retention volumes.

Concentration measurements are usually made with detectors such as differential refractometers or fixed wavelength spectrometers. Such detectors are suitable for homopolymers or species that vary only in branching character. They are not generally applicable to analyses of copolymers because the detector response in that case may be a function of the solute composition as well as its concentration. Attempts to find detectors that are less sensitive to the composition of the eluting species have met with limited success.

Another problem involved in measurement of the size of the eluting species at a given solvent retention time, is that the method that is practiced most generally requires construction of a universal calibration relation for

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the polymer of interest. Since all species that elute with a given solvent retention volume in SEC have the same solvodynamic volume, universal calibration requires the assumption that solvodynamic volume is a function only of molecular size in the SEC solvent. This is true for homopolymers,² barring concentration effects.^{3,4} It is not necessarily valid for copolymers, however, since the solvodynamic volume and SEC retention volume may be a function of the polymer composition as well as of its molecular weight.

As an alternative to universal calibration, the molecular weight of the species in an SEC detector cell may be measured directly by low-angle laser light scattering (LALLS).⁵ This method, also, is not generally applicable to copolymers because the measured turbidity is a function not only of the molecular weight (M) of the polymer but also of the specific refractive index, dn/dc , in the particular solvent. A single value of dn/dc cannot be assumed for a copolymer sample where composition may vary with molecular weight.

These problems will not apply, of course, if the copolymer composition is invariant with molecular weight. In that case, universal calibration procedures can be applied.⁶ More generally, however, the standard current techniques for molecular weight analyses by SEC are not valid for copolymers.

This article describes and illustrates a method for measuring the molecular weight distributions of copolymers of any complexity. The variation of composition with molecular weight can also be determined, in favorable cases.

ANALYTICAL METHOD

This technique uses three detectors:

1. An evaporative detector (ED, or Mass Detector)⁷⁻⁸ to measure the concentration, Δc , of the eluting species. This detector is based on turbidity from solute particles derived from nebulized effluent. Its response appears to be insensitive to chemical composition and molecular weight compared to the usual differential refractometer detector.⁹

2. A differential refractive index detector (DRI) to measure the refractive index difference, Δn , between the solution and solvent at any given elution volume.

3. A LALLS detector that measures the corresponding molecular weight of the eluting solute. This latter measurement is made possible because the appropriate values of $\Delta n/\Delta c$ ($= dn/dc$ for small elution volume increments) are available from the outputs of the other two detectors.

It should be noted, however, that the $\Delta n/\Delta c$ values are obtained with white light, while the LALLS detector operates with 6328Å wavelength light. A conversion factor is calculated for different copolymer compositions by comparing dn/dc values from a laser differential refractometer with those measured with the conventional DRI detector. Good practice entails the determination of this conversion factor for copolymers with a range of compositions, to ensure that the conversion itself is not composition dependent.

With this technique, it is possible to measure dn/dc of the copolymer solution as a function of molecular weight, and hence to follow variations in chemical composition with molecular size. Application of a method de-

scribed elsewhere also permits the optional calculation of the Mark-Houwink constants of the copolymer as a function of molecular weight.¹⁰

The method is illustrated here with data from analyses of a series of ethylene-propylene (EPR) and ethylene-propylene-diene (EPDM) polymers. In this case, the dn/dc values of polyethylene¹¹ and polypropylene¹² are so similar that variations in ethylene/propylene ratios have no significant effect on the specific refractive index of EPR copolymers. Variations in the diene content in EPDMs may affect dn/dc , however.

EXPERIMENTAL

All measurements were made in trichlorobenzene (TCB) at 135°C. Polymer solutions contained 0.1% (w/v) of Santonox (4, 4'-thiobis-3-methyl-6-tert-butyl-phenol) and 0.1% (w/v) of Irgafos D13-168 (2,4-di-tertbutylphenyl phosphite) to prevent polymer degradation during the analyses. In molecular weight analyses of polyolefins it is necessary to ensure that the polymer solutions are free of supermolecular aggregates.^{11,12} For these particular samples, heating at 135°C for 1.5 hours proved to be sufficient to provide molecularly dispersed solutions. This was judged by the absence of "spikes" in the LALLS output.¹¹

For dn/dc determinations, samples were prepared in concentrations ranging between 1 and 3 mg/mL. Specific refractive index increment values were measured at 5328 Å with a Chromatix KMX-16 laser differential refractometer and with white light using a Waters DRI.

SEC measurements were made using a bank of three 11 mm × 300 mm PL Gel columns (1×10^3 , 2×10^6 Å). The eluant flow rate was 1 mL/min. The eluant from the columns was passed through the cell of a Chromatix KMX-6 LALLS unit and then split into two streams with a low-volume connector. One stream passed through the ED and the other was directed to the DRI. The lengths of the tubing sections were adjusted to provide equal flow through both detectors. The tubing was 0.009 inch inside diameter (ID). Optimum tube lengths were found to be 72 cm to the DRI and 96 cm to the ED. Negligible time lag was introduced as a result of this arrangement. The eluant flow rate and tubing diameter were such that the mean flow time through the additional tubing was less than the interval between signal accumulations on our interfaced microcomputer. Splitting of the flow did not result in any noticeable peak broadening or distortion. Flow rates were monitored continuously with a Molytek thermal pulse flowmeter.

Sample preparation for SEC measurements was the same as for dn/dc analyses, except that the concentrations for SEC experiments were 2.5–4.2 mg/mL. An injection volume of 300 μL was used to obtain a good signal from the LALLS detector. The LALLS was employed with an angle of 6°–7° and 0.15-mm field stop to minimize background noise.

The temperature in the chamber of the Applied Chromatography Systems ED was 160°C and the air pressure was 30 psi.

All three detectors and the flowmeter were interfaced with a microcomputer. Computations were based on the following equations:

$$\frac{K_i c_i}{R_{\theta i}} = \frac{1}{M_i} + 2A_2 c_i \quad (1)$$

where K (optical constant) = $408 \times 10^{-8} n^2 (dn_i/dc_i)^2$, with n being the refractive index of the solvent. For TCB at 135°C with 6328 Å wavelength light $n = 1.502$. The specific refractive index (dn_i/dc_i) was measured separately for each eluting species, as described above. In Eq. (1) R_{θ_i} is the excess Rayleigh scattering of the solution as compared to the solvent. It is determined by the LALLS. A_2 is the second virial coefficient of the polymer solution. In this case A_2 was set equal to zero. A_2 is actually a function of the molecular weight of the eluting species. Other investigations in this laboratory have shown that use of a zero A_2 does not have a significant effect on the molecular weight measured for commercial polymers.

Also in Eq. (1), M_i is the molecular weight of the i -th fraction and c_i is its concentration, as determined from the ED response according to:

$$c_i = \frac{mX_i}{V_i \sum X_i} \quad (2)$$

where m is the total mass injected, X_i is the height of the ordinate on the ED chromatogram at the particular elution volume, and V_i is the elution volume increment.

RESULTS AND DISCUSSION

Although a total of 14 samples were analyzed only 7 had different dn/dc values. Table I lists the refractive index increments at 6328 Å and the DRI responses in white light (in arbitrary units) for these materials. Also included is the percent unsaturation in the various samples. These values were supplied by the polymer manufacturer. Unsaturation reflects the incorporation of unconjugated dienes in EPDMs.

The data in Table I show that in this case the DRI response may be used to convert the LALLS response to molecular weight with the relation:

$$\frac{dn}{dc} = -0.083 (\text{DRI response}) \left(\frac{\text{mL}}{\text{mV}} \right) \quad (3)$$

TABLE I
Refractive Index Increments and DRI Response Factors

Sample	Percent unsaturation	dn/dc^a		DRI response ^b		dn/dc
		Mean (mL/mg)	SD	Mean (mV/mg)	SD	DRI ratio
2A	0	-0.101	0.002	+1.22	0.01	-0.083
2D	2.7	-0.098	0.002	+1.18	0.01	-0.083
2B	3.0	-0.097	0.002	+1.17	0.02	-0.083
2F	4.5	-0.094	0.003	+1.13	0.01	-0.083
1A	6.5	-0.091	0.002	+1.10	0.03	-0.083
2C	9.0	-0.087	0.002	+1.05	0.01	-0.083
2H	11.0	-0.084	0.003	+1.01	0.01	-0.083

^a Chromatix KMX-16 laser differential refractometer with 6328Å light; 5 determinations per sample.

^b Waters differential refractometer with white light; 5 determinations per sample.

The same conversion factor holds for all compositions in this series of copolymers.

Table II compares molecular weight averages of the fourteen samples, as measured by two different methods. The DRI-LALLS results are from conventional LALLS-SEC computations, in which it is assumed that the DRI measures concentration only (independent of composition) and in which molecular weight is measured with the LALLS detector, assuming a dn/dc value measured for the whole sample. The DRI-LALLS-ED data are measured, as described, by assessing dn/dc for each fraction.

For the majority of these copolymers, no very great error is introduced by ignoring the effects of compositional drifts with molecular weight. For copolymers 2F, 2H, and 3A, however, the new method produces substantially smaller \bar{M}_n values and larger \bar{M}_w 's than the alternative, inaccurate technique. The reasons for these differences are evident when the dependence of dn/dc values on molecular weight is examined.

Most of the analyses were repeated several times (especially for samples 2F, 2H, and 3A). The reproducibility of \bar{M}_n and \bar{M}_w was found to be within 1%, while that of M_z was within 3%.

Figure 1 shows dn/dc versus M for EPDM copolymers 2F and 3A, each of which has 4.5% unsaturation and a bulk dn/dc (at 6328 Å) of -0.094 mL/g. A similar plot is shown in Figure 2, for sample 2H (11.0% unsaturation, mean $dn/dc = -0.084$ mL/g). In these three cases, dn/dc decreases with increasing molecular weight. Since the measured M_i is inversely proportional to $(dn/dc)^2$, the lower moments of the molecular weight distribution will be erroneously high and the higher moments will be lower than the true values if a constant value of dn/dc is assumed for all species in the sample.

Samples 2D (2.7% unsaturation) and 1A (6.5% unsaturation) by contrast, have uniform dn/dc 's with molecular weight. The data points are shown in Figure 3.

Since the difference between dn/dc values for polyethylene and polypropylene is insignificant, the variations of dn/dc with molecular weight in samples 2F, 3A, and 2H can be ascribed to increasing unsaturation (i.e., diene contents) with increasing molecular weights. Figures 4–6 show the relations between diene content and molecular weight for these three materials.

The diene contents were estimated from the measured dn/dc values using the correlation between percent unsaturation and dn/dc summarized in Table I. The assumption here is that changes in dn/dc correspond only to variations in unsaturation and not to changes in ethylene/propylene ratios (since polyethylene and isotactic polypropylene have very similar dn/dc values).

CONCLUSIONS

The DRI-LALLS detector combination or universal calibration procedures are suitable for the analyses of molecular weight distributions of copolymers, provided the composition of such materials does not vary with molecular weight. More generally, however, a third detector is required to measure concentration independent of copolymer composition or molecular weight.

TABLE II
Comparison of Molecular Weights

Percent unsaturation	Sample	DRI-LALLS-ED				DRI-LALLS			
		\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_{z+1}	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_{z+1}
6.5	1A	82,300	311,000	968,000	1,220,000	81,100	308,000	944,000	1,210,000
0	2A	35,100	192,000	577,000	751,000	36,500	189,000	576,000	764,000
4.5	3A	35,300	128,000	411,000	521,000	34,900	127,000	348,000	512,000
6.5	4A	75,100	341,000	1,481,000	2,070,000	74,500	338,000	1,540,000	2,130,000
0	1B	78,300	361,000	1,630,000	2,280,000	78,100	357,000	1,680,000	2,390,000
3.0	2B	98,100	325,000	911,000	1,860,000	97,300	321,000	921,000	1,940,000
9.0	2C	84,100	273,000	681,000	981,000	86,300	278,000	684,000	976,000
2.7	2D	82,300	289,000	742,000	1,000,000	83,100	284,000	736,000	1,070,000
0	2E	78,500	292,000	801,000	1,130,000	77,400	289,000	793,000	1,130,000
4.5	2F	64,500	368,000	1,210,000	1,680,000	89,200	276,000	781,000	986,000
4.5	2G	95,900	336,000	1,210,000	1,820,000	93,700	348,000	1,300,000	1,890,000
11.0	2H	29,100	228,000	636,000	1,200,000	40,600	169,000	481,000	684,000
4.5	3C	68,100	395,000	1,540,000	2,840,000	91,200	329,000	981,000	1,670,000
4.5	3D	84,200	331,000	1,010,000	1,810,000	86,700	336,000	1,060,000	1,890,000

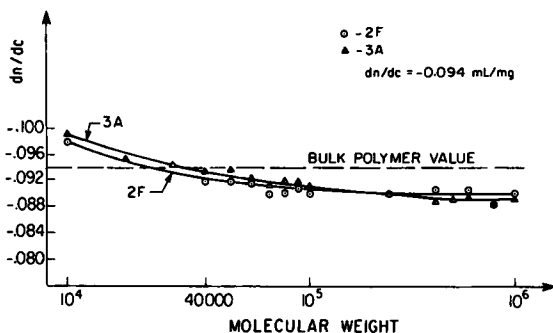


Fig. 1. Plot of dn/dc versus M for samples 2F and 3A both of which contain 4.5% unsaturation.

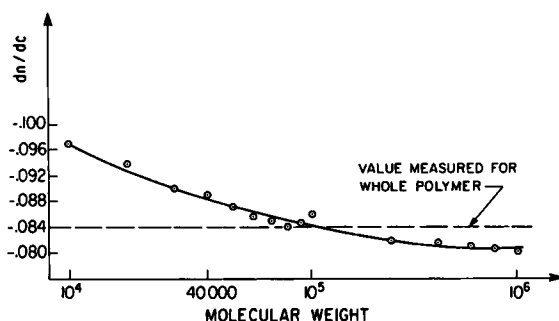


Fig. 2. Relation between dn/dc and M for polymer 2H (11.0% unsaturation).

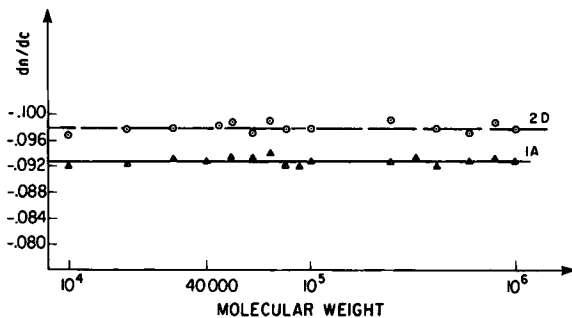


Fig. 3. Plots of dn/dc versus M for samples 2D (2-7% unsaturation) and 1A (6.5% unsaturation).

An evaporative detector (ED) appears to be satisfactory as this third detector. A DRI-LALLS-ED detector system can be used to obtain correct molecular weight distributions of copolymers, in general.

The change in composition of the polymer with molecular weight can also be measured. In a binary copolymer this requires that the dn/dc values of the corresponding homopolymers be sufficiently different. In more complex copolymers, compositional variations can be determined if the dn/dc changes

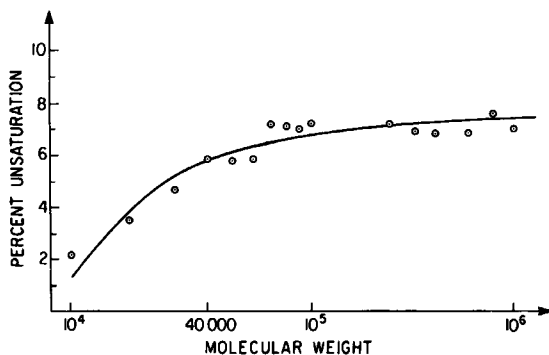


Fig. 4. Diene content (as percent unsaturation) versus molecular weight, for sample 2F.

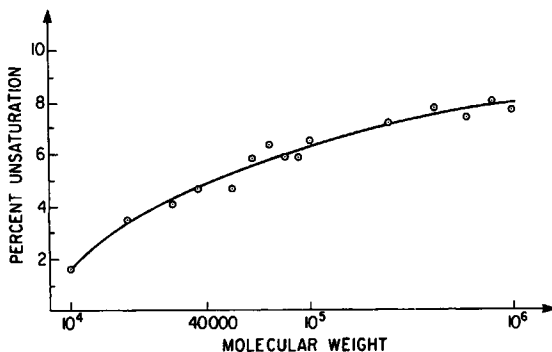


Fig. 5. EPDM 3A; diene content versus molecular weight.

with molecular weight can be attributed to variations in the content of only one of the comonomers.

The LALLS detector measures the molecular weight of species that have the same hydrodynamic volume. This measurement is valid, in general only if the species in the detector cell at any instant also all have the same dn/dc values. Otherwise, \bar{M}_w can be determined accurately only by light-scattering measurements on solutions in a multiplicity of solvents.¹³

The LALLS measurements are believed to be valid with the present EPDM samples, however, since the diene content is constant or increasing with increasing molecular weights (Figs. 3–6). The diene monomer is larger than ethylene or propylene and this means that polymers with the same degree of polymerization and higher diene contents will be larger. This assures relative homogeneity of the composition of the detector cell contents (higher molecular weight polymers will have higher hydrodynamic volumes).

Huang and Barth⁹ showed that the response of the evaporative detector can be a function of the refractive index of the polymer. The detector sensitivity was also reported not to be linear at low concentrations (of nitrocellulose, in this case). The present investigation showed a linear response with concentration, regardless of the refractive indices of the ethylene-propylene copolymers. Other studies have produced the same conclusions for

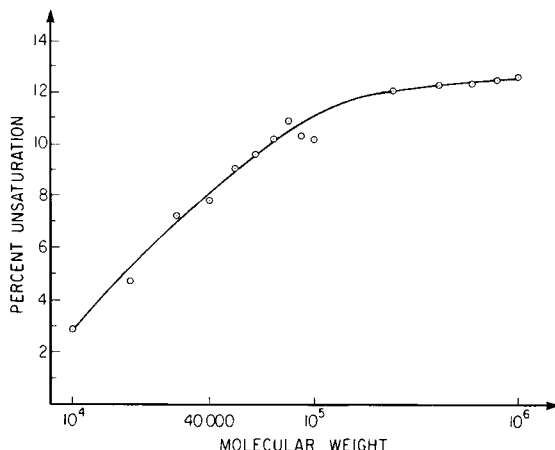


Fig. 6. EPDM 2H; diene content versus molecular weight.

polyethylenes, polystyrenes, and natural rubber samples in several solvents. However, we have noticed nonlinear responses for mixtures of polymers with oils. In that case, low boiling oils may evaporate with the solvent and the ED may not measure the true concentration.

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