

Specific Refractive Index Increments of Ethylene-Vinyl Acetate Copolymers in Trichlorobenzene Solutions at 145°C

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Synopsis

Specific refractive index increments of ethylene/vinyl acetate copolymers have been measured in trichlorobenzene at 145°C. A relationship between these values and copolymer composition has been determined for use in light scattering measurements of weight-average molecular weights of these materials. The data are also required for analysis of molecular weight distributions by size exclusion chromatography with light scattering detection.

INTRODUCTION

Light scattering measurements on polymer solutions can be used to measure the weight-average molecular weight (\bar{M}_w) of the macromolecular species and to provide information about the second virial coefficient (A_2) of the solution as well as the mean radius of gyration of the solvated polymer. The introduction of commercial low-angle laser light scattering (LALLS) photometers has simplified the technique by avoiding the need to extrapolate experimental points to zero viewing angles. The combination of a LALLS detector with a size exclusion chromatograph (SEC) has enhanced the ability of SEC to measure molecular weight distributions.¹ Under favorable circumstances² the SEC-LALLS combination can be used without resort to universal calibration techniques and long chain branch concentrations can also be estimated as a function of polymer molecular weight.³

Generally, however, molecular weight determinations by light scattering measurements apply strictly to homopolymers. Copolymers are not usually amenable to this analysis, without considerable extra precautions and effort.^{4,5} This is because the intensity of light scattered at a given angle, wavelength, and solution concentration is strongly dependent on the refractive index of the solution. The latter usually varies with the chemical composition of the copolymer. Thus, turbidity of copolymer solutions is not generally a single-valued function of the macromolecular size and concentration if the composition of the copolymer is not the same for species of all molecular sizes. The SEC-LALLS combination can be used, with some caution, to measure molecular weight distributions of copolymers in general by employing a combination of detectors.⁶

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Ethylene-vinyl acetate (EVA) copolymers are one of the few types of commercially important copolymers that can be characterized by SEC-LALLS. Numerous studies⁷⁻¹² have shown that these comonomers produce random copolymers in which the comonomer composition is uniform across the molecular weight distribution. Since EVA copolymers are produced in free-radical polymerizations, they tend to contain long branches; conventional SEC universal calibration cannot be used for analyses of their molecular weight distributions. It is necessary, then, to employ a LALLS or continuous viscometer detector in the SEC procedure.¹³

Measurements of the light scattered by polymer solutions yields the weight average molecular weight \bar{M}_w of the solute from the relation

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_2c + \dots \quad (1)$$

where R_θ is the reduced scattering intensity of polymer with concentration c . The optical constant K is defined by

$$K = \frac{2\pi^2 n_0 (dn/dc)^2}{L\lambda^4} \quad (2)$$

Here n_0 is the refractive index of the pure solvent at the experimental temperature and wavelength λ of incident light, L is Avogadro's constant, and dn/dc is the specific refractive index of the polymer solution. The latter parameter varies with copolymer composition. It is necessary to know the appropriate value of dn/dc in order to measure \bar{M}_w of EVA copolymers by light scattering or to determine the molecular weight distribution parameters by SEC-LALLS.

In this investigation, we have measured dn/dc values for a variety of EVA copolymers with a wide range of vinyl acetate contents. The vinyl acetate contents of these copolymers were determined by ¹³C-NMR spectroscopic analyses.¹⁴ A relation is reported here between dn/dc and copolymer composition to facilitate interpolation or cautious extrapolation of our experimental results. These measurements were made in 1,2,4-trichlorobenzene, which is a convenient solvent for SEC of polyolefins.³

EXPERIMENTAL

The EVA copolymers used for this study are all commercial, free-radical polymerized samples with vinyl acetate contents ranging from 1 to 40%, by weight. The NMR spectra of these samples were obtained with a Bruker AM-250 spectrometer operating at 62.5 MHz with 10-mm o.d. tubes and sample concentrations in the 50–60% (w/w) range in 1,2,4-trichlorobenzene (TCB). The spectra were acquired with no nuclear Overhauser effect, 35 s relaxation time, and approximately 2000 scans. These conditions have been shown to give quantitative results in similar analyses of LDPEs.¹⁵

Before inserting the sample tubes into the NMR spectrometer, the solutions were held at 150°C for approximately 30 min (for samples of low vinyl acetate content) or 20 min (for samples of high vinyl acetate content). The polymers

were then analyzed at 100°C in the NMR spectrometer. This procedure has been shown to increase spectral resolution and signal sensitivity of LDPEs while simultaneously minimizing sample degradation during data acquisition.¹⁵ Peak areas from the ¹³C-NMR spectra were measured by planimetry, which is believed to be more accurate than digital integration.

The chemical compositions of the EVA copolymers were determined from the vinyl acetate carbonyl carbon resonance line area (A_{co}) of the NMR spectra, the sum of all spectrum peak areas (A_T), and the following equations:

$$y = \frac{A_{co}}{A_T} \times 1000 \quad (3)$$

$$x = \frac{1000 - 4y}{2} \quad (4)$$

Here x and y are the respective numbers of ethylene and vinyl acetate units per 1000 carbons in the copolymer. The wt% vinyl acetate (W_{ac}) content is given by

$$W_{ac} = \frac{86y}{86y + 28x} \times 100 \quad (5)$$

where 86 and 28 are the respective formula weights of vinyl acetate and ethylene.

The specific refractive index increments were determined with a Chromatix KMX-16 differential refractometer operating with a He-Ne laser source at $\lambda = 6386 \text{ \AA}$. For each copolymer chemical composition, dn/dc values were determined at three to five different concentrations, varying from 1 to 18 g/L. The samples were dissolved in TCB plus 0.1% (w/w) 4,4'-thiobis(3-methyl-6-tert-butylphenol) antioxidant at 145°C for approximately 2 h prior to their analysis in the differential refractometer, which was also at 145°C.

The specific refractive index increment is obtained as the zero concentration intercept of a plot of $\Delta n/c$ vs. c , where Δn is the difference between the solution and solvent refractive indices.¹⁶ However, with the concentrations and copolymers used in this work, $\Delta n/c$ exhibited a very small or negligible dependence on concentration. The dn/dc values quoted here are therefore averages of three to five readings at different concentrations.

RESULTS AND DISCUSSION

Table I summarizes the copolymer chemical composition of the EVA samples used in this work, expressed both as wt and mol % vinyl acetate. It also includes the mean values of the specific refractive index increments. The dn/dc value for sample A (of low vinyl acetate content) is close to that reported elsewhere for the high-pressure, low-density polyethylene homopolymer.¹⁷

In general, one observes an increase (less negative) in dn/dc values with increasing vinyl acetate content. Figure 1 is a plot of dn/dc vs. mol % vinyl acetate. It shows a nonlinear relationship between the two variables. A

TABLE I
Vinyl Acetate Content and dn/dc Values of EVA Copolymers

Sample	Vinyl Acetate (wt %)	Vinyl Acetate (mol %)	dn/dc (mL/g)
A	1.2	0.4	-0.104
B	3.2	1.1	-0.101
C	6.7	2.3	-0.099
D	9.4	3.3	-0.095
E	18.7	7.0	-0.094
F	27.2	10.8	-0.086
G	38.9	17.2	-0.084
H	41.3	18.6	-0.084

least-squares polynomial regression analysis of the data yields the following second-order polynomial with a 0.985 correlation coefficient:

$$\frac{dn}{dc} = 2.2394 \times 10^{-3}F_v - 6.4127 \times 10^{-5}F_v^2 - 0.1036 \quad (6)$$

where F_v is the mol % vinyl acetate in the copolymer. The correlation coefficient for the above relationship is good considering that the samples

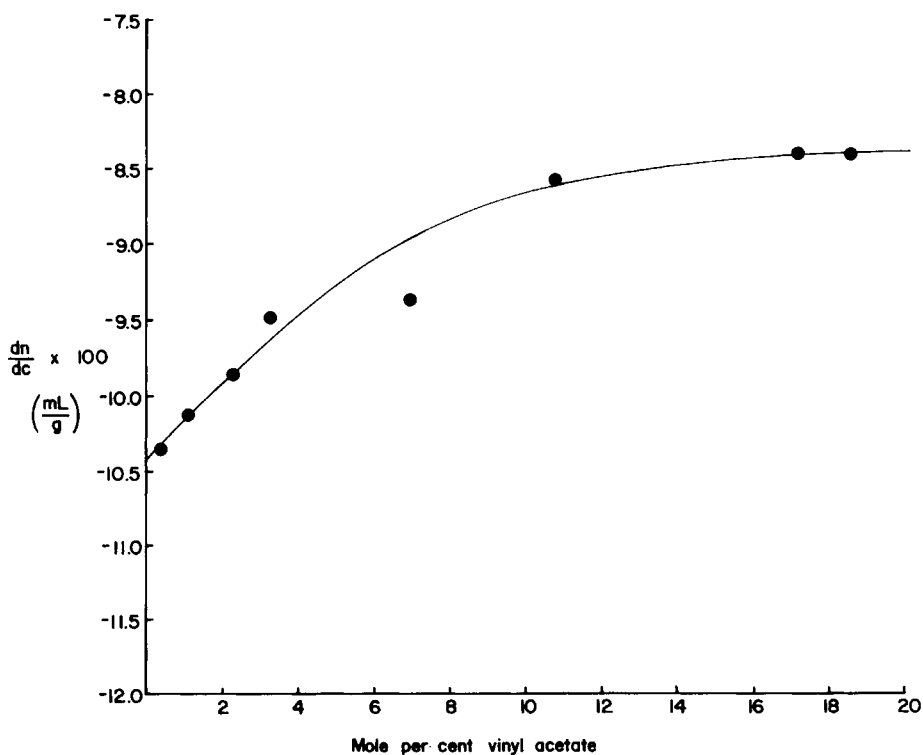


Fig. 1. Specific refractive increments vs. mol % vinyl acetate in EVA copolymers.

originate from different manufacturers. Furthermore, the constant -0.1036 in eq. (6) should correspond to the specific refractive index increment for zero vinyl acetate content. This value agrees well with the figure reported elsewhere for high pressure, low-density polyethylene.¹⁷

Equation (6) may be used to determine copolymer chemical composition from a known specific refractive index increment, although this analytical method is probably more tedious than alternative techniques.

The data reported here are needed for analyses of EVA copolymers. There are nevertheless some problems with the measurement technique that should be recorded for those who wish to extend these data to a wider range of copolymer compositions or to other copolymers. These are as follows: The windows of the differential refractometer fog readily at the temperatures that are needed for SEC analyses of polyolefins. It was necessary to clear the windows about once per minute. Some inaccuracies may arise from convection currents and evaporation of solvent from the cell. The NMR analyses of vinyl acetate content are probably accurate to about 10% of the reported values. Finally, it was noted that the particular antioxidant [which is used in SEC analyses¹⁷] degrades, so that the solutions may acquire a yellow tinge which may affect the dn/dc measurements.

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