Measurement of Number-Average Molecular Weights and Second Viral Coefficients of Polyolefins using an Improved Vapor Pressure Osmometer

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Synopsis

Operation of an improved design of a vapor pressure osmometer for polyolefins at 140°C is described. Reproducibility of $\pm 10\%$ of the measured number-average molecular weight $(\overline{M}_n)$ was obtained with a maximum $\overline{M}_n$ of about 45,000–50,000. Results are reported for some standard and commercial, linear and branched polyethylenes and for commercial polypropylenes.

INTRODUCTION

The methods used to measure the number-average molecular weight $(\overline{M}_n)$ of high polymers have continued to attract significant interest despite the sophistication achieved by the technique of gel permeation chromatography (GPC) which permits the measurement of all molecular weight averages in one experiment. The continued interest in the measurement of $\overline{M}_n$ usually arises from a special interest in the relationship between polymer properties and the nature of the low-molecular-weight fraction of a broad-molecular-weight-distribution polymer. Additionally, there is an interest in comparing $\overline{M}_n$ obtained by GPC and independent methods. Significant work has been conducted in the development of four colligative methods to measure $\overline{M}_n$: cryoscopy,[1,2] ebulliometry,[1,3–5] membrane osmometry,[1,3,5] and vapor pressure osmometry.[3,6–12] The ease of measurement and greater sensitivity[13] of membrane osmometry and vapor pressure osmometry have made these techniques preferable to and more widely reported than cryoscopy and ebulliometry. However, several experimental difficulties have been reported for membrane osmometry at high temperature and with broad-molecular-weight polyolefins. The necessity to operate at high temperature when analyzing polyolefins causes problems primarily related to membrane instability. The author has experienced rapid membrane embrittlement, causing unstable solvent baseline readings when various types of cellulosic membranes (gel cellophane and deacetylated acetyl cellulose) were used at 140°C in *ortho*-dichlorobenzene, and this behavior has been reported by others.[14] Secondly, large errors in the measurement of $\overline{M}_n$ of broad-molecular-weight-distribution polymers because of diffusion of low-molecular-weight species through the membrane yielding fallaciously high $\overline{M}_n$ have been noted.[3,15] In the present work, it was found that with an improved vapor pressure osmometer the measurements of $\overline{M}_n$ and A_2 of polyolefins can be performed rather easily with good precision. Data are presented for broad-molecular-weight-distribution branched polyethylenes and polypropylenes and narrow- and broad-molecular-weight-distribution linear polyethylenes.

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EXPERIMENTAL

Materials

The solvent used throughout this work was distilled in glass 1,2,4-trichloro-benzene (TCB), as supplied by Rho Chemical Co., Joliet, IL. The calibration standard was sucrose octaacetate (M_w = 678.6) 99+% purity as supplied by Wescan Instrument Co., Santa Clara, CA.

Polymer standards were used as supplied. The polyethylene standards were used as supplied. The polyethylene standards were obtained from National Bureau of Standards, Washington, D.C., and ArRO Laboratories, Joliet, IL. The polystyrene standards were obtained from Pressure Chemical Co., Pittsburgh, PA. The various broad-molecular-weight-distribution industrial polyolefins were analyzed as supplied by the various manufacturers. The hydrogenated polybutadienes (HPB) were obtained from Dr. W. Graessley, Northwestern University, Evanston, IL.

Vapor Pressure Osmometer

The vapor pressure osmometer (VPO) was a Corona/Wescan model 232A molecular weight apparatus, Wescan Instrument Co., Santa Clara, CA. The operating conditions were as follows: cell temperature 140°C, syringe holder temperature 151°C, bridge current 195 μA, thermistor temperature match setting 754, and sensitivity 10X. The operation of this instrument has been described[12] in detail.

VPO Procedure

The polymer solutions were prepared at room temperature in TCB and the concentrations at operating temperature were calculated using the change in density of TCB according to

$$d = 1.4783364 - 0.0012016T \tag{1}$$

where d is the density in g/ml and T is the temperature in °C. Each solution concentration was prepared by independent weighing of the sample and dilution in a known volume of solvent. Solutions were established at 150°C and transferred to the heated syringe holder of the Corona/Wescan VPO and held at 151°C. Measurements of ΔV, change in voltage across the thermistors, were taken at 140°C for each solution concentration. At least five solution concentrations were measured for each polymer sample.

Gel Permeation Chromatography

Gel permeation chromatography was performed on a Waters GPC-200 instrument with six Styragel columns (10^3, 3×10^3, 10^4, 10^5, 10^6, and 10^7 Å) with refractive index detection. Injection volume was 2 cm^3 at a concentration of 3.5 g/liter in TCB. Columns and detector were maintained at 140°C. No correction was applied for axial dispersion.

RESULTS AND DISCUSSION

The VPO calculations were performed as described below. The calibration constant K was determined with sucrose octaacetate in TCB and was about 22,000 for the conditions described in this work. The calibration constant was assumed to be independent of molecular weight in accordance with the observations of Wachter and Simon[6] and Burge,[12] who found that low-molecular-weight calibration standards could be used for polymers with molecular weights up to 100,000 daltons with an instrument of the type used in this work. The Corona/Wescan VPO uses a platinum screen over each thermistor as shown in Figure 1. A thin sheet of liquid is held on these platinum screens so that reproducibility of the volume of liquid on each thermistor is excellent, unlike VPO designs where droplets are held on the thermistors. The reproducibility of the surface area of the thin sheets of liquid also appears to eliminate the dependence of the calibration constant K on molecular weight. This dependence has generally been ascribed to a diffusion-controlled surface concentration which is different from the bulk concentration.[7,8] The configuration of a thin sheet of liquid, as used in this work, yields a much larger surface-to-volume ratio than for a spherical drop and the metallic screen promotes rapid thermal equilibration in the sheet of liquid. Consequently, concentration gradients are minimized or eliminated and condensation heating owing to solvent condensation into the drop is equilibrated rapidly in the sheet of liquid. This apparently leads rapidly to the true change in temperature ΔT because of the vapor pressure difference of solvent and solution and eliminates the dependence of K on molecular weight. The values of voltage differences ΔV (which are proportional to ΔT) concentration C in g/liter and K in units of μV liter mole^{-1} were used to calculate $\overline{M}_n$ and the second virial coefficient A_2 from

$$\Delta V/C = K (1/\overline{M}_n) + A_2C \qquad (2)$$

and by plotting $\Delta V/C$ vs. C and extrapolating to zero concentration. A linear least-squares curve-fitting regression was applied to the data to obtain $\overline{M}_n$ and A_2 from the intercept and slope, respectively. The solution concentrations were kept as low as possible while insuring sufficient response from the VPO. Concentrations of 0.5–2.0 g/liter were used for $\overline{M}_n$ up to 3000, 2–10 g/liter for $\overline{M}_n$ up to 15,000, and 10–25 g/liter for $\overline{M}_n$ up to the maximum values of about 40,000. At these concentrations the data were quite linear and did not exhibit curvature within experimental error. This is in agreement with the results of Wachter and Simon[6] and appeared to obviate any need for quadratic fitting or plotting of $(\Delta V/C)^{1/2}$ vs. C. Typical data are shown in Figure 2 for a commercial polypropylene.
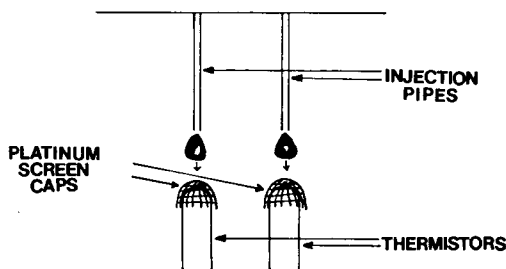

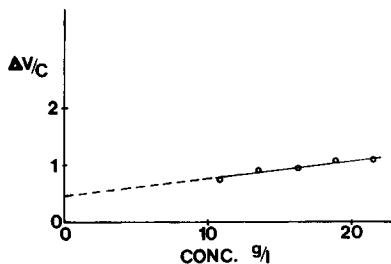Fig. 1. Thermistor configuration in Wescan 232A vapor pressure osmometer.

Fig. 2. Typical plot of vapor pressure osmometry data for a commercial polypropylene.

Table I presents the results for some standard polyethylenes. The agreement among certificate, VPO, and GPC values is good for the linear polyethylene NBS standards SRM 1482 and 1483. The GPC values are lower for these narrow molecular-weight-distribution (MWD) samples because of axial dispersion in the GPC. The results for the linear whole polyethylene NBS SRM 1475 and the branched whole polyethylene NBS SRM 1476 are surprising. The VPO showed consistently the values of $\overline{M}_n$ for each of the polymers to be about one-half of the published and GPC values. The VPO is very sensitive to any low-molecular-weight materials present in a sample and these will lower the measured $\overline{M}_n$. The NBS certificates report that NBS SRM 1475 contains 111 ppm of Irganox 1010 (molecular weight, 1178) and NBS SRM 1476 contains 50 ppm of Santanox (molecular weight, 358). However, calculations of the effect of these additives shows that they have a negligible contribution toward lowering the measured $\overline{M}_n$. In the case of NBS SRM 1475, the Irganox 1010 present was calculated to lower the measured $\overline{M}_n$ by 0.1%, and for NBS SRM 1476, the Santanox present was calculated to lower the measured $\overline{M}_n$ by 0.2%. Thus, it appears that the VPO was sensitive to low-molecular-weight material present in NBS SRM 1475 and 1476 beyond the resolution capacity of the GPC, by which the published values of $\overline{M}_n$ were obtained. Such low-molecular-weight materials would probably not be sensed in a membrane osmometer either, since they would most likely pass through the membrane.

TABLE I
Molecular Parameter Data from VPO and GPC for Polyethylene Standards

| | | $\overline{M}_n$ | | $A_2 \times 10^3$ | $D = \overline{M}_w/\overline{M}_n$ |
| | | Certificate or | | (mole cm³/g²) | |
Sample	VPO	published value	GPC	VPO	GPC
NBS SRM 1482	12,120	11,400[a]	11,200	4.11	1.11
	13,380				
NBS SRM 1483	32,940	28,900[a]	24,000	4.52	1.22
	33,500				
NBS SRM 1475	11,300	18,310[b]	18,400	4.06	2.33
	11,900				
NBS SRM 1476	13,600	20,100[c]	20,400	4.11	4.56
	12,000				
	12,900				

[a] Certificate value, MO.
[b] Certificate value, GPC.
[c] Ref. 16.

TABLE II
Molecular Parameter Data from VPO for Various Polyethylenes

Sample	$\overline{M}_n$ VPO	$\overline{M}_n$ GPC	$A_2 \times 10^3$ (mole cm³/g²) VPO	$D = \overline{M}_w/\overline{M}_n$ GPC
	Whole, branched polyethylenes			
LDPE 3	19,400	22,700	2.17	9.24
	17,300			
LDPE 8	16,600	17,600	2.64	22.96
	17,200			
LDPE 9	26,200	26,600	3.22	18.59
	33,100			
	Narrow, linear polyethylenes			
AC No. 6	3,770	4,500	4.36	1.39
HPB-1	1,750	2,100	20.11	1.03
	2,060		34.37	
	1,790		20.78	
HPB-2	3,720	3,700	6.70	1.04
	3,530		7.59	
HPB-3	22,950	19,600	4.17	1.08
	24,800		4.17	

Table II shows the results for some linear and branched polyethylenes. Agreement between VPO and GPC $\overline{M}_n$ are quite good. Figure 3 shows the sharp decrease in A_2 with increasing molecular weight.

Table III shows results for some commercial polypropylenes. Agreement between VPO and GPC results are fairly good for PP1 and PP3. The VPO results are consistently lower, probably because of the higher sensitivity of VPO to low-molecular-weight materials. The upper limit of the VPO at the conditions described in this work is apparently $\overline{M}_n$ of about 45,000–50,000, based on the results for PP2. The reproducibility of the $\overline{M}_n$ obtained for five determinations on PP1 was good, being less than ±10% standard deviation.

TABLE III
Molecular Parameter Data from VPO and GPC for Polypropylenes

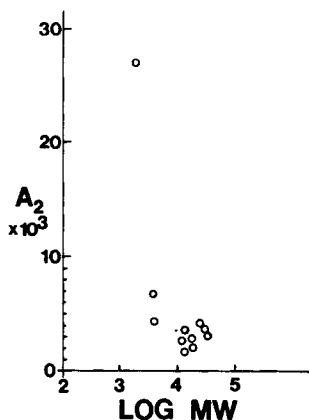| Sample	$\overline{M}_n$ VPO	$\overline{M}_n$ GPC	$A_2 \times 10^3$ (mole cm³/g²) VPO	$D = \overline{M}_w/\overline{M}_n$ GPC
PP1	25,800	33,400	1.25	10.00
	28,000		1.30	
	23,000		1.20	
	27,900		1.69	
	26,600		1.63	
	Mean ± SD			
	26,300 ± 2000			
PP2	47,600	65,800	1.25	5.70
	44,500		1.50	
	49,800		1.44	
PP3	37,100	38,100	2.24	8.60
	34,700		2.38	

Fig. 3. Variation of the second virial coefficient A_2 [(mole cm^3)/g^2] with log molecular weight (log MW).

CONCLUSIONS

The VPO design used in this work offers some advantages over older designs. $\overline{M}_n$ can be obtained without correction for variations in drop size or dependence of calibration constant K on molecular weight. The VPO was easily operated at 140°C for polyolefins up to about $\overline{M}_n$ of 45,000–50,000, with reproducibility of ±10%.

One very important aspect of VPO measurements is that it is very sensitive to low-molecular-weight materials, including additives, residual solvents, and oligomers. Thus, $\overline{M}_n$ obtained by VPO is usually lower than that obtained by GPC or membrane osmometry. One must determine if such materials will render useless the values of $\overline{M}_n$ obtained. If such materials are present and would interfere in the measurement, they must be removed for VPO work. Otherwise, another method should be used, such as GPC, where they can be resolved from the polymeric material, or membrane osmometry, where they will pass through the membrane.

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