

# Molecular Weights of Polyethylene and Polypropylene by Vapor Pressure Osmometry at Elevated Temperatures

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## Synopsis

The Wescan Model 232-A VPO was modified with a 12 volt regulated power supply for supplying bridge current and with thermocouples to allow for direct digital readout of the syringe box and measuring chamber temperatures. The modified instrument was used to measure  $\bar{M}_n$  of standard (NBS) polyethylenes. Agreement with NBS values was good (within 10%) for  $\bar{M}_n < 3 \times 10^4$  and fair (within 20%) for  $\bar{M}_n = 1 \times 10^5$ . Results on  $\bar{M}_n$  of commercial polypropylenes are also reported.

## INTRODUCTION

Recent improvements in commercially available vapor pressure osmometers have resulted in instruments which are capable of reliably measuring molecular weights as high as about  $10^{5,1,2}$ . These new instruments reproducibly control drop size and yield number-average molecular weights ( $\bar{M}_n$ ) for polymers that are independent of the molecular weight of the material used to calibrate the instrument.

Because of the high polydispersity of many commercial polyolefins, membrane osmometry (MO) experiments are frequently complicated by diffusion of low molecular weight polymeric components through the membrane. The result is that  $\bar{M}_n$  values measured by MO under such conditions are erroneously high. Consequently, the application of vapor pressure osmometry (VPO) to measure  $\bar{M}_n$  of polyolefins appears to be an important area, particularly in view of the widespread commercial use of these materials.

In this paper, we report results from VPO experiments with standard polyethylenes and commercial isotactic polypropylenes. Our results are compared with  $\bar{M}_n$  values reported by the suppliers and, in some cases, with VPO results reported by Mirabella.<sup>3</sup>

## EXPERIMENTAL

VPO experiments were conducted in purified, stabilized 1,2,4-trichlorobenzene (TCB) containing 0.15% Irganox 1010 using the Wescan Model 232-A molecular weight apparatus. Solutions were prepared by heating in an oven for about 4 h, with intermittent swirling of the solutions. Oven temperatures of 155 and 170°C were used for polyethylene and polypropylene, respectively. Solvent and gas-tight "Luer-Lok" syringes were also preheated in the oven before use. Samples were quickly loaded into the hot syringes (normally without filtration) and attached to the injection tubing in the heated (150°C) syringe box. The box was covered and the temperature was allowed to

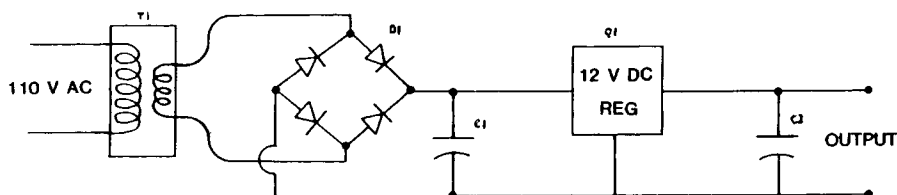


Fig. 1. 12-V regulated DC power supply for the VPO Bridge. Parts specifications are as follow: T1 is a power transformer (input = 120 VAC, output = 12.6 VAC, 60 Hz). D1 is a bridge rectifier (forward current = 1 A, peak reverse voltage = 600). Q1 is a 12-V regulator (maximum DC output current = 100 mA, maximum input voltage = 35, minimum input voltage = 14, wattage = 0.7). C1 is a capacitor (50  $\mu$ F at 50 V). C2 is a capacitor (0.1  $\mu$ F at 100 V).

equilibrate for 15 min. The syringe-box temperature is set somewhat higher than the actual measurement chamber temperature to compensate for any cooling that might occur in the 5.5 in. of injection tubing between the syringe box and measuring cell, which is not insulated.

Measurement temperatures of 130 and 142°C were used for polyethylene and polypropylene, respectively. The instrument was modified to allow for digital readout of both the cell temperature and the heated syringe compartment temperature. This was done by inserting thermocouples attached to a digital readout thermocouple thermometer. An additional modification involved the installation of a 12 V, regulated DC power supply for the VPO bridge. A schematic for this power supply is shown in Figure 1.

Calibration was carried out using sucrose octaacetate as the standard. Standard polyethylenes were obtained from the National Bureau of Standards (NBS). The polypropylenes used are commercial products of Hercules Incorporated. Four to six polymer solutions for each sample were used to generate plots of  $(\Delta V/c)^{1/2}$  vs  $c$ , where  $\Delta V$  is the voltage imbalance for the solution minus the voltage imbalance for the solvent and  $c$  is concentration in units of  $\text{gL}^{-1}$ .

We emphasize the importance of careful and frequent cleaning of the VPO cell during work at elevated temperatures; otherwise, drifting can be a problem. In addition, care must be taken to avoid heating polyolefins too long at elevated temperatures, so that thermal degradation of the polymer is avoided.

Size exclusion chromatography (SEC) results were obtained using a Waters 150C instrument at 145°C with TCB as the mobile phase. A flow rate of 0.5  $\text{mL min}^{-1}$  was used, and a universal calibration curve based on narrow molecular weight distribution polystyrenes (Pressured Chemical Co.) and polyethylenes (NBS) was employed.

## RESULTS AND DISCUSSION

Results from VPO experiments with NBS standard polyethylenes are given in Table I, along with characterization data supplied by NBS and VPO data taken from Ref. 3. Data for NBS 1483 are also plotted in Figure 2. Our results are within a range of 3–11% lower as compared to NBS values with the exception of NBS 1484 which is about 20% lower than the certified value of  $\bar{M}_n = 101,000$ .

For NBS 1482 and NBS 1483, our results are also in reasonable agreement with VPO data reported by Mirabella.<sup>3</sup> Mirabella's results for NBS 1475 are

TABLE I  
 Molecular Weight Data for NBS Polyethylenes

Sample	$\bar{M}_n$ (VPO)	$\bar{M}_n$ (NBS)	$\bar{M}_n$ (VPO, Ref. 3)	$\bar{M}_w/\bar{M}_n$ (NBS)
NBS 1475	17,800	18,300 <sup>a</sup>	11,600	2.90
NBS 1482	10,300	11,400 <sup>b</sup>	12,800	1.19
NBS 1483	25,800	28,900 <sup>b</sup>	33,200	1.11
NBS 1484	82,000	101,000 <sup>b</sup>	—	1.19

<sup>a</sup> Determined by SEC.

<sup>b</sup> Determined by MO.

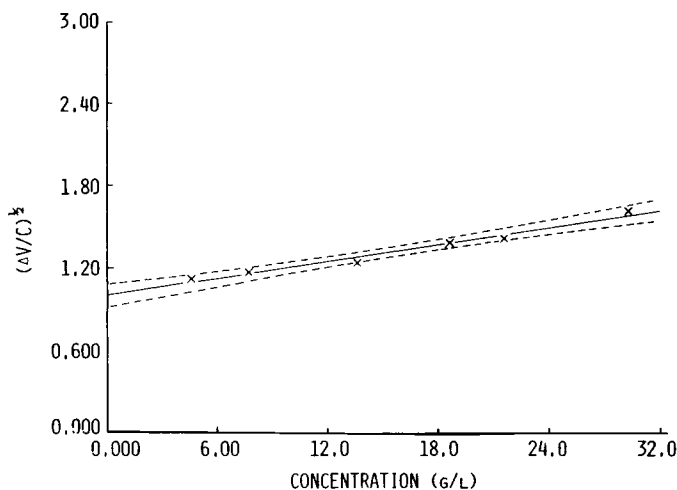


Fig. 2. Plot of  $(\Delta V/c)^{1/2}$  vs  $c$  for NBS 1483 standard polyethylene (dotted lines indicate 95% confidence limits).

 TABLE II  
 Molecular Weight Data for Commercial Polypropylenes

Sample	$\bar{M}_n$ (VPO)	$\bar{M}_n$ (SEC)	$\bar{M}_w/\bar{M}_n$ (SEC)
Pro-Fax 6301-A	27,000	30,000	10
Pro-Fax 6301-B	28,000	37,000	8.4
Pro-Fax 6401-A	15,000	33,000	10
Pro-Fax 6401-B	38,000	40,000	8.3
Pro-Fax 6501-A	49,000	45,000	10
Pro-Fax 6501-B	43,000	59,000	8.0
Pro-Fax 6601	35,000	65,000	7.9
Pro-Fax 6801	38,000	90,000	10

considerably lower than either our results or NBS results. Reasons for this discrepancy are not clear, particularly in view of the fact that Mirabella used the same VPO instrument and solvent used in this work.

Table II gives molecular weight data for commercial isotactic polypropylene samples. For the lower molecular weight samples, with some exceptions, we

find good agreement between VPO and SEC results, with the VPO values being lower. These results suggest the possible presence of low molecular weight components not detected by SEC. Also, some thermal degradation during sample preparation and analysis at elevated temperatures cannot be ruled out.

In the case of Pro-Fax 6801 polypropylene, we feel that the molecular weight is too high to obtain reliable VPO results. Polydispersity appears to be important here. Even though  $\bar{M}_n$  (SEC) was  $9 \times 10^4$ , solutions high enough in concentration to give reliable  $\Delta V$  readings were very viscous, implying substantial polymer-polymer interactions. A simple estimation of the coil overlap concentration,  $c^* \approx 1/[\eta]$ , for this polymer gives a value of  $2 \text{ gL}^{-1}$ . The concentrations used in the VPO work were thus well above  $c^*$  ( $6\text{--}20 \text{ gL}^{-1}$ ), that is, truly dilute solutions were not employed. Because the equations used in handling VPO data were derived for the case of dilute solutions, the erroneous  $\bar{M}_n$  value found for Pro-Fax 6801 using more concentrated solutions is not surprising. NBS 1484 polyethylene, with a comparable  $\bar{M}_n$  value but low polydispersity, yielded much less viscous solutions at similar concentrations due to the absence of very high molecular weight components. Consequently, polydispersity is also an important consideration when defining the upper limit for reasonable accuracy using high temperature VPO. Based on our experience, we feel that  $\bar{M}_n$  of  $5 \times 10^4$  is a reasonable upper limit provided polydispersity is not too great. In addition, our experience thus far indicates a relative standard deviation of about 10% based on multiple analyses of the same sample.

In summary, recent improvements in commercial vapor pressure osmometers have significantly extended the range of molecular weights which can be measured by such instruments. The application of high temperature VPO to polyolefins is of considerable importance due to difficulties in characterizing polydisperse samples of modest molecular weights by MO. VPO is useful for measuring  $\bar{M}_n \leq 50,000$  provided that care is taken to avoid thermal degradation. Our results lend support to Mirabella's<sup>3</sup> conclusion that, in view of the extreme sensitivity of VPO to low molecular weight components, care must be taken to remove low molecular weight additives and contaminants if good agreement with  $\bar{M}_n$  values measured by MO and SEC is to be realized.

We would like to express our sincere appreciation to J. R. Barnes for designing and implementing the DC power supply.

### References

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