

NOTES

Calibration of the Gel Permeation Chromatography Polyester Resins

Applications of polyester resins have grown rapidly in recent years. The molecular weight (MW) and molecular weight distribution (MWD) data are important to characterize these resins for their end uses. Gel permeation chromatography (GPC) is now a powerful and popular technique for the determination of MW and MWD of high polymers. Constructing a calibration curve for the polymer of interest is one of the most important parts of the technique. Direct calibration of GPC columns in terms of MW of narrow MMD standards of the same polymer type is still the method of choice. If there are no standards of the polymer of interest other methods must be employed. One of the widely used techniques is the so-called "Q"-factor method.^{1,2} Another is the well-known "universal calibration method."³

Industrial polyester resins are broad MWD and low MW polymers which often display adsorption effects on the column substrates. There are no narrow MWD standards of polyester type available commercially. The "Q" factor method or the universal calibration method seems to be the alternative for calibrating the GPC for polyester resins. However, the value of Q is difficult to determine; it varies with different GPC conditions. If the universal calibration method is applied the Mark-Houwink constants for polyester resins must be determined.

Furthermore, the elution volume is uniquely determined by molecular size in the case of pure exclusion chromatography, but interaction between polymer and substrates, e.g., adsorption can lead to enhanced retentions. Such effects cannot be taken into account by the universal calibration method. Preparation of a calibration curve for low MW polymers may be achieved by measuring molecular dimensions.⁴⁻⁶ These methods are tedious and have limited success for specific cases.

This note describes a relatively simple and direct calibration method for polyester resins.

EXPERIMENTAL

The GPC instrument was a Perkin-Elmer Liquid Chromatograph 1240 equipped with a UV detector. The columns were two 2.7 × 500 mm Sephadex LH-20 and two 2.7 × 500 mm CPG-10-75. The GPC was run with tetrahydrofuran as solvent at a column temperature of 55°C and at a flow rate of 0.5 ml/min. A Knauer vapor pressure osmometer (VPO) was used to determine the number average MW of polyester resin using ethyl methyl ketone as solvent. Calculation was effected by time-sharing computer facilities.

METHOD, RESULTS, AND DISCUSSION

The first step is to pick a polyester resin sample and its number average molecular weight, assigned as \bar{M}_n (VPO), is determined accurately by VPO technique. Obtain GPC data for very low MW (<10,000) polystyrene standards, as usual. Prepare a calibration curve (normally a straight line) from these data by plotting either the molecular size (in angstrom units) or molecular weight against retention volume at the peak point of its GPC curve. Obtain a GPC chromatogram of the same polyester resin sample and calculate the number average MW according to eqs. (1) or (2):

$$\bar{M}_n(\text{GPC}) = \frac{\sum H_i}{\sum H_i/A_i} \times K_1 \quad (1)$$

$$\bar{M}_n(\text{GPC}) = \frac{\sum H_i}{\sum H_i/M_i} \times K_2 \quad (2)$$

where H_i is the height of the chromatogram at retention volume i ; A_i is the size in angstrom of molecules at retention volume i , obtained from the polystyrene standards calibration curve; M_i is the molecular weight at retention volume i , obtained from the polystyrene standards calibration curve; and K_1, K_2 are the correction factors.

Now search a value of K_1 or K_2 until the difference of $\bar{M}_n(\text{GPC})$ and $\bar{M}_n(\text{VPO})$ becomes as small

TABLE I
 \bar{M}_n of Polyester Resin as Determined by VPO and GPC

Polyester	VPO	GPC	Difference (%) ^a
A	1304	1357	4.0
B	2680	2652	1.0
C	1926	1854	3.7
D	1490	1480	0.6
E	713	778	9.1
F	3566	3539	0.7
G	1984	1924	3.0
H	2452	2440	0.5

^a Based on the result of VPO.

as possible. To construct a calibration curve for polyester resin plot $\log_{10}(K_1A_i)$ or $\log_{10}(K_2M_i)$ against retention volume i . Table I gives \bar{M}_n values for a number of polyester resins as determined by VPO and the GPC method described here. The agreement is generally good.

Since the same kind of sample is used as calibration standard any effect due to interaction between sample and column substrates has been accounted for. In this regard the method could be suitable for other types of low MW polymers, especially for those with polar functional groups. One of the advantages of the present method is to use only one polyester resin sample as a standard. It is not necessary for this sample to be narrow in molecular weight distribution. This method does not correct band spreading, a major problem of the GPC technique.

The difficult part of the present method is to search for a K value. However this can be made easy by using computer. A computer program in BASIC for searching K and plotting the final calibration curve is available from the author on request.

Thanks are due to A. Dearden for the VPO measurements.

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Received July 18, 1977
 Revised September 15, 1977